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Thomas Vincent Rowland
(Ph. D. thesis)

October 1975

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Contents

OXYGEN-17 NMR STUDIES OF THE RATE OF WATER EXCHANGE
FROM PARTIALLY COMPLEXED NICKEL ION

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ABSTRACT

The oxygen-17 bulk water NMR linewidth and chemical shifts for an
aqueous solution of the nickel iminodiacetate complex, NiIDA, have been
measured from 0°C to 140°C at 8.134 MHz in order to determine both the
rate of chemical exchange between the two chemically non-equivalent
first coordination sphere sites and the bulk solvent and also the
scalar coupling constants, A/h. Linewidth measurements from 0°C to
100°C for a $Ni(IDA)_2^{2-}$ sample yielded estimates of the per cent time
of dissociation for the carboxylate arms and the resulting rate of
water exchange.

Two distinct rates of water exchange were measured for the three
waters of the NiIDA complex: one slow exchanging site with
$k_{298°} = 5.3 \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = 11.8$ kcal., $\Delta S^{\ddagger} = 2.7$ eu, and
$A/h = 1.8 \times 10^7$ Hz and two equivalent fast exchanging sites with
$k_{298°} = 2.4 \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 11.4$ kcal., $\Delta S^{\ddagger} = 4.6$ eu, and
$A/h = 1.9 \times 10^7$ Hz. The difference in exchange rates is thought to be
due to the bond strain about the coordinated nitrogen group which is
partially relieved by a tendency to eliminate one of the two water
positions cis to the nitrogen group, while the third water position
remains unaffected by the strain.

For the $Ni(IDA)_2^{2-}$ complex, the per cent time of dissociation of some one of the four carboxylate arms was measured to be ca. 1.5%, while the rate of water exchange was estimated to be 4×10^5 sec^{-1}, assuming that the scalar coupling constants were similar to those measured for NiIDA.

Ligand labilization trends are discussed relative to these and other complexes containing coordinated nitrogen and carboxylate groups for which water exchange rates appear in the literature. Electron donor effects, configurational strain and conformational effects are considered in this treatment, and it is concluded that the effect of bond strain is important for the IDA complex in the labilization of the remaining water molecules.

I. INTRODUCTION

Nuclear magnetic resonance spectroscopy has become a widely applied technique used in measuring the rate of water exchange between the first hydration sphere of metal ions and the bulk solvent in cases where rapid exchange occurs. Temperature studies of the broadening of the bulk water oxygen-17 NMR signal by paramagnetic transition metal ions have in the past provided much information about water exchange rates for these ions.[1a,b,c] More recently similar temperature studies on partially substituted metal ion complexes have been reported.[2] Much of the work has been done on systems utilizing ligands coordinated at nitrogen and/or oxygen positions such as NH_3, en, dien, EDTA, etc, and paramagnetic transition metal ions such as cobalt and nickel. It has been generally shown that the rate of replacement of water in the first sphere of hydration is definitely affected by the presence of the other coordinated ligands bound to the metal ion. In general, coordinated nitrogens appear to increase the lability of the remaining water molecules while for coordinated oxygens the case is not as clear.[2,3a,b]

The purpose of this thesis is to measure the rates of water exchange from the partially substituted nickel iminodiacetate complex, $NiNH(CH_2COO)_2$ or NiIDA, and to attempt to determine the reasons for the labilization of the remaining waters. The NiIDA complex has three remaining water molecules in the first coordination sphere, two of which are equivalent. This ligand is believed to be complexed with nickel in a cis (facial) manner, that is with the carboxylate groups on axes 90° from each other rather than 180°.[4a,b] Nickel has been chosen as

the paramagnetic metal ion in this experiment since the oxygen-17

nuclear magnetic relaxation has been well characterized for the

hexaquo ion, with both the chemical exchange control and relaxation

control regions reached over the easily attainable temperature range

of 0°C to 140°C. At lower temperatures (below about 60°C) relaxation

is controlled by the rate of chemical exchange of the water molecules,

while in the mid temperature region relaxation is controlled by the $\Delta\omega$

mechanism. At higher temperatures scalar coupling relaxation also

contributes appreciably.[1c] These same relaxation regions are expected

to be found over this temperature range for the partially complexed

NiIDA.

Previous work[5a,b] on the nickel nitrilotriacetate complex,

$NiN(CH_2COO)_3^-$ or NiNTA, which has two nonequivalent waters remaining

in the first coordination sphere, one trans and the other cis to the

coordinated nitrogen, has indicated that these two water molecules

exchange at considerably different rates ($k_1 = \sim 2 \times 10^4$ sec^{-1},

$k_2 = \sim 1 \times 10^6$ sec^{-1}). From the results of the oxygen-17 line broadening

temperature study it is not possible to determine which site is the

faster exchanging site. However, the case for the IDA complex, similar

to the NTA complex but with one less coordinated carboxylate arm, is

theoretically different. Since the broadening of the NMR signal is a

function of the concentration of both the paramagnetic ion and the

number of identical water coordination positions, and because for the

NiIDA complex there are two water molecules of one type (cis to nitrogen)

and one of another type (trans to nitrogen), the fast exchanging position (s) may be distinguished from the slow position(s) as long as the difference in exchange rates is large enough to be detectable.

In order to measure accurately the paramagnetic line broadening of the oxygen-17 signal, three corrections must be known. First, the natural oxygen-17 pure water linewidth must be subtracted from the experimentally observed bulk water linewidth. Although normally a trivial process, in this case where for stoichiometric reasons the NiIDA sample solution was held at a pH of 8.5, this correction was more difficult to make due to the dependancy of the oxygen-17 linewidth on pH in the pH range of about 4.0 to 9.0 at room temperature and lower. In the neutral region where the proton exchange rate from a water mole-cule is considerably slower than in an acidic or basic solution, the oxygen-17 linewidth becomes broadened due to the spin-spin splitting of the signal by the protons.[6] A study was undertaken to determine the pH of the sample solution as a function of temperature and NMR data were collected so as to know the proper linewidth blank correction both as a function of pH and temperature.

A second correction which is of interest in itself was determined by measuring the paramagnetic broadening which occurs in a fully complexed $Ni(IDA)_2^{2-}$ sample. Theoretically if the IDA were bound strongly enough to the nickel ion, there would be no paramagnetic broadening since the totally complexed nickel would not interact with the bulk water in a manner which would cause nuclear magnetic relaxation,

unless of course second sphere interactions were strong enough to contribute to the bulk water oxygen-17 relaxation. Although it was determined that the correction required due to the presence of $Ni(IDA)_2^{2-}$ in the NiIDA sample was negligible, it still provides a direct measurement of the complexing strength of the carboxylate groups in the IDA molecule. Whenever a carboxylate arm comes free from its coordinated position and allows a water molecule to exchange in and out of this position, paramagnetic broadening will occur. This effect has been measured and will be discussed. Additionally, the correction for broadening due to free nickel ion in the NiIDA sample solution was easily made using Neely's data for the nickel hexaquo ion.[1c]

Measurement of the chemical shift of the bulk water resonance position of the NiIDA sample solution relative to the resonance position of a pure H_2O^{17} sample has also been undertaken. This experiment also provides information on the water exchange rates of the NiIDA complex as well as assisting in the determination of the relevant scalar coupling constants.

II. THEORY

In general, the theory involved in interpreting the experimental results obtained consists of arriving at equations to handle both the NMR linewidth and chemical shift data. The well known Bloch equations[7] provide a phenomenological description of the macroscopic properties of nuclei in an external magnetic field H_o in terms of a longitudinal relaxation time T_1 and a transverse relaxation time T_2. When solved for the steady state, slow passage condition with no RF saturation, using audio frequency modulation side band detection methods,[8] the Bloch equations yield for the absorption mode first side band signal strength

$$S = (2/\beta) \; \frac{[J_1(\beta)]^2 \gamma H_1 T_2 M_0}{1 + T_2^2 (\Delta\omega_0 \pm \omega_m)^2} \tag{1}$$

where $\beta = \gamma H_m/\omega_m$, γ is the magnetogyric ratio of the observed nucleus, H_m is the amplitude of the audio modulation in gauss, J_1 is the first Bessel function of the first kind, H_1 is one half the amplitude of the RF field in gauss, M_0 is the equilibrium magnetization, $\Delta\omega_0 = \omega_0 - \omega$, ω_0 is the Larmor precessional frequency of the observed nucleus in the field H_0, and ω_m is the frequency of the audio modulation. The second term in the denominator of this equation may be more meaningful if rearranged and written in terms of the first side band resonance frequency, $\omega_0 \pm \omega_m$, giving $T_2^2 [(\omega_0 \pm \omega_m) - \omega]^2$. The signal will have a maximum height when $(\omega_0 \pm \omega_m) - \omega = 0$ or $\omega_0 = \gamma H_0 = \pm \omega_m + \omega$, and S will be at half height when $\{T_2[(\omega_0 \pm \omega_m) - \omega]\}^2 = 1$ or

$\frac{1}{T_2} = (\omega_0 \pm \omega_m) - \omega_{1/2} = \Delta\omega_{1/2}$, where $\Delta\omega_{1/2}$ is seen to be the half width of the signal at half height.

In general for dilute aqueous solutions of paramagnetic ions, the oxygen-17 transverse relaxation rate can be divided into two contributions,

$$\frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2p}} \tag{2}$$

where $\frac{1}{T_{2H_2O}}$ is the natural oxygen-17 linewidth of pure water and $\frac{1}{T_{2p}}$ represents the line broadening due to the presence of paramagnetic ions. For dilute solutions, where exchange is occurring between bulk and bound waters, $\frac{1}{T_{2p}}$ can be described by the following equation,[1a]

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m} \cdot \frac{\frac{1}{T_{2m}^2} + \frac{1}{T_{2m}\tau_m} + \Delta\omega_m^2}{\left[\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2\right]} \tag{3}$$

where τ_m is the lifetime of a water molecule in the first coordination sphere of the metal ion, $\frac{1}{T_{2m}}$ is the transverse relaxation rate of the coordinated or bound water molecules, $\Delta\omega_m$ is the frequency difference between the bound water oxygen-17 and the bulk water oxygen-17 signals in the paramagnetic solution, and P_m is the mole ratio of the bound waters to the bulk waters, defined by

$$P_m = \frac{x_m}{x_{H_2O}} = \frac{n[Ni^{2+}]}{55.5 - n[Ni^{2+}]} \tag{4}$$

where n is the number of water coordination sites on the paramagnetic ion and $[Ni^{2+}]$ is the molality of the paramagnetic ion.

To handle the NiIDA problem, where there are two chemically nonequivalent bound water environments, the above equation must be written as derived by Swift and Connick[1a] for three sites, where exchange is allowed from bound positions to bulk positions only and not from one bound position to another bound position. The equation then becomes

$$\frac{1}{T_{2p}} = \frac{P_{m_1}}{\tau_{m_1}} \left[\frac{\dfrac{1}{T_{2m_1}^2} + \dfrac{1}{T_{2m_1}\tau_{m_1}} + \Delta\omega_{m_1}^2}{\left(\dfrac{1}{T_{2m_1}} + \dfrac{1}{\tau_{m_1}}\right)^2 + \Delta\omega_{m_1}^2} \right]$$

$$+ \frac{P_{m_2}}{\tau_{m_2}} \left[\frac{\dfrac{1}{T_{2m_2}^2} + \dfrac{1}{T_{2m_2}\tau_{m_2}} + \Delta\omega_{m_2}^2}{\left(\dfrac{1}{T_{2m_2}} + \dfrac{1}{\tau_{m_2}}\right)^2 + \Delta\omega_{m_2}^2} \right]$$

$$(5)$$

where the subscript "1" signifies the single water coordination position and the subscript "2" signifies the remaining two equivalent water positions on the NiIDA complex, and thus P_{m_1} = [NiIDA]/(55.5 - 3[NiIDA]) and P_{m_2} = 2[NiIDA]/(55.5 - 3[NiIDA]). This equation cannot be simplified and still describe the full temperature range over which data were collected, since a T_{2m} relaxation region, a $\Delta\omega_m$ relaxation region, and an exchange controlled region are all present.

