Contribution from the Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia, and the Department of Chemistry, Washington State University, Pullman, Washington 99164

Oxygen-17 Magnetic Resonance and Temperature-Jump Spectrophotometric Study of the Square Planar–Octahedral Equilibrium in the 1,4,7,10-Tetraazacyclododecanenickel(II) System

JOHN H. COATES, DEWAN A. HADI, STEPHEN F. LINCOLN,* HAROLD W. DODGEN, and JOHN P. HUNT*

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A kinetic study of the system

$$\mathrm{Ni([12]aneN_4)^{2+} + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni([12]aneN_4)H_2O^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ni([12]aneN_4)(H_2O)_2{}^{2+}}$$

in which the equilibrium k_1/k_{-1} is considered to be rate determining in the establishment of the overall equilibrium between the square-planar and octahedral species is reported. Oxygen-17 NMR studies at 5.75, 11.5, and 13.2 MHz in 3.00 mol dm^{-3} aqueous $LiClO_4$ solution give an exchange rate constant for a single aquo ligand in $Ni([12]aneN_4)(H_2O)_2{}^{2+}$: k_{H_2O} ($=k_{-2}/2$) = (2.10 ± 0.17) × 10^7 s^{-1} (298.2 K) ($\Delta H^* = 32.7 \pm 1.1$ kJ mol^{-1} and $\Delta S^* = 5.0 \pm 4.6$ J K^{-1} mol^{-1}). Spectrophotometric temperature-jump and equilibrium studies yield k_1(298.2 K) = (5.8 ± 0.3) × 10^3 mol^{-1} dm^3 s^{-1}, ΔH = 43.1 ± 1.7 kJ mol^{-1}, $\Delta S^* = -28.2 \pm 5.9$ J K^{-1} mol^{-1}, k_{-1}/k_2(298.2 K) = 0.016 mol dm^{-3}, and an overall equilibrium constant K_{eq}(298.2 K) = $[Ni([12]aneN_4)^{2+}]/[Ni([12]aneN_4)(H_2O)_2{}^{2+}]$ = (490 ± 20) × 10^{-4}, $\Delta H^\circ = 15.0 \pm 0.3$ kJ mol^{-1}, and $\Delta S^\circ = 25.1 \pm 0.9$ J K^{-1} mol^{-1} in 3.00 mol dm^{-3} aqueous $LiClO_4$. Data obtained at additional $LiClO_4$ concentrations are reported, and comparisons are made with related nickel(II) systems.

Introduction

The equilibrium in (1) between the low-spin square-planar

$$\underset{\text{low spin}}{\mathrm{NiL^{2+}}} + 2\mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NiLH_2O^{2+}} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{high spin}}{\mathrm{NiL(H_2O)_2{}^{2+}}} \quad (1)$$

($^1A_{1g}$) and high-spin octahedral ($^3A_{2g}$) nickel(II) complexes with tetradentate polyamine ligands (L) has been the subject of considerable investigation;[1-7] nevertheless there is no report of a study in which the reaction dynamics of the sequential equilibria k_1/k_{-1} and k_2/k_{-2} have been separately characterized. It is desirable to gain an insight into the factors which control the lability of these equilibria and to try to determine which of them embraces the rate-determining step for the square planar to octahedral interconversion. For this study 1,4,7,10-tetraazacyclododecane,[8,9] $[12]aneN_4$, has been chosen to represent L in (1) as it comes from a series of macrocyclic tetraaza ligands for which the nickel(II) complexes have been particularly well characterized spectroscopically and thermodynamically.[1-3] The smallest of the macrocyclic tetraaza ligands, $[12]aneN_4$, presents a macrocyclic hole which is variously estimated to constrain the metal–nitrogen distance to 1.70[2] or 1.81 Å[10] whereas the observed averaged low-spin and high-spin nickel(II) distances in polyamine complexes are 1.89 ± 0.03 and 2.10 ± 0.05 Å, respectively.[2,3,10,11] Thus coplanarity of nickel(II) and the four donor nitrogen atoms in $Ni([12]aneN_4)(H_2O)_2{}^{2+}$ is improbable and cis stereochemistry is inferred from spectroscopic data[11] and studies of *cis*-$Co([12]aneN_4)X_2{}^{3+}$ complexes,[8] whereas such coplanarity in low-spin $Ni([12]aneN_4)^{2+}$ is more readily achieved. (The cis stereochemistry of high-spin $Ni([13]aneN_4)X_2$ may be similarly explained.[12]) These low- and high-spin species exist in concentrations in aqueous solution which facilitate both temperature-jump spectrophotometric and ^{17}O NMR kinetic studies of the system under identical conditions; and the high stability of the two complexes and the very slow dissociation of the $[12]aneN_4$ ligand even under strongly acidic or basic conditions precludes the interference of other reactions with the study of the square planar–octahedral equilibrium.

Experimental Section

Synthesis of 1,4,7,10-Tetraazacyclododecanenickel(II) Diperchlorate, $[Ni([12]aneN_4)](ClO_4)_2$. $Ni(ClO_4)_2 \cdot 6H_2O$ (1.5 g) was dissolved in boiling ethanol (50 cm^3), and $[12]aneN_4$[9] (0.8 g) in ethanol (30 cm^3) was added dropwise with stirring. The reaction mixture was refluxed for 15 min and was then evaporated to dryness. The brownish yellow product was dried over silica gel prior to thorough digestion in four 30-cm^3 lots of chloroform (in which $[Ni([12]aneN_4)](ClO_4)_2$ is insoluble) to remove residual excess $[12]aneN_4$. The last traces of water were removed by digestion in triethyl orthoformate for 2 h. The product was then filtered and washed with chloroform under dry nitrogen (yield 1.3 g). Anal. Calcd for $[Ni(C_8H_{20}N_4)](ClO_4)_2$: Ni, 13.66; C, 22.35; H, 4.69; N, 13.03. Found: Ni, 13.45; C, 21.9; H, 4.71; N, 12.52. The $[Ni([13]aneN_4)](ClO_4)_2$ complex was prepared in the same way. Anal. Calcd for $[Ni(C_9H_{22}N_4)](ClO_4)_2$: Ni, 13.23; C, 24.35; H, 5.00; N, 12.62. Found: Ni, 13.08; C, 24.83; H, 5.20; N, 12.72. The two macrocyclic ligands gave good microanalyses also, but as it was found that the published preparative method[9] can sometimes give significant amounts of other macrocyclic species, the purity of the ligands was also checked by ^{13}C NMR. In D_2O, $[12]aneN_4$ is characterized by a single resonance 14.2 ppm downfield and $[13]aneN_4$ by resonances 16.7, 16.5, 15.7, and 15.4 ppm downfield and one resonance 3.3 ppm upfield (which is assigned to the central carbon in the C_3 segment) from the CH_3 resonance of *tert*-butyl alcohol in a capillary. All other chemicals used in this study were of good reagent grade and were used without further purification.

Instrumental Methods. The magnetic moment of solid $[Ni([12]aneN_4)](ClO_4)_2$ was determined by using the Gouy method,[13] and diamagnetic susceptibility corrections were calculated from Pascal's

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* To whom correspondence should be addressed: S.F.L., University of Adelaide; J.P.H., Washington State University.

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Table I. Spectrophotometric Equilibrium and Kinetic Data for the $Ni([12]aneN_4)^{2+}/Ni([12]aneN_4)(H_2O)_2{}^{2+}$ System[a]

$[LiClO_4]$, mol dm^{-3}	10^4K_{eq} (298.2 K)	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}	$10^6\tau$, s	10^3k_1 (298.5 K), mol^{-1} dm^3 s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
0	30.0 ± 2.0	23.6 ± 0.3	30.8 ± 1.1				
0.10	33.0 ± 2.0	24.2 ± 0.8	33.7 ± 2.7				
1.00	79.0 ± 4.0	22.1 ± 0.2	34.0 ± 0.7				
2.00	200 ± 10	19.6 ± 0.5	33.3 ± 1.5	4.4 ± 0.2 (286.1 K), 3.4 ± 0.2 (291.5 K), 2.2 ± 0.1 (296.4 K)	9.5 ± 0.5	44.5 ± 9.3	−19.4 ± 32
3.00	490 ± 20	15.0 ± 0.3	25.1 ± 0.9	7.0 ± 0.3 (287.2 K), 4.5 ± 0.2 (293.4 K), 3.3 ± 0.2 (298.8 K)	5.8 ± 0.3	43.1 ± 1.7	−28.2 ± 5.9
4.00	1070 ± 50	13.9 ± 0.3	27.9 ± 0.9	2.8 ± 0.1 (305.8 K), 2.3 ± 0.1 (310.6 K), 2.0 ± 0.1 (316.0 K)	5.6 ± 0.3	20.9 ± 6.1	−103 ± 20

[a] In 2.00, 3.00, and 4.00 mol dm^{-3} $LiClO_4$, $[H_2O]$ = 50.9, 48.6, and 46.1 mol dm^{-3}, respectively. Each τ value represents the average of at least five determinations.