The chemical shift measurements made on the NiIDA complex system may be handled in the following manner. The bulk water chemical shift, $\Delta\omega_{H_2O}$, which is the difference between the resonance frequency of pure water and that of the bulk water in the paramagnetic solution, for dilute solutions obeys the equation[1a]

$$\Delta\omega_{H_2O} = \frac{-P_m \Delta\omega_m}{\tau_m^2 \left[\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2\right]} \tag{6}$$

or for the NiIDA case with two chemically different bound water sites

$$\Delta\omega_{H_2O} = \frac{-P_{m_1} \Delta\omega_{m_1}}{\tau_{m_1}^2 \left[\left(\frac{1}{T_{2m_1}} + \frac{1}{\tau_{m_1}}\right)^2 + \Delta\omega_{m_1}^2\right]} + \frac{-P_{m_2} \Delta\omega_{m_2}}{\tau_{m_2}^2 \left[\left(\frac{1}{T_{2m_2}} + \frac{1}{\tau_{m_2}}\right)^2 + \Delta\omega_{m_2}^2\right]} \tag{7}$$

where all terms have been previously defined. At high temperature, or more specifically when $\frac{1}{\tau_m} \gg \frac{1}{T_{2m}}$, $\Delta\omega_m^2\tau_m$, then

$$\Delta\omega_{H_2O} = -P_m \Delta\omega_m = -P_{m_1} \Delta\omega_{m_1} - P_{m_2} \Delta\omega_{m_2} \tag{8}$$

and the bulk water chemical shift experiment gives a direct measurement of the value of the relaxation parameter $\Delta\omega_m$. Bloembergen's equation[9] gives the chemical shift of the bound waters relative to pure water, $\Delta\omega_{H_2O-m}$, and can be set approximately equal to $\Delta\omega_m$ for the dilute solution case where the bound water shift will be considerably greater than the bulk water shift,

$$\Delta\omega_{H_2O-m} = \Delta\omega_m - \Delta\omega_{H_2O} = \omega S(S + 1) \frac{\gamma_S}{\gamma_I} \frac{A}{3kT} \cong \Delta\omega_m \qquad (9)$$

where ω is the precessional frequency of the observed nuclei, S is the electron spin quantum number, γ_S and γ_I are the gyromagnetic ratios of the unpaired electron and the observed nucleus, A is the scalar coupling constant in ergs, which will be discussed later, k is Boltzmann's constant, and T is the temperature. Again, for the NiIDA case there will be two different scalar coupling constants, A_1 and A_2, representing the two different water sites. The value of γ_S was calculated from the relationship

$$\gamma_S = g_{eff}\beta = \frac{\mu_{eff}}{\sqrt{S(S + 1)}} \qquad (10)$$

where g_{eff} is the effective spectroscopic splitting factor or g-factor, β is the Bohr magneton, and μ_{eff} is the effective magnetic moment for nickel ion in aqueous solution.[10] Using μ_{eff} equal to 3.22 as the observed value reported in Tables of Constants and Numerical Data (U.I.C.P.A.), No. 7, Constantes Selectionnees Diamagnetisme et Paramagnetisme by G. Foex, Masson, and Cie, Paris (1957), a value of 2.28 was obtained for g_{eff}. This is in good agreement with the value of 2.25 obtained from ESR work on hydrated nickel salts.[11]

Both the equation for the paramagnetic line broadening, $\frac{1}{T_{2p}}$, and the equation for the bulk water chemical shift, $\Delta\omega_{H_2O}$, contain the parameters τ_m and T_{2m} in addition to the above defined $\Delta\omega_m$. The exchange lifetime, τ_m, should have the normal temperature dependence expressed by the Eyring equation,

$$\tau_m = \frac{h}{kT} \exp\left[\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right] \tag{11}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for water exchange.

It has been shown that the oxygen-17 relaxation caused by the hydrated paramagnetic nickel ion, $\frac{1}{T_{2p}}$, is due to the scalar coupling mechanism,[1c] and the same is expected for the partially complexed nickel case. The scalar coupling interaction has the form $A\vec{I}\cdot\vec{S}$ where A is called the scalar coupling constant and is in effect a measure of the amount of unpaired electron overlap at the position of the nucleus I. The relaxation rate due to this scalar interaction is described by the equation[12]

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3}\left(\frac{A}{h}\right)^2\left[\tau_{c_1} + \frac{\tau_{c_2}}{1 + \omega_S^2\tau_{c_2}^2}\right] \tag{12}$$

where it has been assumed that $\omega_I \ll \omega_S$ and where

$$\frac{1}{\tau_{c_1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}}, \qquad \frac{1}{\tau_{c_2}} = \frac{1}{\tau_m} + \frac{1}{T_{2e}} \tag{13}$$

where T_{1e} and T_{2e} are the longitudinal and transverse electronic relaxation times. In the case of nickel, since $\tau_m \gg T_{1e}$, T_{2e}, the scalar coupling correlation time which will be designated τ_e may be written

$$\tau_e = T_{1e} + \frac{T_{2e}}{1 + \omega_S^2 T_{2e}^2} \quad . \tag{14}$$

Again, similar equations for $\frac{1}{T_{2m_1}}$ and $\frac{1}{T_{2m_2}}$ must be written

utilizing the scalar coupling constants A_1 and A_2 respectively for

the NiIDA case. In general, since the T_{1e} and T_{2e} contributions to the

correlation time cannot be distinguished in the following experiments,

for computer fitting purposes the equation for the correlation time

can be simplified to the form

$$\tau_e = \tau_e^o \exp \frac{V}{RT} \tag{15}$$

where V represents the activation energy for the electronic relaxation.

III. EXPERIMENTAL

A. Sample Preparation

The pH vs. temperature line broadening study of pure water to determine blank corrections for the NiIDA samples was conducted using 10% H_2O^{17} buffered with 0.1 M NH_4ClO_4 and adjusted to the desired pH with NaOH. Multiple samples were run with pH's varying from 8.00 to 9.00 over the temperature range of 0°C to 45°C. Above 45°C at pH 8.2 or higher no additional correction above the normal (acidic or basic) H_2O^{17} linewidth is required.

NiIDA sample solutions were prepared from recrystallized $Ni(ClO_4)_2 \cdot 6H_2O$ (GFS) and iminodiacetic acid (Eastman Kodak) recrystallized successively from acidic water and ethanol. The recrystallized $Ni(ClO_4)_2$ was analyzed spectroscopically to be free of other paramagnetic impurities. Solutions of about 2 ml. volume were prepared by weight to be approximately 0.025 M in both the mono and bis complexes of nickel IDA using ~10% enriched H_2O^{17}. The pH of the sample solutions was adjusted to 8.5 using high purity NaOH, and all samples contained ~5×10^{-4} M NH_4ClO_4 as a buffer. Concentration calculations were made using the complexing constants shown in Table I taken from Sillen and Martell's compilation, Stability Constants of Metal-Ion Complexes,[13] and sample conditions (pH, concentration of constituents) were such as to maximize NiIDA concentration while minimizing dependency on the nickel iminodiacetate complexing constants without suffering nickel hydroxide solubility problems.

Table I. Equilibrium Constants for the NiIDA and $Ni(IDA)_2^{2-}$ Complexes[13]

| Reaction	$\log K_{30°K}$ (mole^{-1} litre)	ΔH^O (kcal)	ΔS^O (eu)
Acid Dissociation Constants:			
$H^+ + IDA^{2-} = H(IDA)^-$	9.12	-8.15	15.4
$H^+ + H(IDA)^- = H_2(IDA)$	2.98		
Nickel Complexing Constants:			
$Ni^{2+} + IDA^{2-} = Ni(IDA)$	8.26	-5.05	20.0
$Ni(IDA) + IDA^{2-} = Ni(IDA)_2^{2-}$	6.35	-4.5	13.1
Nickel Hydroxide Solubility Product:			
$Ni^{2+} + 2(OH^-) = Ni(OH)_2 \downarrow$	-15.0	-6.7	

The bis nickel IDA complex solutions were prepared in a similar manner, but with a $Ni(IDA)_2^{2-}$ concentration of approximately 0.50 M and negligible NiIDA concentration, and with pH adjusted to about 9.2. A similar $Zn(IDA)_2^{2-}$ sample was prepared as a diamagnetic water blank having similar properties.

Between the temperatures of 0°C and 60°C all samples were run in 11 mm. O.D. Pyrex tubes (~2ml. volume) constructed with thermocouple wells immersed in the solution, and were sealed under vacuum. Above 60°C, machined teflon sample tubes of similar dimensions were used for reasons explained below. These tubes, which utilized threaded pressure caps, were tested to 140°C (3.5 atm.) for leaks and were sealed at atmospheric pressure. Difficulty was experienced in holding the pH of the 0.025 NiIDA samples constant for the duration of an NMR temperature study. At high temperatures a reaction occurred within the sample cell manifesting itself by the appearance of a small amount of white precipitate and a decline in pH. Depending on the temperature and length of heating, the initial pH of 8.4 declined as much as one pH unit, causing a considerable amount of neutral region linebroadening. The precipitate was analyzed to be high in both boron and silicon while all sample constituents were analyzed free of these contaminants, leading one to suspect the glass. Using a teflon sample cell and 0.025 M NiIDA at a pH of 8.44 resulted in considerably less pH change (-0.24 pH units) and the appearance of no ppt. after heating for six hours at 105°C, while the same treatment resulted in a much larger change (-0.84 pH units) for an identical sample in a pyrex tube.

Care was taken in sample preparation to use no soft glassware and all glass sample cells were sealed in such a manner as to preclude direct heating of the sample solution. The pH of the sample was checked upon transfer from pyrex to teflon tube for the high temperature work and after each run above 100°C to ensure that a negligible pH change had taken place.

B. NMR Linewidth Measurements

For all linewidth measurements a Varian Associates model V4200 wide line spectrometer was used in conjunction with a model V4311 fixed frequency transmitter/receiver operating at 8.134 MHz. The diode or leakage detection mode was employed and care was taken to avoid RF power saturation, with power settings between 0.04 and 0.23 volts rms depending on the linewidth. A Princeton Applied Research model HR-8 lock-in amplifier was used to provide audio modulation and phase sensitive detection. The modulation amplitude setting was determined to maximize the peak height of the first sidebands and the audio frequency was set such that the half width of the resonance signal was always at least an order of magnitude smaller than the modulation frequency. A diagram of the spectrometer as used for the linewidth measurements is shown in the right half of Fig. 1. Data were collected by scanning continuously through the upfield and downfield first sidebands four times, allowing eight linewidth measurements. Since the separation of the first sidebands is exactly twice the modulation frequency, the linewidths may be easily calculated.