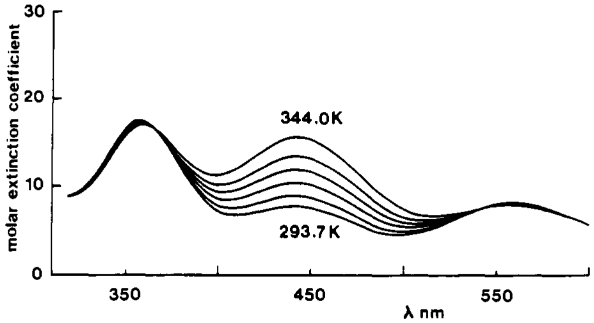

Figure 1. The solid lines are the spectra of the $Ni([12]aneN_4)^{2+}$/$Ni([12]aneN_4)(H_2O)_2{}^{2+}$ system in aqueous 4.00 mol dm^{-3} $LiClO_4$ solution. The peak at 443 nm shows a progressive increase in intensity in the spectra recorded at 293.7, 302.5, 313.2, 323.0, 332.3, and 344.0 K, respectively.

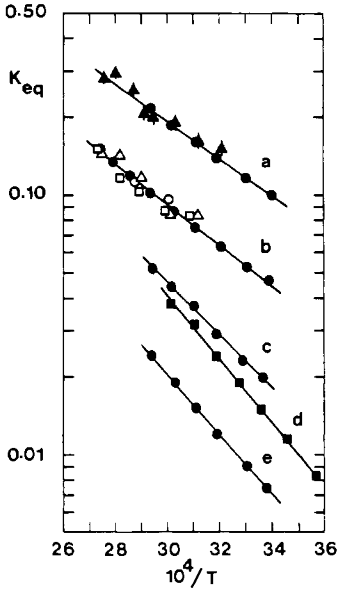

Figure 2. Variation of K_{eq} with temperature and $[LiClO_4]$. The filled circles and squares represent spectrophotometric data obtained in (a) 4.00, (b) 3.00, (c) 2.00, (d) 0.00 (plotted as $5K_{eq}$), and (e) 1.00 mol dm^{-3} aqueous $LiClO_4$ solution, and the solid lines represent the linear regression lines. The filled triangles represent data obtained from magnetic moment measurements in 4.00 mol dm^{-3} aqueous $LiClO_4$ solution. The open squares, circles, and triangles represent data obtained from ^{17}O NMR shift studies at 5.75, 11.5, and 13.2 MHz in 3.00 mol dm^{-3} aqueous $LiClO_4$ solution.

constants. Magnetic moments in solution were determined by the Evans method,[14] using precision coaxial NMR tubes (Wilmad) and a Bruker HX90E spectrometer for which temperature control was ±0.3 K. Corrections were made for the experimentally determined density variation of the solutions with temperature. Diamagnetic corrections were calculated from Pascal's constants, and the bulk susceptibility of aqueous 4.00 mol dm^{-3} $LiClO_4$ was determined with use of the Gouy method ($\chi = -0.5328 \times 10^{-6}$ cgsu/g). The reference signals for the CH_3NO_2 and aqueous $LiClO_4$ solutions were provided by 3% w/w tetramethylsilane and *tert*-butyl alcohol, respectively. Oxygen-17 NMR measurements were carried out on a variable-field spectrometer built in these laboratories (Pullman) at 13.2, 11.5, and 5.75 MHz. The ^{17}O resonances were observed in the absorption mode and the half-width at half-maximum amplitude, *W*, was derived through a computer fit of the Lorentzian line shape. Sample temperature control was ±0.1 K. The ^{17}O water was 10% ^{17}O (normalized in H content) and was obtained from YEDA R and D Co., Ltd., Rehovot, Israel.

Spectrophotometric measurements were made with a Zeiss DMR 10 spectrophotometer (cell temperature control ±0.2 K), and temperature-jump spectrophotometer measurements were carried out on equipment constructed (Adelaide) in a manner similar to that described in the literature.[15] The heating relaxation time for a 10-K temperature jump ≤0.4 μs in the 2.00–4.00 mol dm^{-3} aqueous $LiClO_4$ solutions was determined with the use of phenol red indicator. Longer heating relaxation times were observed in the <2.00 mol dm^{-3} $LiClO_4$ solutions, and hence no relaxation studies of the $[12]aneN_4$ system were carried out under these conditions.