PROTON LOCK SYSTEM   O^{17} NMR SPECTROMETER
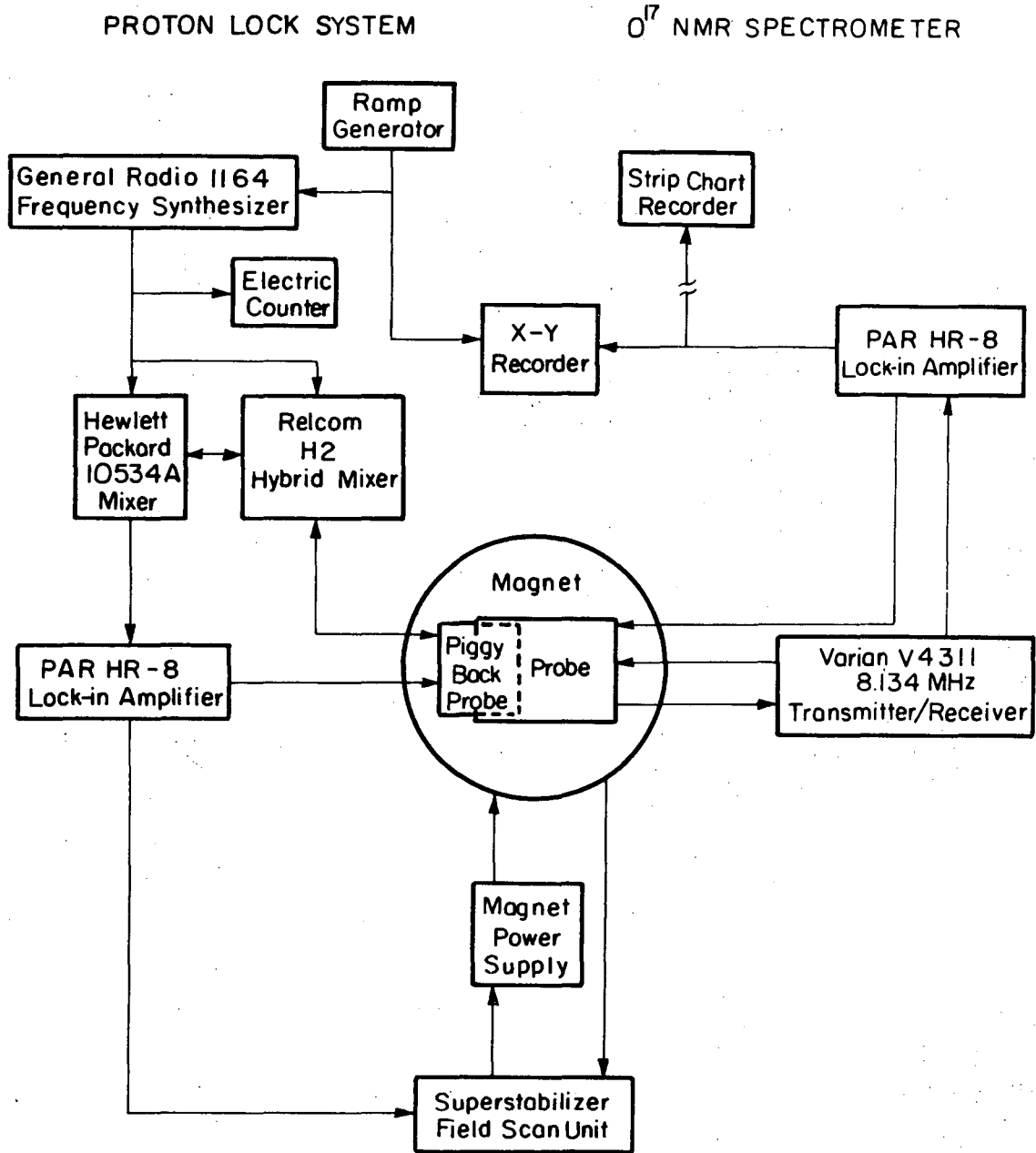
XBL 759-7194

Fig. 1. Schematic of oxygen-17 NMR spectrometer and proton lock
         system as used in linewidth and chemical shift measure-
         ments.

C. Chemical Shift Measurements

Chemical shift measurements of the bulk water resonance relative

to the pure H_2O^{17} resonance were made using the same spectrometer,

but additionally utilizing an external NMR proton lock system which

was used for both locking and scanning purposes. This system consisted

of a scannable 60 MHz radio frequency source, a Varian piggy back probe

containing a doped water sample which was fitted inside the main probe

body, a passive RF detection system, and an additional phase sensitive

lock-in amplifier for audio modulation and detection in the lock system

as shown in the left half of Fig. 1. During the chemical shift experiment

the magnetic field was scanned by driving the frequency synthesizer with

a ramp generator, causing the proton RF to change which in turn caused

the superstablizer/scan unit to scan the magnetic field. This system

allowed accurate calibration of the magnetic field strength by counting

the proton lock frequency at the beginning and end of each scan, and

thus the absolute position of the resonance lines could be measured

accurately to determine the chemical shifts. The results of four scans

on both the water blank and the NiIDA samples were averaged to give

a single data point.

The temperature of the sample in the probe was controlled by

flowing heated or cooled dry nitrogen gas past the sample tube which was

surrounded by a Dewared probe insert. The temperature for each run

was taken as the average reading of two copper-constantan thermocouples

read to 0.1°C, one placed in the nitrogen stream directly below the

sample tube, the other in the thermocouple well in the top portion of

the sample tube. Both thermocouples were read immediately before and
after each run, with temperature differences between top and bottom
ranging from zero at room temperature to 5°C at 140°C. In all runs
utilizing teflon sample tubes, in order to facilitate rapid temperature
equilibration within the probe, the sample tubes were preheated in an
external oil heat bath before being transferred to the probe. This
reduced the total time the sample remained at elevated temperatures
in order to minimize the possibility of decomposition due to heat.

D. Computer Fitting Programs

The linewidth data were fitted to Eq. (5) using the Oak Ridge
General Least Squares (ORGLS) computer program.[14] The standard
deviation (68% confidence interval) in the eight linewidths measured
for each data point was used as the weighting factor. A correlation
matrix consisting of an array of correlation coefficients which describe
the linear dependence of each parameter on each other parameter (where
one represents complete correlation)[15] was printed at the end of the
output section.

The results of the linewidth and chemical shift measurements were
simultaneously fitted to Eq. (5) and Eq. (7) using the Dye and Nicely
General Purpose Curvefitting Program.[16] Again standard deviations were
used as weighting factors for both sets of data and a list of multiple
correlation coefficients which describe the total linear dependence of
each parameter on all other parameters[15] was printed in the output of
the program. The curvefitting subroutine contained IF statements
directing the program to fit the proper data set to the proper equation,

as shown in Appendix II. Fortuitously, the numerical values of the linewidths and chemical shifts were of the same order of magnitude in the NiIDA experiment as were the weighting factors for both experimental data sets. Were this not true, one data set would have to be normalized to the other to provide a reasonably weighted fit.

IV.   RESULTS AND DISCUSSION

A.   Introduction: NiNTA Complex
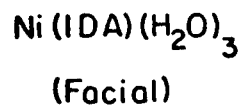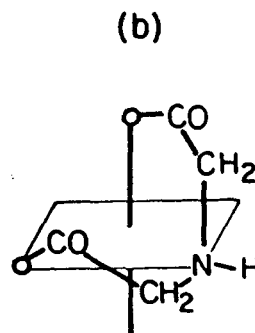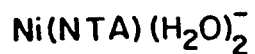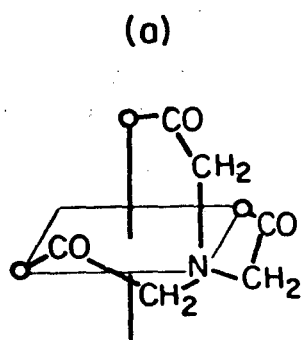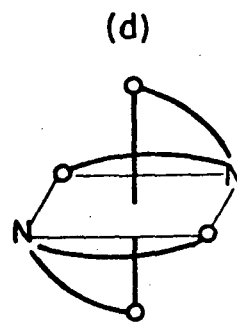
In 1968 Kustin and Vriesenga, in work done in this laboratory,[5]
observed two distinct water exchange rates from the first coordination
sphere of the nickel nitrilotriacetate complex, $NiNTA(H_2O)_2^-$, which
is shown in Fig. 2(a). It is evident from the figure that the two
remaining water molecules are not structurally equivalent, one being
trans to a tertiary nitrogen, the other being cis to the nitrogen
and in the plane of coordination of the carboxylate groups. Preliminary
results from this experiment, to be published later, have shown that
the two exchange rates differ by about a factor of seventy at room
temperature. The linebroadening measurements, as a function of
temperature, produce two easily distinguishable minima when plotted
as T_{2p} vs. $10^3/T$, showing two exchange controlled and two $\Delta\omega_m$ relaxation
regions. The chemical shift measurements also show two flat "rapid
exchange" areas as expected when plotted as $\Delta\omega_{H_2O}$ vs. $10^3/T$.
Unfortunately, while the large difference in rates for the two exchange
positions appears to confirm the structural non-equivalence of these
sites, the oxygen-17 NMR experiment does not identify the fast or slow
site.

Vriesenga has treated the linewidth and chemical shift data in
two manners.[5b] The first method was to determine the scalar coupling
constants, A_1 and A_2, from the best visual fit of the chemical shift
plot, then choosing the activation parameters $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$

(a)

Ni(NTA)(H$_2$O)$_2^-$

(b)

Ni(IDA)(H$_2$O)$_3$

(Facial)

(c)

Ni(IDA)$_2^{2-}$

Cis-Facial

(d)

Ni(IDA)$_2^{2-}$
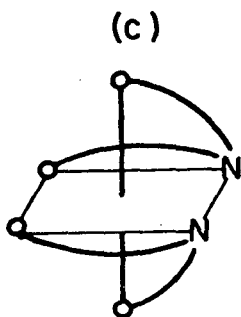
Trans-Facial

XBL 759-7195

Fig. 2. (a) Configuration of the nickel nitrilotriacetate (NiNTA$^-$) complex.
(b) Configuration of the facial isomer of the mono nickel iminodiacetate (NiIDA) complex.
(c) and (d) Configuration of the two possible facial isomers of the bis nickel iminodiacetate [Ni(IDA)$_2^-$] complex.

to give the best visual fit of the linewidth plot. A constant value
for the contribution due to the scalar coupling relaxation mechanism,
$1/T_{2m}$, which becomes appreciable only at high temperatures was assumed.
This procedure yielded the following parameters:

$$A_1/h = 3.2 \times 10^7 \text{ Hz} \qquad A_2/h = 2.9 \times 10^7 \text{ Hz}$$

$$\Delta H_1^{\ddagger} = 11.0 \text{ kcal} \qquad \Delta H_2^{\ddagger} = 11.3 \text{ kcal}$$

$$\Delta S_1^{\ddagger} = 5.6 \text{ eu} \qquad \Delta S_2^{\ddagger} = -0.7 \text{ eu}$$

$$k_{1_{298°}} = 1.1 \times 10^6 \text{ sec}^{-1} \qquad k_{2_{298°}} = 1.7 \times 10^4 \text{ sec}^{-1}$$

The rate constant $k_{298°}$ represents the rate of exchange of a water
molecule at a particular site on the coordinated ion. Rigorously,
$k_{298°}$ is defined as $1/\tau_m$ (the reciprocal of Eq. 11), where τ_m is the
mean lifetime of a water in a bound site.