Results

The visible spectrum of the aqueous nickel(II)–$[12]aneN_4$ system is markedly dependent upon temperature and ionic strength (Figure 1 and Table I) such that an increase in either variable produces a shift in the square planar–octahedral equilibrium toward the former state.[16] The two isosbestic points illustrated for 4.00 mol dm^{-3} aqueous $LiClO_4$ solution in Figure 1 and similarly observed in the other solutions listed in Table I suggest the occurrence of two predominant species: high-spin $Ni([12]aneN_4)(H_2O)_2{}^{2+}$, most probably in the cis configuration,[11,12] and low-spin $Ni([12]aneN_4)^{2+}$. For the purposes of determining the equilibrium constant, K_{eq} = [square planar]/[octahedral], the molar extinction coefficient (71.0, 443 nm) of $Ni([12]aneN_4)^{2+}$ in nitromethane, determined from 3.49×10^{-3} and 1.49×10^{-2} mol dm^{-3} solutions, was assumed to be identical with that of the square-planar species in aqueous solution. The spectrum of an aqueous solution 4.53×10^{-2} mol dm^{-3} in the complex alone, from which the band at 443 nm was absent at 274 K, was taken as the spectrum of $Ni([12]aneN_4)(H_2O)_2{}^{2+}$. The K_{eq} values

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Table II. Kinetic and ^{17}O NMR Parameters for Water Exchange on Nickel(II) Species

species	Ni([12]ane N$_4$)-(H$_2$O)$_2^{2+}$	Ni-(H$_2$O)$_6^{2+}$ [a]	Ni(trien)-(H$_2$O)$_2^{2+}$ [b]
τ_M (298.2 K), s	$(4.76 \pm 0.39) \times 10^{-8}$	3.18×10^{-5}	1.75×10^{-6}
k_{H_2O} (298.2 K), s^{-1}	$(2.10 \pm 0.17) \times 10^{7}$	3.14×10^{4}	5.7×10^{5}
$\Delta H^\ddagger$, kJ mol^{-1}	32.7 ± 1.1	56.9	34.4
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	5.0 ± 4.6	32.1	−19.2
T_{2M}°, s	$(2.56 \pm 0.08) \times 10^{-6}$		
E, kJ mol^{-1}	-9.04 ± 0.54		
T_{2M}', s kHz^2	119 ± 6		
E', kJ mol^{-1}	-14.2 ± 1.4		
A/h, MHz	23.2	22.2	22.5

[a] Data from ref 19. [b] Data from ref 23.

are plotted in Figure 2 and the associated thermodynamic parameters appear in Table I.

In the solid state and in nitromethane solution, [Ni([12]aneN$_4$)](ClO$_4$)$_2$ was found to be diamagnetic by using the Gouy[13] and Evans[14] methods, respectively. The magnetic moment, μ_{eff}, of Ni([12]aneN$_4$)(H$_2$O)$_2^{2+}$ was determined to be 2.90 μ_B by Evans' method in aqueous 0.101 mol dm^{-3} solutions of the complex alone at 274 K. This value compares with μ_{eff} = 3.06, 3.16, and 3.15 μ_B respectively for the analogous dichloro, dibromo, and dinitrato[11] species in the solid state. In 4.00 mol dm^{-3} aqueous LiClO$_4$ solution, K_{eq} was determined from the observed magnetic moment, μ_{obsd}, of a solution of 4.06×10^{-2} mol dm^{-3} in the complex, within the temperature range 288.3–362.5 K, by using eq 2 and by assuming the square-planar species to be diamagnetic in aqueous solution.[17] These data are seen to be in reasonable agreement with the spectrophotometric data (Figure 2).

$$K_{eq} = (\mu_{obsd}^2 - \mu_{eff}^2)/\mu_{obsd}^2 \tag{2}$$

The temperature-jump relaxation of the square planar–octahedral equilibrium observed at 443 nm in 2.00, 3.00, and 4.00 mol dm^{-3} aqueous LiClO$_4$ in the complex concentration range 0.047–0.140 mol dm^{-3} is characterized by a single concentration-independent relaxation time (Table I). These τ values are $>10^2\tau_M$, the lifetime of a water molecule in Ni([12]aneN$_4$)(H$_2$O)$_2^{2+}$, derived from the ^{17}O NMR studies (Table II) discussed below, and thus τ characterizes the equilibrium between Ni([12]aneN$_4$)$^{2+}$ and Ni([12]aneN$_4$)H$_2$O^{2+} shown in eq 1. Under these conditions, τ is related[4,18] to the rate constants of eq 1 through eq 3. With use of the K_{eq} data from Table I, the k_1 and associated $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values may be derived through eq 3 as may k_{-1}/k_2(298.2 K) = 0.016 mol dm^{-3} for 3.00 mol dm^{-3} aqueous LiClO$_4$ solution by substituting $k_{-2} = 2k_{H_2O}$ (Table II). In the Ni([13]aneN$_4$)(H$_2$O)$_2^{2+}$ system a spectral change consistent with a shift in the square planar–octahedral equilibrium was observed in temperature-jump experiments, but it occurred at the same rate as the temperature rise in the cell, indicating that $\tau \leq 0.4$ μs.