However, a second treatment of the NiNTA linewidth data utilizing
a six parameter non-linear least square computer fitting program
yielded a slightly different set of parameters:

$$A_1/h = 2.9 \times 10^7 \text{ Hz} \qquad A_2/h = 2.6 \times 10^7 \text{ Hz}$$

$$\Delta H_1^{\ddagger} = 13.6 \text{ kcal} \qquad \Delta H_2^{\ddagger} = 13.6 \text{ kcal}$$

$$\Delta S_1^{\ddagger} = 15.1 \text{ eu} \qquad \Delta S_2^{\ddagger} = 6.6 \text{ eu}$$

$$k_{1_{298°}} = 1.3 \times 10^6 \text{ sec}^{-1} \qquad k_{2_{298°}} = 1.8 \times 10^4 \text{ sec}^{-1}$$

Both the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are larger in this treatment than from the original hand fitting procedure. However, the computer program does show a strong correlation between the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ pairs, suggesting that the curve can be fit fairly well with a number of different enthalpy/entropy values. Additionally, the rates calculated from the two different data treatments do not differ greatly and the ratio k_1/k_2 is quite similar in both cases, 65 for the hand fit and 72 for the computer fit.

Data have also been collected by Vriesenga at 2 MHz as well as at 8 MHz in the work described above in the hope of fixing the parameters more accurately. Proton NMR work where the proton signals of the NTA ligand have been studied as a function of temperature suggests that the faster water exchanging site is cis to the nitrogen coordinating position. This work has served as background and stimulation for the NiIDA investigation, whose main purpose has been in measuring the water exchange rates to determine which site exchanges more rapidly and the reasons for this labilization.

B.   NiIDA Linewidth Measurements and Results

A plot of the oxygen-17 water blank relaxation time, $T_{2(H_2O)}$, used in determining T_{2p} for the NiIDA system is shown in Fig. 3 plotted against $10^3/T$. This curve has been drawn to represent the proper water blank correction for a buffered 0.025 M NiIDA sample. Since the pH of the sample varies slightly with temperature (from pH 8.3 at 45°C to 8.7 at 0°C) and the linewidth varies with pH, a number of water samples adjusted to slightly different pH values had to be run within the
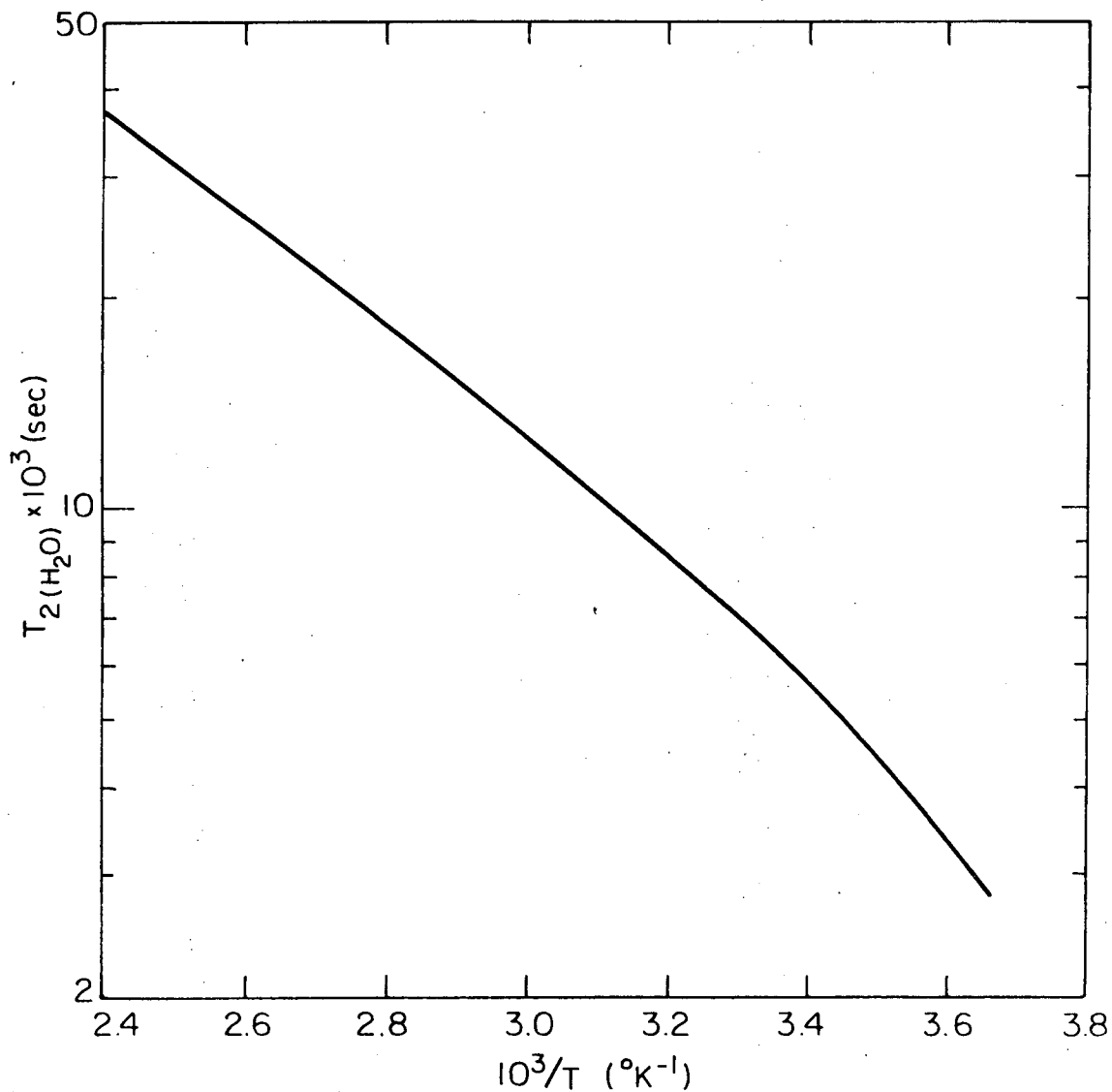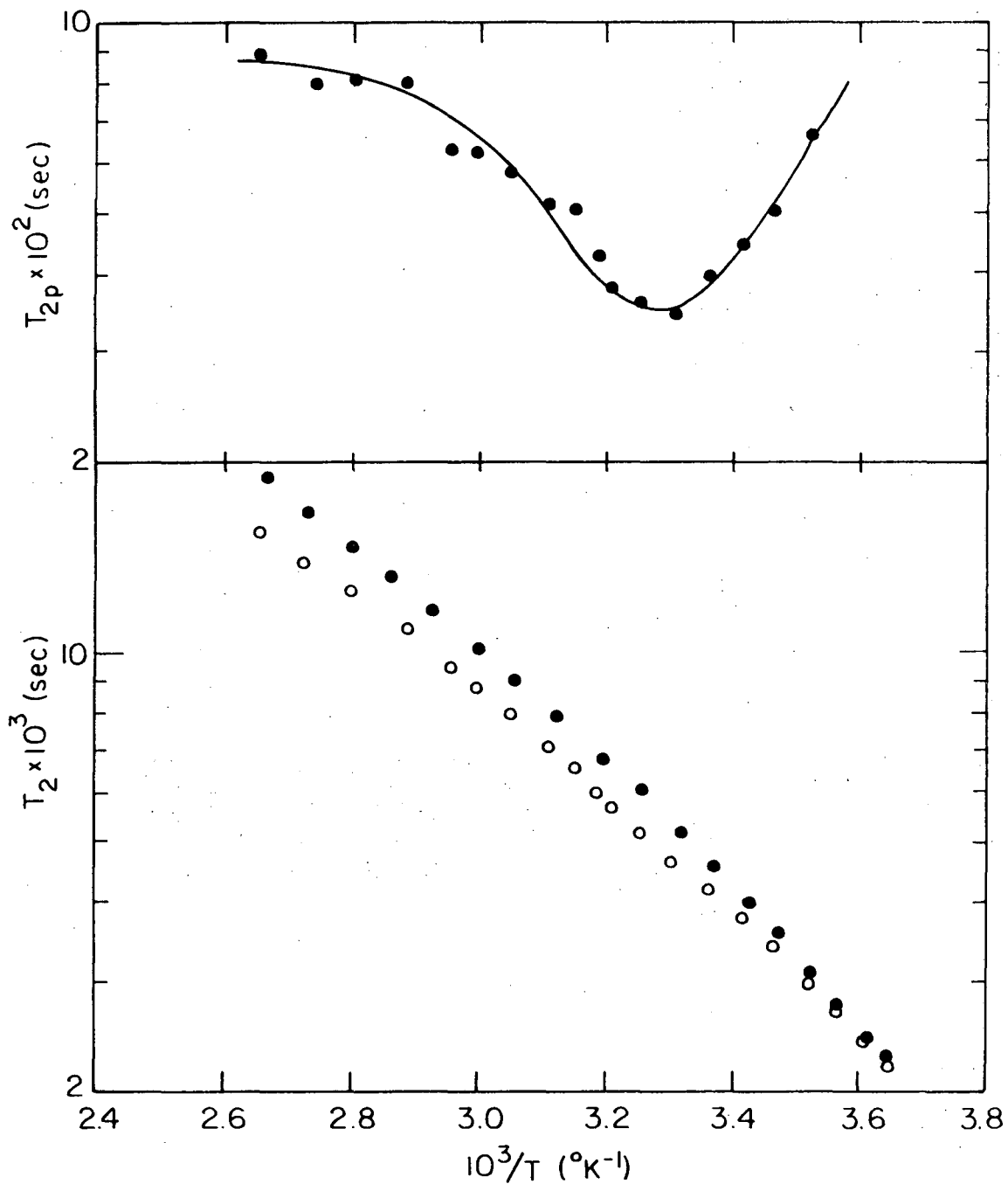
Fig. 3. $T_{2(H_2O)} \times 10^3$ versus the reciprocal of absolute temperature
for the oxygen-17 NMR of a water solution buffered with
0.10 M NH_4ClO_4 and adjusted to pH $\sim$ 8.4 at 25° with NaOH.
For exact pH adjustment as a function of temperature see
data table in the appendix.