$$\begin{aligned} 1/\tau &= k_1[H_2O](1 + k_{-1}k_{-2}/(k_1k_2[H_2O]^2)) \\ &= k_1[H_2O](1 + K_{eq}) \end{aligned} \tag{3}$$

Shift and broadening measurements of the ^{17}O-water resonance of a 0.0498 mol kg^{-1} solution of [Ni([12]aneN$_4$)](ClO$_4$)$_2$ using pure water as a reference were made at 11.5 MHz over the temperature range 273–363 K. More extensive measurements were made on a solution 0.0498 mol kg^{-1} in [Ni([12]aneN$_4$)](ClO$_4$)$_2$ and 3.00 mol dm^{-3} in LiClO$_4$ by using an aqueous 3.00 mol dm^{-3} LiClO$_4$ solution as reference over the temperature range 253–363 K at 5.75, 11.5, and 13.2 MHz. These data are plotted in Figure 3.

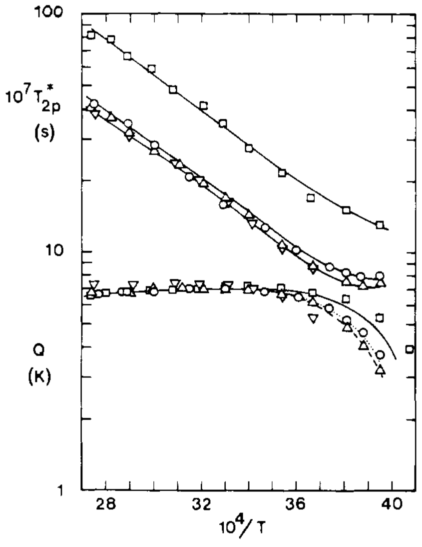

Figure 3. Oxygen-17 NMR data obtained in 3.00 mol dm^{-3} at 5.75, 11.5, and 13.2 MHz are shown as squares, circles, and triangles, respectively, and data obtained in the absence of LiClO$_4$ at 11.5 MHz are shown as inverted triangles. The upper and lower sets of solid curves are respectively the simultaneous nonlinear least-squares best fits of the line broadening, T_{2p}*, and shift, Q, data obtained in 3.00 mol dm^{-3} aqueous LiClO$_4$ solution from eq 8 and 9.

The ^{17}O shift and line-broadening data yield Q and T_{2p}* through eq 4 and 5, respectively, where m is the [Ni([12]aneN$_4$)](ClO$_4$)$_2$ concentration in mol kg^{-1}, Δf and ΔW are the shift and increase in half-width (in Hz) at half-maximum amplitude, respectively, of the ^{17}O resonance of the [Ni([12]aneN$_4$)](ClO$_4$)$_2$ solution relative to that of the reference solution, f_0 is the spectrometer frequency, and T is the absolute temperature. In the NMR fast-exchange limit Q should become independent of temperature and reach a limiting value Q_{lim}^0 provided that a single species is present and that the magnetic moment of Ni([12]aneN$_4$)(H$_2$O)$_2^{2+}$ obeys Curie's law. (For example solutions of Ni(H$_2$O)$_6^{2+}$ exhibit this behavior with Q_{lim}^0 = 24.[19]) With the assumption that Ni([12]aneN$_4$)$^{2+}$ neither shifts nor broadens the ^{17}O resonance, the actual Q_{lim} value is given by eq 6, where χ_p is the mole fraction of Ni([12]aneN$_4$)(H$_2$O)$_2^{2+}$ present.

$$Q = T(\Delta f/f_0)(55.5/m) \tag{4}$$

$$\frac{1}{T_{2p}^*} = \frac{1}{T_{2p}} - \frac{1}{T_{2o}} = \frac{55.5(2\pi)(\Delta W)}{m} \tag{5}$$

$$Q_{lim} = \chi_p Q_{lim}^0 \tag{6}$$

Equations 1 and 6 give

$$K_{eq} = (Q_{lim}^0 - Q_{lim})/Q_{lim} \tag{7}$$

Equation 7 may be used to calculate K_{eq} from the high-temperature shift measurements if Q_{lim}^0 is known. In practice Q_{lim}^0 cannot be determined precisely from the NMR data alone, but K_{eq} calculated with Q_{lim}^0 = 7.5 for the 3.00 mol dm^{-3} LiClO$_4$ solution is in excellent agreement with the spectrophotometrically determined K_{eq} values (Figure 2 and Table I) and is also consistent with the maximum value of Q_{lim} =