temperature range of 0°C to 45°C. Data for these samples and their pH
values are listed in Appendix I. Above 45°C the curve in Fig. 3
represents the relaxation time of pure basic or acidic water, the rate
of proton exchange from the water molecule being fast enough to eliminate
the neutral region linebroadening effect.[6] Water blank correction
values for the NiIDA data points are also listed in Appendix I.
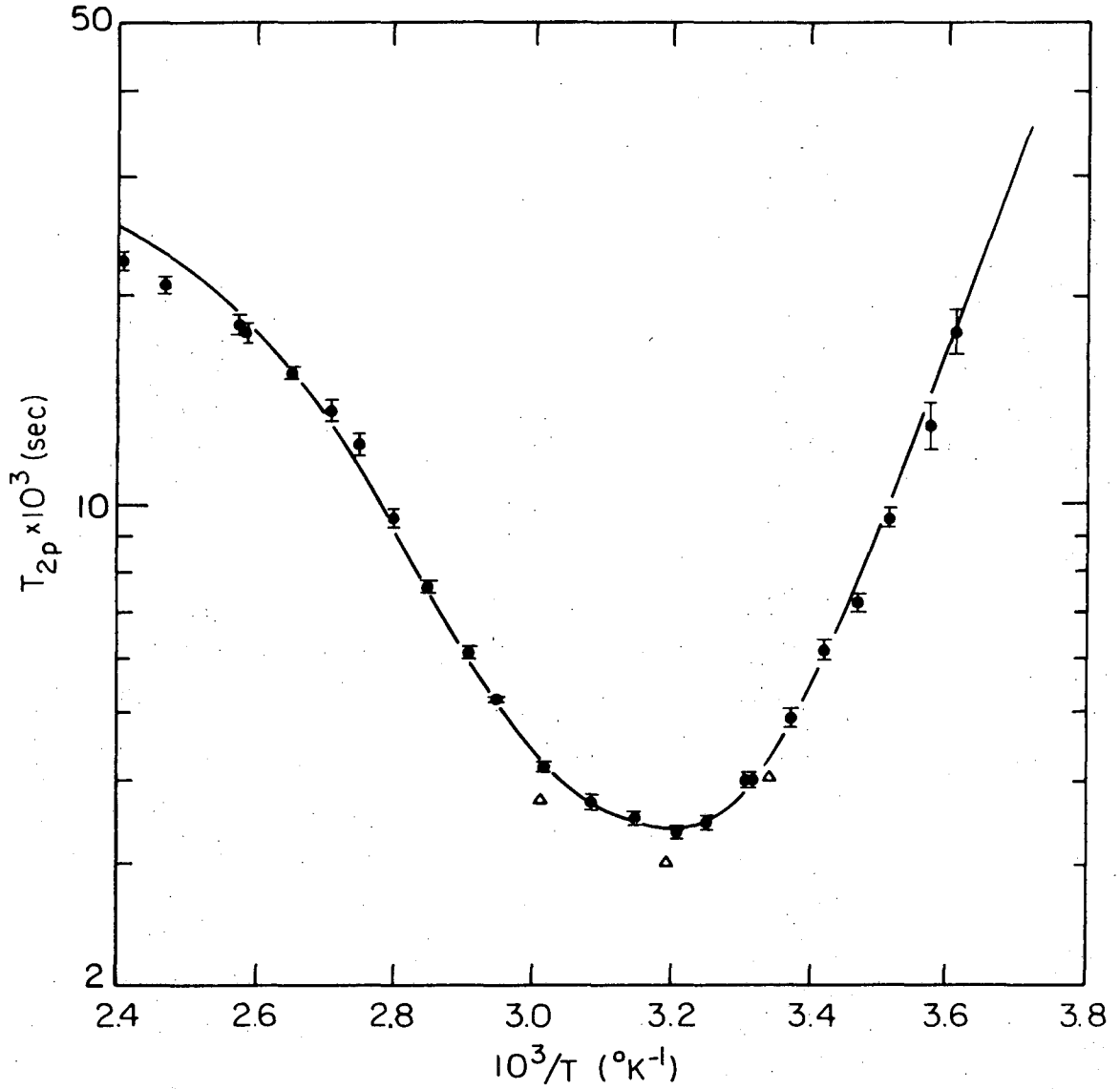
The correction for the free hexaquo nickel ion in the NiIDA
solution was calculated from Neely's data[1c] for a room temperature
concentration of 2.99×10^{-4} M Ni^{2+} and is listed in Appendix I as
$T_{2(Ni^{2+})}$. In addition, a correction for the cis complex, $Ni(IDA)_2^{2-}$,
whose concentration is approximately equivalent to that of the NiIDA
species, must be considered. A plot of T_{2p} vs. $10^3/T$ for this complex
is shown in the upper portion of Fig. 4. Although detectable line-
broadening has been observed with a sample of 0.5 M $Ni(IDA)_2^{2-}$, the
broadening due to the presence of this species in the NiIDA sample is
negligible relative to the NiIDA linebroadening itself. For example,
at room temperature for the 0.0249 M NiIDA sample, the linewidth
contribution due to the 0.0249 M $Ni(IDA)_2^{2-}$ species will be approximately
0.3 Hz where the total paramagnetic linewidth is about 40 Hz; thus the
$Ni(IDA)_2^{2-}$ can be seen to contribute less than 1% of the total
linebroadening. At higher and lower temperatures the per cent contribu-
tion is similar. The linebroadening data for $Ni(IDA)_2^{2-}$ will be
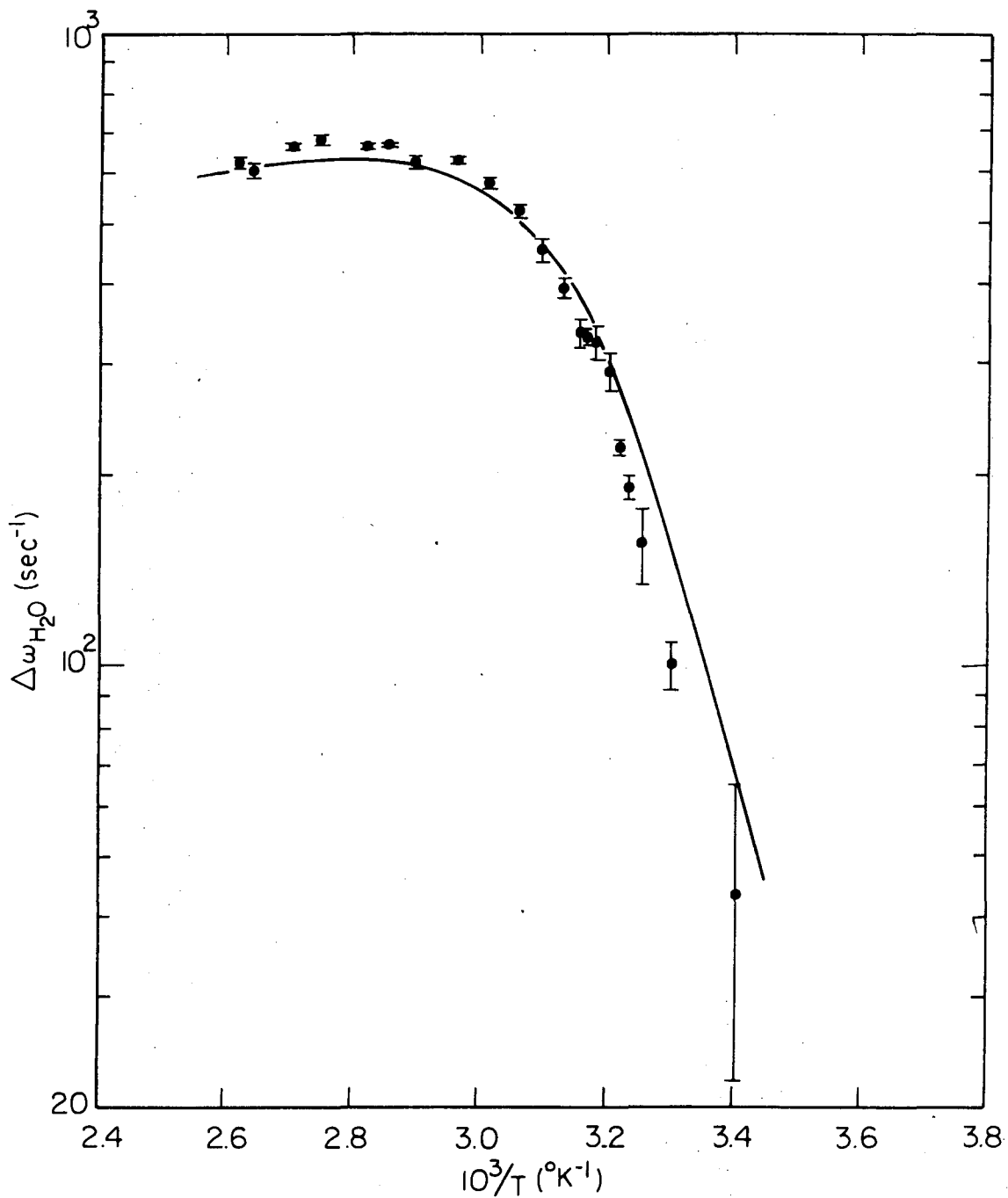discussed in a later section for additional meaning.

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Fig. 4. Upper: $T_{2p} \times 10^2$ versus the reciprocal of absolute temperature for the oxygen-17 NMR of a 0.4970 M Ni(IDA)$_2$$^{2-}$ sample at pH 9.2 at 25°. Lower: $T_2 \times 10^3$ versus the reciprocal of absolute temperature for ● - 0.515 M Zn(IDA)$_2$$^{2-}$ at pH 9.2. O - 0.497 M Ni(IDA)$_2$$^{2-}$ at pH 9.2.

A plot of T_{2p} vs. $10^3/T$ for the NiIDA complex is shown in Fig. 5,
where the curve drawn through the data points represents a six parameter
computer fit (ORGLS) for these linewidth data. Figure 6 shows the
chemical shift of the bulk water resonance position relative to pure
H_2O^{17}, $\Delta\omega_{H_2O}$, plotted against $10^3/T$ for a similar NiIDA sample where
the solid line has been calculated using the parameters from the
linewidth fit. Figure 7 shows the linewidth curve with the individual
fitting for chemical exchange, $\Delta\omega_m$ relaxation, and scalar coupling
relaxation for both the fast and slow exchanging sites. These lines
were also calculated from the best fit parameters of the computer
program. The intersection of the chemical exchange line, τ_{m_1}/P_{m_1},
and the $\Delta\omega_m$ line, $1/(P_{m_1}\tau_{m_1}\Delta\omega_{m_1}^2)$, can be seen to be to the left of
and about a factor of two higher than the intersection of the other
exchange line and $\Delta\omega_m$ line. Thus the fit indicates that there are two
fast exchange sites and one slow site. Note that neither T_{2p} nor $\Delta\omega_{H_2O}$
has been multiplied by the concentration factor P_m as this may prove to
be misleading when dealing with a curve fitted by an equation involving
more than one P_m value (in this case P_{m_1} and P_{m_2} where $P_{m_2} = 2P_{m_1}$).
The data points may of course be multiplied by $P_m = P_{m_1} + P_{m_2} = 3P_{m_1}$
for the purpose of comparison with samples of different concentration
or with different chemical systems, but the fitting lines representing
chemical exchange in Fig. 7 then become $\frac{3}{2}\tau_{m_2}$ and $3\tau_{m_1}$ instead of
the simpler τ_{m_2}/P_{m_2} and τ_{m_1}/P_{m_1}, and similarly for the chemical shift
curve.

XBL 759-7198

Fig. 5. $T_{2p} \times 10^3$ versus the reciprocal of absolute temperature
for the oxygen-17 NMR of a 0.0249 M NiIDA sample at
pH 8.4 at 25°. The curve was calculated using Eq. (5)
and the "linewidth only" computer fitting parameters
in Table II. Δ - 0.0147 M NiIDA at pH 3.1.

Fig. 6. $\Delta\omega_{H_2O}$ versus the reciprocal of absolute temperature for the oxygen-17 chemical shift of the bulk water in an aqueous solution of 0.0259 M NiIDA. The curve was calculated using Eq. (7) and the "linewidth only" computer fitting parameters in Table II.
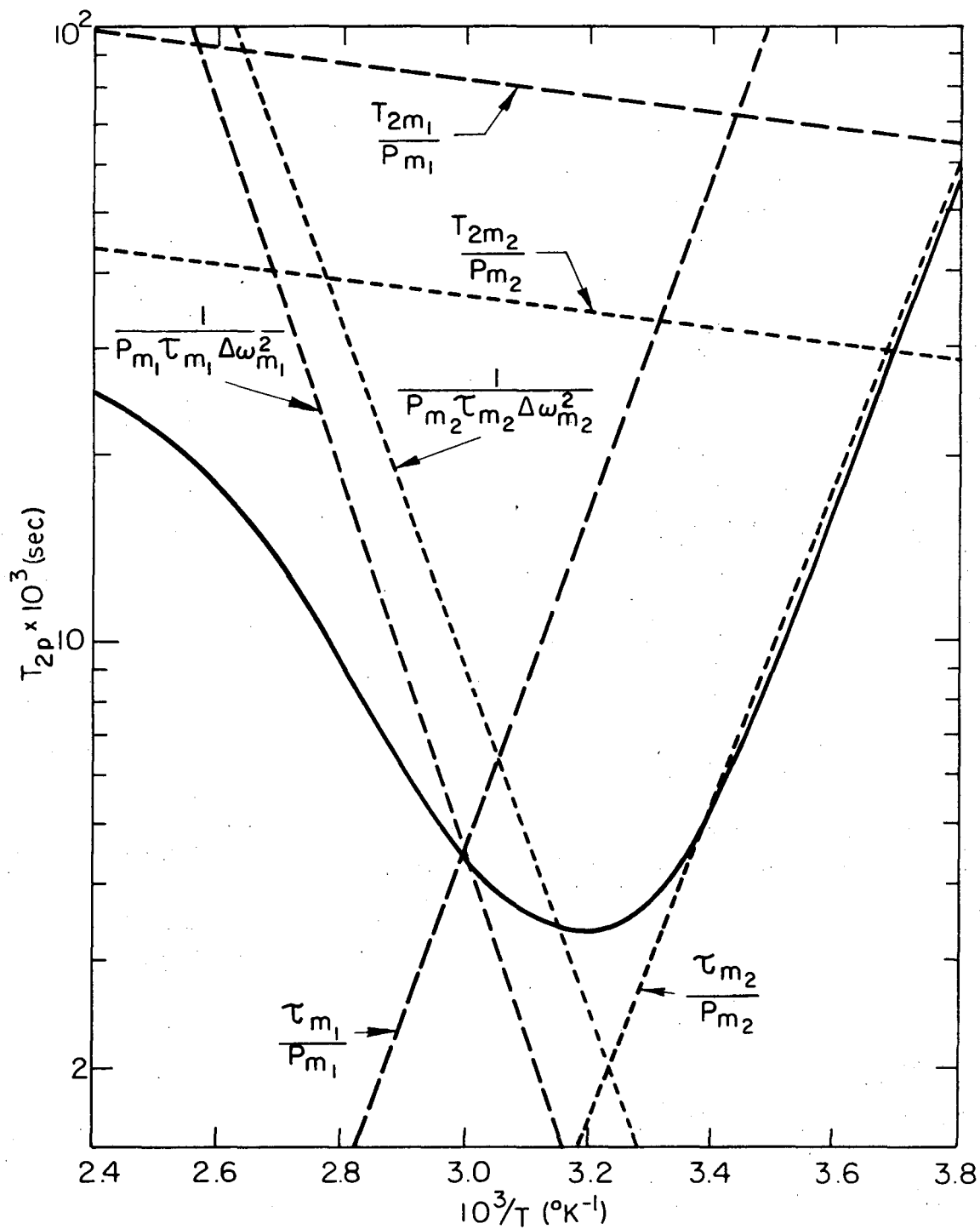
XBL 759-7199

XBL 759-7200

Fig. 7. $T_{2p} \times 10^3$ versus the reciprocal of absolute temperature for the oxygen-17 NMR of 0.0249 M NiIDA where the curve represents the "linewidth only" computer fit. The long dashed lines represent the individual fit lines as labeled for site 1; the short dashed lines represent the same for site 2.

A preliminary oxygen-17 NMR study of an acidic (pH 3.09) NiIDA

sample was undertaken by Vriesenga[5b] and is in general agreement with

the high pH results reported here. In the present study a number of

linewidth points were also recorded for an acidic (pH 3.13) 0.0147 M NiIDA

sample and are shown with the proper concentration normalization as

triangles in Fig. 5 and in the data table in Appendix I. The appropriate

corrections have been made for other nickel species in the solution.

The agreement is again reasonable and suggests that there are no large

pH effects on the rate of water exchange from the NiIDA complex.

C. NiIDA Chemical Shift Measurements

The correction for the shift caused by hexaquo nickel ion in the

NiIDA solution was also calculated from Neely's data.[1c] Since no

appreciable chemical exchange was observed from the $Ni(IDA)_2^{2-}$ species,

no correction to the shift data was required. However, because the

chemical shift measurements were done in cylindrical tubes rather than

spherical tubes in order to improve the signal to noise ratio, a

magnetic susceptibility correction was necessary. This correction was

determined using the normal equation for the field inside a long

cylindrical tube,[17]

$$H = H_o(1 + \frac{2\pi}{3} \kappa) \tag{16}$$

where κ, the volume susceptibility of the sample, was determined from the

relationships[18]

$$\kappa = [Ni]\chi_m \tag{17}$$

and

$$\chi_m = \frac{Ng_{eff}^2\beta^2}{3kT} \, S(S+1) + 2N\beta^2\Lambda \tag{18}$$

where N is Avogadro's number, and $\Lambda = \frac{4}{\Delta}$ for nickel where Δ is the crystal field splitting in cm^{-1}. The first term is the spin only term (quenched orbital angular momentum is assumed) written with g_{eff} to take into account the spin orbit coupling. The second term is a second order term arising from orbital contributions only. These corrections are tabulated in the NiIDA chemical shift data table in the appendix.

An additional correction was made to the chemical shift data in order to compensate for the fact that a non-logarithmic plot of $\Delta\omega_{H_2O}$ vs. $10^3/T$ as shown by the solid circles in Fig. 8 does not appear to approach zero asymptotically at low temperature as is expected from the equation for the shift, but rather approaches some negative value. At low temperature where for a nickel sample

$$\Delta\omega_m^2 \gg \frac{1}{\tau_m^2} \, , \, \frac{1}{T_{2m}} \, ,$$

the chemical shift equation can be reduced to

$$\Delta\omega_{H_2O} = \frac{-P_m}{\tau_m^2\Delta\omega_m} \tag{19}$$

and thus the correctional factor can be determined by adding a constant to the data points in the non-logarithmic plot until the curve approaches zero at low temperature or by adding a constant to the

low temperature points in a semi-log plot and checking them against
a straight line fit. The second method was employed, using the seven
lowest temperature data points, adding a small constant and checking
the straight line fit by programmable calculator until a constant
was found which best allowed the log of the data points to approximate
a straight line. Although the higher temperature points used in this
fitting procedure do not meet the condition $\Delta\omega_m^2 \gg 1/\tau_m^2$, the
resulting constant, when added to the data points can be seen (open
circles in Fig. 8) to give values which closely approach zero at low
temperature. The value of this constant as shown in Fig. 8 and the
chemical shift data table was determined to be 44 sec^{-1} which is
approximately a 7% correction to the high temperature region of the
curve. Although this baseline correction is not based on direct
experimental observation, since there is no reason to expect that Eq. (7)
is not valid for this experimental system, it was assumed that the
normal low temperature chemical shift behavior would occur. Such a
residual shift might be attributable to some unknown systematic error
or to improper susceptibility corrections due either to irregular
sample cell shape or to the paramagnetism of the glass sample cell
itself. The susceptibility correction calculations made using Eq. (16)
for an infinite cylinder yielded values on the order of 21 sec^{-1}.
This correction is of the same size as the probable error for each
data point, which is on the average about 15 sec^{-1}. A quick check at
room temperature using a spherical sample cell for the paramagnetic
nickel sample solution showed a chemical shift virtually identical to
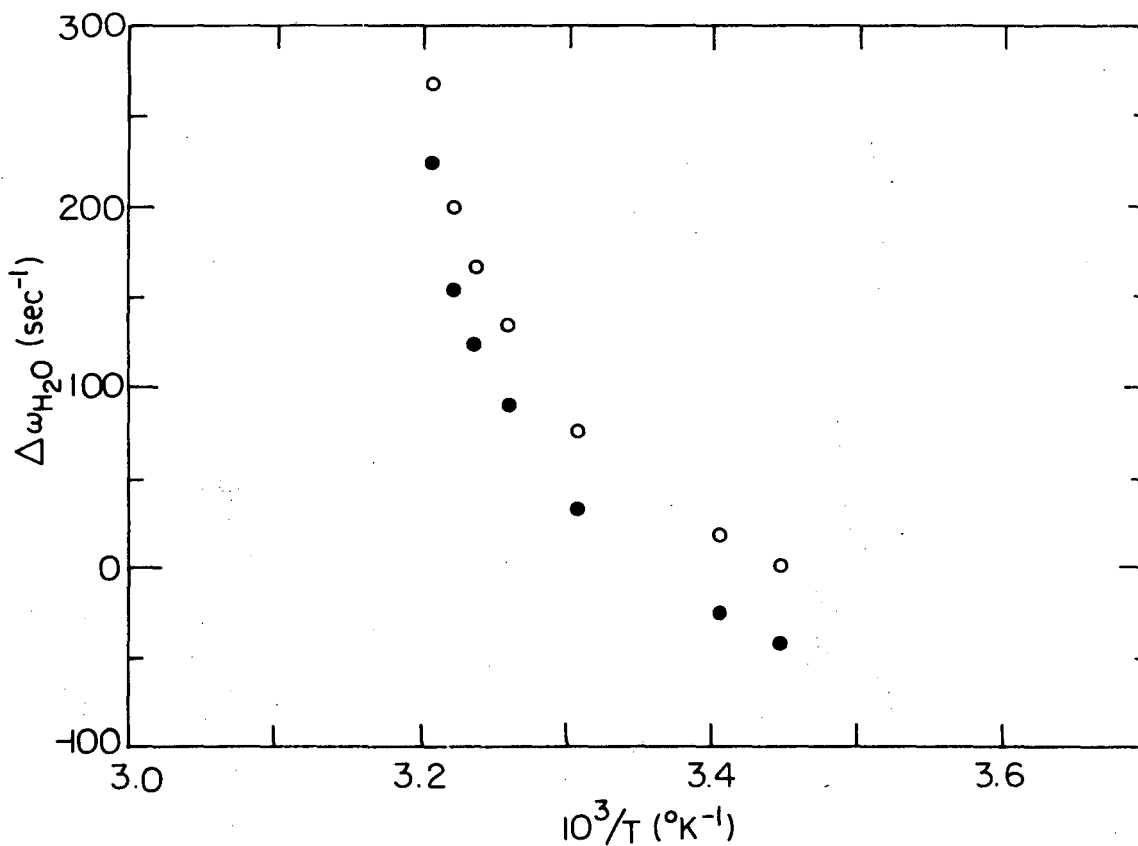
XBL 759-7203

Fig. 8. Cartesian plot of $\Delta\omega_{H_2O}$ versus the reciprocal of absolute temperature for the oxygen-17 chemical shift of the bulk water in a 0.0259 M NiIDA solution showing:

● - original low temperature data points approaching a
     negative value at low temperature.