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7.38 observed in the absence of $LiClO_4$. The spectrophotometrically determined K_{eq}, ΔH°, and ΔS° values obtained in 3.00 mol dm^{-3} $LiClO_4$ solution together with $Q_{lim}{}^0 = 7.5$ were used in the simultaneous fitting of the Q and $T_{2p}{}^*$ data to the Swift and Connick equations[20] (8) and (9), using the Dye and Nicely[21] nonlinear least-squares program. In eq 8 and 9, n is the number of coordinated water molecules (here set equal to 2 on the basis of the A/h value as discussed below), T_{2M} is the ^{17}O transverse relaxation time of coordinated water, τ_M is the mean lifetime of one coordinated water molecule, $\Delta\omega_M$ is the frequency shift (rad/s) between the ^{17}O resonances of coordinated and bulk water, and Q_o is the portion of $Q_{lim}{}^0$ arising from interactions outside the first coordination sphere. Other relevant equations used are (10)–(13). Equation 10

$$Q = \chi_p\left[\frac{n[T(\Delta\omega_M)/\omega_0]}{\tau_M{}^2\left[\left(\frac{1}{T_{2M}}+\frac{1}{\tau_M}\right)^2+(\Delta\omega_M)^2\right]}+Q_o\right] \qquad (8)$$

$$\frac{1}{T_{2p}{}^*} = \chi_p\frac{n}{\tau_M}\,\frac{\dfrac{1}{T_{2M}{}^2}+\dfrac{1}{T_{2M}\tau_M}+(\Delta\omega_M)^2}{\left(\dfrac{1}{T_{2M}}+\dfrac{1}{\tau_M}\right)^2+(\Delta\omega_M)^2} \qquad (9)$$

$$\chi_p = 1/(1+K) \qquad (10)$$

$$\tau_M = \frac{h}{kT}e^{-\Delta S^*/R}e^{\Delta H^*/RT} \qquad (11)$$

$$\frac{nT(\Delta\omega_M)}{\omega_0} = Q_{lim}{}^0 - Q_o \qquad (12)$$

$$T_{2M} = T_{2M}{}^0e^{E(X-X_0)/R} + \frac{T_{2M}{}'}{f_0{}^2}e^{E'(X-X_0)/R} \qquad (13)$$

$$X = 10^3/T \qquad X_0 = 10^3/298.2$$

is based upon equilibrium 1, and eq 11, in which ΔH^* and ΔS^* are the enthalpy and entropy of activation for the exchange of a water molecule in the first coordination sphere, arises from the absolute reaction rate theory. Equation 12 arises from the high-temperature limiting form of (8). Equation 13 is a phenomenological equation constructed to reproduce the frequency and temperature dependence of T_{2M} indicated by the data. The form of eq 13 may be arrived at by considering a combination of rotationally modulated zero-field splitting and an anisotropic **g** tensor as sources of electron spin relaxation in the system, but in the data treatment it is simply used as an empirical equation. Initial attempts to fit the data indicated that an equation based on an impact or rotationally modulated zero-field splitting[22] alone was inadequate.

In fitting the shift and line-broadening data to eq 8 and 9, ΔH^*, ΔS^*, $T_{2M}{}^0$, $T_{2M}{}'$, E, and E' were all allowed to vary. As the shift data do not extend significantly into the region where τ_M is dominant in determining the magnitude of Q, where Q_o would become important, a value of 0.3 was assigned to Q_o on the basis of previous observations on nickel(II).[19] The parameters derived from the data fitting appear in Table I, and the best-fit computed curves appear in Figure 3. The value of the scalar coupling constant A/h was calculated from eq 12 in which $\Delta\omega_M = [S(S+1)/3k_BT](A/h)h\omega_S$ where S is the summed unpaired electron spin, k_B is Boltzmann's constant, and ω_S is the electronic Larmor precession frequency. The value of A/h calculated in this way is close to that observed[19,23] (Table II) for $Ni(H_2O)_6{}^{2+}$ and $Ni(trien)(H_2O)_2{}^{2+}$ (trien = triethylenetetramine) and, on the assumption that A/h is not significantly dependent upon the composition of the first coordination sphere, indicates that two water molecules are coordinated per nickel(II), consistent with the stoichiometry $Ni([12]aneN_4)(H_2O)_2{}^{2+}$. The Q and $T_{2p}{}^*$ data obtained in the absence of $LiClO_4$ were not fitted, but the proximity of these data to those obtained in 3.00 mol dm^{-3} solution suggests that τ_{H_2O} is probably not markedly dependent upon electrolyte concentration.

The spectrophotometric and ^{17}O NMR data together indicate that $Ni([12]aneN_4)H_2O^{2+}$ is unlikely to exist in concentrations of more than a few percent of the total nickel(II) concentration, and subsequent discussion is based upon this assessment.