O - corrected data points, raised by a constant 44 sec^{-1},
     approaching zero at low temperature.

the shift measured using the cylindrical sample tube where the infinite cylinder correction had been made. However the probable error in this set of measurements was larger (25 sec^{-1}) than for those made in cylinders due to the loss in the signal to noise ratio because of the diminished sample volume. According to Dickenson,[17b] for a sample tube with this length to diameter ratio, approximately 70% of the full infinite cylinder correction should be used. Because of the large probable errors involved, this comparison does not really allow a more accurate calculation of the susceptibility correction, but serves only to show that within experimental error compatible chemical shift values could be measured in both spherical and cylindrical tubes. Thus, the full infinite cylinder correction was used, the difference between this and Dickenson's suggested 70% value being small relative to the probable error of the measurements. Although the spherical sample comparison does not rule out the possibility of an improper susceptibility correction (indeed, the combination of the probable errors from the cylinder and sphere measurements is not much less than the 44 sec^{-1} correction), the baseline correction made by fitting the low temperature data appears to be a reasonable manner in which to handle the data.

D. Computer Fitting Results

The curves through the data points of Figs. 5 and 6 represent the theoretically calculated curves using Eqs. (5) and (7) respectively and the computer fitted parameters listed in Table II, where the computer fit is to the linewidth data only.

Table II. Curve Fitting Parameters for 0.0249 M NiIDA Linewidth Data

and for 0.0259 M NiIDA Chemical Shift Data

Linewidth Fit Only	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (eu)	$\frac{A}{h}$ (Hz)	$\tau_e^o (\sec^{-1})$	k_{298° $(\sec^{-1})$
Site 1	11.8	2.7	1.8×10^7	1.3×10^{-12}	5.3×10^4
Site 2	11.4	4.6	1.9×10^7	1.3×10^{-12}	2.4×10^5
Linewidth & Chemical Shift					
Site 1	13.8	8.8	1.9×10^7	1.5×10^{-12}	4.3×10^4
Site 2	12.1	7.2	2.0×10^7	1.5×10^{-12}	2.9×10^5

The second set of values comes from a similar computer fit, but where

both the linewidth and chemical shift data were fit simultaneously

as shown by the solid lines in Figs. 9 and 10. The quantities $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$

and A/h were fitted parameters in all programs; however, the value of

V in the electronic correlation time, τ_e, as defined by Eq. (15), was

assumed to be 0.6 kcal for all sites. The fit is quite insensitive

to the value of V, and 0.6 kcal was chosen as this value was suggested

in the case of a similar treatment of Ni^{2+} by Neely.[1c] Values between

0.3 and 1.2 kcal change the resulting exchange parameters negligibly.

The value of τ_e^o was varied manually in the computer program about a

value determined by a hand fit of the high temperature linewidth data

where the scalar coupling relaxation mechanism contributes appreciably,

until the best fit of the data was obtained. No attempt was made to fit

τ_e^o and V simultaneously with the other parameters since there are few

data points in the region where scalar coupling relaxation becomes the

dominant mechanism.

It is, in fact, difficult to fit the linewidth data well with a

six parameter ($\Delta H_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta S_2^{\ddagger}$, A_1, A_2) computer program, as seen in

Fig. 5. The computer shows a best fit for values of τ_e^o and the scalar

coupling constants A_1 and A_2 which visually do not fit the high temperature

region well, while fitting the remainder of the curve quite well. As

seen in Fig. 6 the solid curve calculated from these linewidth parameters

is in reasonably good quantitative agreement with the chemical shift

data collected; however the fit is not excellent in either the high

or low temperature regions. In order to determine better the scalar
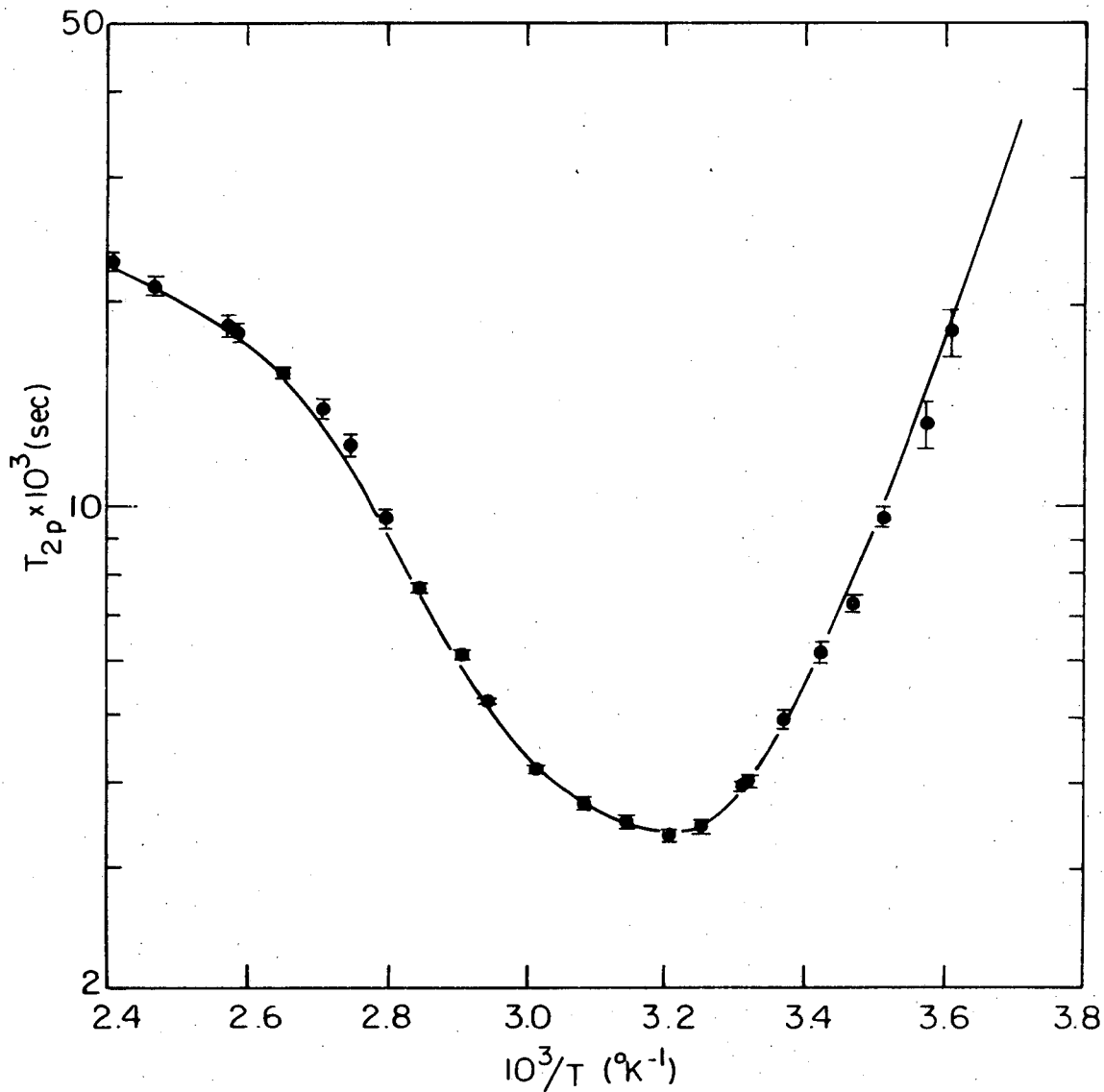
Fig. 9. $T_{2p} \times 10^3$ versus the reciprocal of absolute temperature for the oxygen-17 NMR of 0.0249 M NiIDA at pH 8.4 at 25° where the curve represents the best fit to the linewidth and chemical shift data simultaneously. Fitting parameters are listed in Table II.
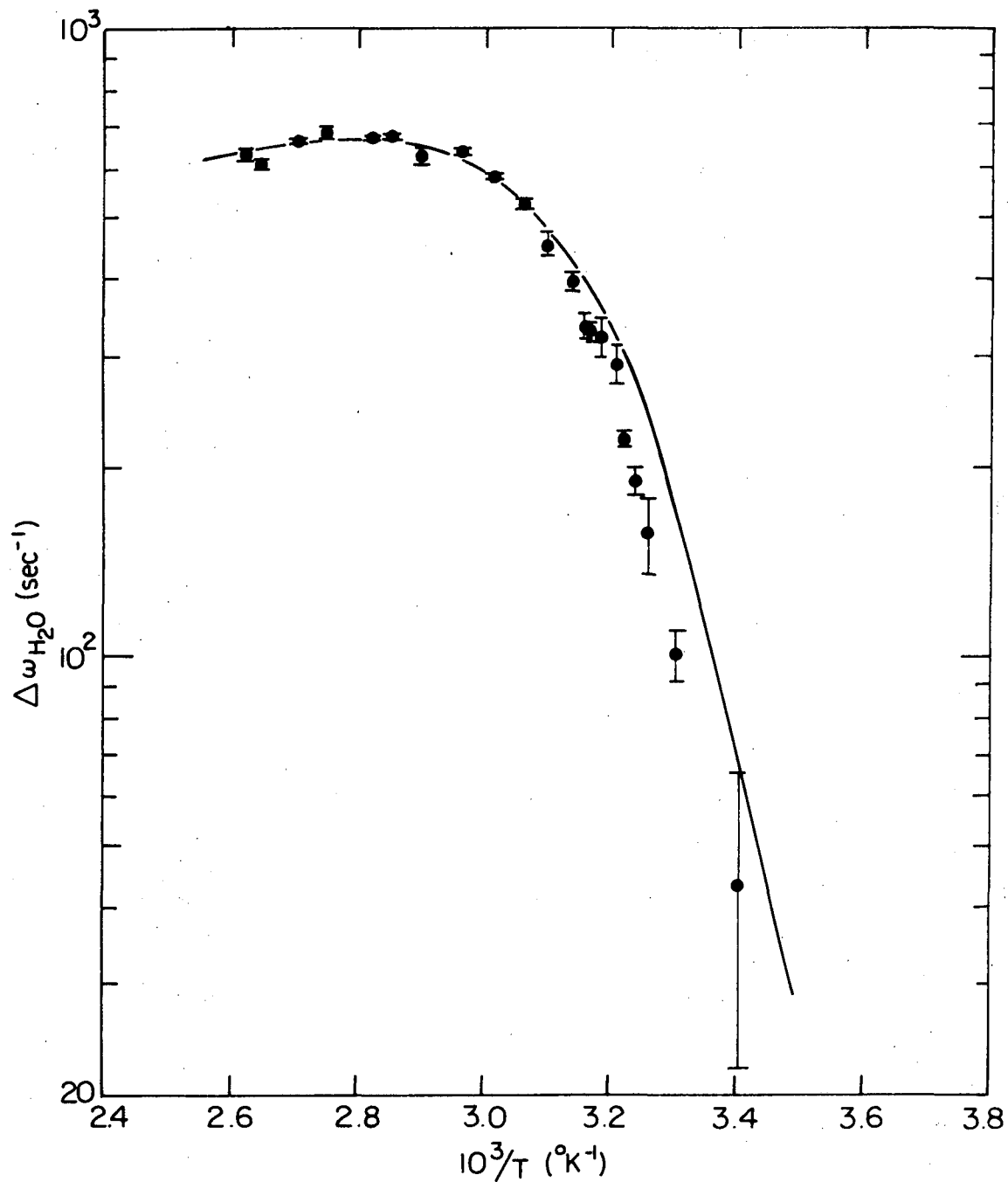
Fig. 10. $\Delta\omega_{H_2O}$ versus the reciprocal of absolute temperature for the oxygen-17 chemical shift of the bulk water in an aqueous solution of 0.0259 M NiIDA. The curve represents the best fit to the linewidth and chemical shift data simultaneously. Fitting parameters are listed in Table II.