Discussion

The increased lability of $Ni([12]aneN_4)(H_2O)_2{}^{2+}$ over $Ni(H_2O)_6{}^{2+}$ (Table II) is consistent with the well-established tendency of coordinated amines to labilize aquo ligands in octahedral nickel(II) systems.[23,24] The larger ΔH^* term characterizing $Ni(H_2O)_6{}^{2+}$ is the major thermodynamic factor for the reduced lability of this species by comparison to $Ni([12]aneN_4)(H_2O)_2{}^{2+}$. It has been suggested, most recently on the basis of ΔV^* measurements,[25] that $Ni(H_2O)_6{}^{2+}$ undergoes water exchange through an I_d mechanism. This idea suggests using eq 1 to discuss both water-exchange and the species-interconversion mechanisms in terms of the equilibria given there, although, of course, other possibilities exist. The greater lability of the $Ni([12]aneN_4)(H_2O)_2{}^{2+}$ system is largely a consequence of its ΔS^* being small whereas that characterizing $Ni(trien)(H_2O)_2{}^{2+}$ is significantly negative. In principle the $Ni(trien)(H_2O)_2{}^{2+}$ species may exist as the α-cis and β-cis isomers, in which the aquo ligands are respectively equivalent and nonequivalent, and also as the trans isomer.[6,7] From spectroscopic data it appears that the cis configuration is preferred,[6] and the observation of a single water-exchange process in the ^{17}O studies (exchange rates differing by a factor of <3 are unlikely to be separately distinguished) suggests either that one isomer predominates in solution or that the rates of exchange of water in the various isomeric sites available in $Ni(trien)(H_2O)_2{}^{2+}$ are very similar. As a consequence of this uncertainty, it is not possible to present detailed stereochemical arguments in explanation of the kinetic differences between the $Ni([12]aneN_4)(H_2O)_2{}^{2+}$ and $Ni(trien)(H_2O)_2{}^{2+}$ systems. Nevertheless it is possible that the ligand restraint which requires nickel(II) to be out of the plane of the four nitrogen atoms in $Ni([12]aneN_4)(H_2O)_2{}^{2+}$ results in a relatively small stereochemical rearrangement to form the high-spin transition state and intermediate species $Ni([12]aneN_4)H_2O^{2+}$ in which the nickel(II) is out of the ligand N_4 plane also. (The five-coordinate high-spin species $Ni(tb[12]aneN_4)X^+$, where X is Cl, Br, or SCN and tb[12]aneN$_4$ is 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane, are reported[11] to have trigonal-bipyramidal geometry, but in view of the small energetic differences[26] between this geometry and square-based pyramidal geometry it is possible that $Ni([12]aneN_4)H_2O^{2+}$ could have either geometry.) In the case of $Ni(trien)(H_2O)_2{}^{2+}$ the greater flexibility of trien should permit a greater stereochemical rearrangement in the formation of the transition state. This is conjunction with the concurrent solvent rearrangements is the origin of the ΔS^*

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difference between the two systems.

A comparison of the τ values derived from the temperature-jump data (Table I) and τ_{H_2O} (Table II) suggests that the rate-determining equilibrium in the square planar to octahedral interconversion is that between high-spin Ni([12]aneN$_4$)H$_2$O^{2+} and low-spin Ni([12]aneN$_4$)$^{2+}$. Two extreme mechanisms for the spin change are possible. In the first mechanism the spin change occurs in Ni([12]aneN$_4$)H$_2$O^{2+} prior to any stereochemical arrangement, and nickel(II) subsequently moves into the N$_4$ plane with the prior, synchronous, or subsequent loss of the aquo ligand. The second mechanism differs only in that the spin change occurs subsequently to nickel(II) achieving coplanarity with the N$_4$ plane. The much shorter τ characterizing the interconversion in the Ni([13]aneN$_4$)(H$_2$O)$_2$$^{2+}$ system in which the larger macrocyclic hole (1.80 to 1.92 Å)[2,11] should ease the movement of high-spin nickel(II) into the N$_4$ plane suggests that the second mechanism may be operative. Data from linear tetraamine systems also lend some support for this thesis. Spectrophotometric studies of the square planar to octahedral interconversion in the Ni(trien)(H$_2$O)$_2$$^{2+}$ and Ni(2,3,2-tet)(H$_2$O)$_2$$^{2+}$ systems (where 2,3,2-tet is 1,4,8,11-tetraazaundecane) have been interpreted in terms of the equilibrium between high-spin Ni(trien)(H$_2$O)$^{2+}$ and low-spin Ni(trien)$^{2+}$ being rate determing in the overall square planar–octahedral interconversion.[4] A reexamination of the data suggests that this may not be so since for the Ni(trien)(H$_2$O)$_2$$^{2+}$ system the spectrophotometrically determined τ is approximately equal to 0.6 μs (296.2 K), whereas τ for the Ni(trien)(H$_2$O)$_2$$^{2+}$/Ni(trien)(H$_2$O)$^{2+}$ equilibrium will be ~0.9 μs ($1/\tau = 2/\tau_{H_2O} + k_2$—see eq 1 and Table II). It is improbable that such similar τ values could be separately distinguished from the spectrophotometric data, and thus in the Ni(trien)(H$_2$O)$_2$$^{2+}$ system either the τ values characterizing the sequential equilibrium in eq 1 are very similar or else the octahedral–five-coordinate equilibrium is rate determining.[27] In the Ni(2,3,2-tet)(H$_2$O)$_2$$^{2+}$ system, the spectrophotometrically determined τ is equal to 0.28 μs, but in this case τ_{H_2O} is not available for comparison. Nevertheless the salient fact which emerges is that the more flexible Ni(trien)(H$_2$O)$_2$$^{2+}$ and the analogous 2,3,2-tet and [13]aneN$_4$ systems are characterized by a more labile four- to five-coordinate interconversion than is Ni([12]aneN$_4$)(H$_2$O)$_2$$^{2+}$, which suggests that the ability of high-spin nickel(II) to achieve coplanarity with the N$_4$ plane is an important factor in the spin-change dynamics.

The shift in equilibrium toward the square-planar species with increase in temperature and electrolyte concentration (Table I) is consistent with such observations in related systems.[2,3,16,28] As [LiClO$_4$] increases, $\Delta H°$ decreases systematically whereas $\Delta S°$ exhibits a smaller and nonsystematic variation. Ion pairing between the nickel(II) species and ClO$_4$$^-$ ($K_{IP} \approx 0.1$, calculated from the Fuoss[29] equation) will occur to an increasing extent as [LiClO$_4$] increases and consequently the observed $\Delta H°$ and $\Delta S°$ values are composed of contributions from the ion-paired and nonpaired nickel(II) species. In both the solid and solution states, ClO$_4$$^-$ does not interact sufficiently with the nickel(II) center to perturb the low-spin state of Ni([12]aneN$_4$)$^{2+}$. Thus it is improbable that ClO$_4$$^-$ significantly modifies the component of $\Delta H°$ which arises from the bonding between nickel(II) and the ligands in the first coordination sphere of the ion-paired species. However, if significant solvation changes accompany changes in spin state and stereochemistry, ion pairing with ClO$_4$$^-$ may modify the component of $\Delta H°$ arising from such solvation changes. In the Ni([12]aneN$_4$)$^{2+}$ClO$_4$$^-$ ion pair, ClO$_4$$^-$ is likely to be in a position perpendicular to the N$_4$ plane, thereby blocking access of a potential aquo ligand to this axial coordination site, and also, as a consequence of the net difference in charge distribution between the ion pair and Ni([12]aneN$_4$)$^{2+}$, causing a change in solvation. Mechanistically the first effect attributed to ion pairing should reduce the magnitude of k_1 as is seen to be the trend (Table I) as [LiClO$_4$] increases from 2.00 to 4.00 mol dm^{-3}. This trend is also accompanied by a decrease in $\Delta H^{\ddagger}$ and a tendency for $\Delta S^{\ddagger}$ to become more negative as [LiClO$_4$] increases; but because of the possible accumulation of errors in k_1 data as a consequence of its derivation through eq 3, a detailed mechanistic interpretation of these activation data is not warranted.

We plan to carry out $\Delta V^{\ddagger}$ measurements on this system to further clarify the mechanism involved.

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Registry No. [Ni([12]aneN$_4$)](ClO$_4$)$_2$, 71911-56-3; [Ni([13]aneN$_4$)](ClO$_4$)$_2$, 71901-50-3; Ni([12]aneN$_4$)$^{2+}$, 56647-83-7; Ni([12]aneN$_4$)(H$_2$O)$_2$$^{2+}$, 71901-52-5.

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[27] It has recently been shown from microwave temperature-jump and ^{14}N NMR studies that the octahedral to five-coordinate interconversion is the rate-determining step in the overall octahedral to square-planar interconversion in the system Ni(bbh) + 2L ⇌ Ni(bbh)L + L ⇌ Ni(bbh)L$_2$ where bbh is tetradentate biacetyl bis(α-hydroxybenzylidene)hydrazone(2−)-*N*^{1},*N*$^{1'}$,*O*,*O'* and L is a substituted pyridine: Cusumano, M. *J. Chem. Soc., Dalton Trans.* **1976**, 2133, 2137. Sachinidis, J.; Grant, M. W. *J. Chem. Soc., Chem. Commun.* **1978**, 157.

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