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coupling constants a computer fitting routine was developed which could simultaneously fit the linewidth and the chemical shift data. It was hoped that this more complete utilization of the experimental data would provide a more accurate fix on the exchange parameters as well. The simultaneous fitting procedure can be seen in Fig. 9 to give a visually satisfying fit to the linewidth data over the full temperature range studied, including the scalar coupling region. However, it should be noted that although the values for $\Delta H_1^\ddagger$, $\Delta S_1^\ddagger$ and $\Delta H_2^\ddagger$, $\Delta S_2^\ddagger$ differ somewhat in the two different fitting procedures, the values for the rate of water exchange as shown in Table II are reasonably similar. The correlation matrices and the multiple correlation coefficients in the output of the computer programs indicated a strong correlation between the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for a particular site in both the linewidth only and the simultaneous fitting procedures, as one would suspect in fitting an equation of this nature. There is a lesser degree of correlation between the two scalar coupling constants A_1 and A_2 as shown in Table III below, where plus or minus one represents complete correlation and zero no correlation at all.

E. Discussion of the Electronic Correlation Time, τ_e

The value of τ_e at 120°C, which is in the region of interest, as defined by Eq. (15) can be calculated from the parameters in Table I to be 2.8×10^{-12} sec for the linewidth fitting case and 3.2×10^{-12} sec for the simultaneous fitting routine. Neely[1c] found the value of τ_e for the hexaquo nickel ion to be 8.2×10^{-12} sec at 120°C while Hynes[19]

Table III. Correlation Matrix for the "Linewidth-Only" Fit of the

NiIDA Data.

	A_1	A_2	$\Delta H^{\ddagger}_1$	$\Delta H^{\ddagger}_2$	$\Delta S^{\ddagger}_1$	$\Delta S^{\ddagger}_2$
A_1	1.0000	-0.9748	-0.8812	0.8331	-0.8499	0.8288
A_2		1.0000	0.9369	-0.7264	0.9136	-0.7188
$\Delta H^{\ddagger}_1$			1.0000	-0.6626	0.9979	-0.6511
$\Delta H^{\ddagger}_2$				1.0000	-0.6336	0.9996
$\Delta S^{\ddagger}_1$					1.0000	-0.6216
$\Delta S^{\ddagger}_2$						1.0000

has calculated from proton NMR work a value of approximately 5×10^{-12} sec

at 40°C for the same ion. Other values in this range have been reported

elsewhere.[20,21] Although the value of τ_e is not well defined by the

present experimental work since such a small portion of the curve is

determined by the scalar coupling relaxation mechanism, the values

reported here for the NiIDA system are reasonable when compared to those

reported for $Ni(H_2O)_6^{2+}$. One would in general expect a shorter T_{1e}

and T_{2e} and thus τ_e (as related in Eq. 14) for the NiIDA complex where

there is a lower degree of symmetry than the hexaquo ion,[22] as is

observed here.

F. Discussion of Fitting Parameters and Curves

As previously noted, the visual fit of the linewidth data in the

chemical exchange controlled region of the curve in Fig. 5 is excellent,

with only three points further than one standard deviation from the

calculated line, while these same parameters give substantial agreement

with the chemical shift data in Fig. 6. It should be noted that although

the high temperature linewidth data in the scalar coupling relaxation

region could possibly have been fit better using a higher value for V

in the expression for the electronic correlation time (Eq. 15), this

would have little effect on the fitting of the same temperature region

of the chemical shift curve where in the limit of rapid exchange Eq. (8),

which is dependent only on $\Delta\omega_m$ or the fitting parameters A_1 and A_2,

determines the shape of the curve. Obviously a slightly increased value

for $A_1 + A_2$ would produce a better fit in this region, but at the cost

of the fit of the linewidth data, as seen below. This would also raise the calculated chemical shift curve in the low temperature region, moving it away from the experimental points even further.

The linewidth data fit obtained from the simultaneous fitting procedure, while giving an excellent overall fit, greatly improves the fit in the high temperature scalar coupling relaxation region. Only seven of the twenty five points are more than one standard deviation from the calculated T_{2p} line over the entire temperature range studied. In the high temperature portion of the chemical shift curve the fit is excellent suggesting a good fix on the two scalar coupling constants. However, below 50°C there is an obvious, consistent positive deviation of the calculated line from the experimental points. This inconsistency does not appear to be due to any instrumental or experimental error of a constant nature as this was tested by the addition of a constant value equal to the difference between the experimental and calculated points at 29°C ($10^3/T$ = 3.305) to each experimental point and this new data set was then used in the simultaneous fitting routine. While this procedure results in a calculated chemical shift curve much better fitted to this contrived data set than the former curve to the original data set, the fit of the linewidth data deteriorates greatly. This is in large part due to the increased value of the scalar coupling constants produced by the addition of the constant to the high temperature chemical shift data. This artificially high value for the scalar coupling constants gives a bad fit of the minima of the linewidth curve. The result is in a sense gratifying as it is reassuring to see

that with this six parameter fitting program the other variables do not
tend to easily hide the fact that a particular variable or pair of
variables has taken on an unreasonable value. Thus this procedure
actually allows one to gain a measure of confidence in the sensitivity
of the fitting procedure.

In order to remedy the discrepancy in the chemical shift fit it
appears that a correction which is large at low temperature (on the
order of 70 sec^{-1}) and decreases to little or no correction above
50°C is necessary. Actually it may be necessary to add to this the base-
line correction which has already been made earlier in order to
determine the real size or the discrepancy which must be dealt with.
Thus, at low temperature the calculated curve would be about 112 sec^{-1}
from the data points while at high temperature the discrepancy would be
reduced to the baseline correction value of 44 sec^{-1}. A correction
with such a temperature dependence would not arise from a paramagnetic
impurity, nor is there any reason from the linebroadening data to
suspect that an additional relaxation mechanism might be operative.
There is of course a possibility that some unknown complexed nickel
species is present in varying concentration over the affected temperature
range, but this also is reasonably well precluded by both the line-
broadening data and a visible spectroscopy study which showed no evidence
of such an additional species. Although the reason(s) for this discrepancy
cannot be pin-pointed, it should not in any case greatly alter the results
of the computer fit of the linebroadening data or conclusions drawn from
the fitting parameters.

In general, the linebroadening data appear to be more reliable than the chemical shift data as the blank corrections to the linewidth data were known more accurately. Also, the standard deviations for the linewidth points were generally smaller for a series of measurements than for the chemical shift points. For these reasons, the fitting parameters from the linewidth only computer fit will be used in the section on water exchange rate comparisons.

G. $Ni(IDA)_2^{2-}$ Results and Discussion

As shown in Fig. 4, a solution of approximately 0.5 M $Ni(IDA)_2^{2-}$ produces an observable linebroadening compared to a $Zn(IDA)_2^{2-}$ blank. The effect is thought to be caused by water exchange at the carboxylate coordinating sites. These samples, unlike the NiIDA samples, were run at a pH of 9.2, eliminating the problem of neutral region broadening of the water blank. Since the effect was small relative to the blank, with the maximum broadening being only about 15% of the blank linewidth, and since the total metal complex concentration was fairly high, it was necessary to use a blank which would be, if possible, a diamagnetic duplicate of the $Ni(IDA)_2^{2-}$, giving a sample with virtually identical non-magnetic properties such as viscosity which would affect the unbound water oxygen-17 linewidth. It should be noted that the curve drawn in the upper section of Fig. 4 is quite approximate due to the size of the paramagnetic broadening relative to the zinc blank (about 4 Hz broadening to a 30 Hz zinc blank at room temperature). However, the shape of this curve itself precludes the broadening from being a second

sphere effect, as the rate of chemical exchange from a second sphere position for nickel ion is fast enough that an exchange controlled region such as appears at the low temperature end of this plot could not be obtained for either a dipolar or scalar relaxation mechanism. Although the high temperature end of the curve bends over more rapidly than the curve for the mono nickel IDA complex, rough calculations show that neither a scalar or dipolar interaction would cause a broadening of this order of magnitude, and thus this effect is probably attributable either to the uncertainty in the data, or to a longer electronic correlation time (closer to that of nickel hexaquo ion) for this complex.

The minimum seen in Fig. 4 resembles that of Fig. 5, although not as wide and shifted to a slightly lower temperature. This broadening effect can be used in a qualitative numerical calculation to determine the per cent of the time that some one of the carboxylate groups will be dissociated from its coordinating position, along with the rate of water replacement at the carboxylate position by either another water or the carboxylate group. It would be advantageous to measure the chemical shift for the $Ni(IDA)_2^{2-}$ system as a function of temperature in the limit of rapid exchange and, by assuming scalar coupling constants similar to those for NiIDA, determine P_m, thereby allowing the direct calculation of the per cent of the time that some one of the carboxylate arms is dissociated; however the shift is too small to be measured accurately with present instrumentation.

Although the structure of the $Ni(IDA)_2^{2-}$ complex has not been resolved satisfactorily, with one group reporting approximately a 60/40

cis-facial/trans facial ratio[4a] while another reported an 80/20 ratio,[4b]

it is not unreasonable to assume a mixture having a two to one ratio of

the cis-facial species. As seen in Fig. 2, the cis-facial complex has

two carboxylate sites which when dissociated provide water exchange

positions which are cis to the coordinated nitrogen of the other

ligand. These sites approximate the fast exchange positions of the

mono complex where the strain on the carboxylate arms causes a

labilization of the cis water positions, as will be discussed later.

The remaining two sites on the cis-facial complex provide water sites

trans to the coordinated nitrogen of the other ligand corresponding

to the slow exchange position of the mono complex. For the trans-facial

complex, all possible sites resemble fast exchanging positions. Thus

with a two to one concentration ratio of these isomers, one also obtains

a two to one fast site to slow site ratio, which is identical to the

fast site to slow site ratio in the NiIDA complex. Assuming, then,

that the ratio of fast to slow exchange lifetimes are the same for both

the NiIDA complex and the $Ni(IDA)_2^{2-}$ complex and also that the scalar

coupling constants are identical for both systems, the two linebroadening

curves (Figs. 4 and 5) can be compared and both a value of the per cent

time of dissociation and the rate of water replacement can be estimated.

Thus for single exchange site systems at the cross point of the exchange

line, τ_m/P_m, and the $\Delta\omega_m$ relaxation line, $1/(P_m \tau_m \Delta\omega_m^2)$, a comparison of

the paramagnetic linewidths gives the ratio of the P_m's for the two

systems if it is assumed that the $\Delta\omega_m$ values are the same. Using the

values of $1/T_{2p}$ at the minima of the two curves and the known value of P_m for the NiIDA system, the value of P_m for the $Ni(IDA)_2^{2-}$ system was calculated to be 1.3×10^{-4} and the per cent of the time that some one of the four carboxylate groups is dissociated was calculated to be 1.5%. Assuming the same percentage dissociation will hold at 25°C, and that the activation energy is about the same as for the NiIDA fast site, the rate of water replacement from a fast site on the bis complex was calculated to be $4 \times 10^5 \, sec^{-1}$. It should be noted that it is not known whether the water is being replaced by another water molecule or by the acetate arm.

Since the T_{2p} minimum in the $Ni(IDA)_2^{2-}$ curve is somewhat narrower than that for the NiIDA, a value for the rate of water replacement and the per cent time of dissociation was also estimated assuming that only one exchange rate exists for the $Ni(IDA)_2^{2-}$ complex. In this case the site 2 theoretical lines of Fig. 7 were used for comparison and the per cent of the time that some one of the carboxylate groups is dissociated was calculated to be 1.2%. The rate of water replacement was calculated to be $3 \times 10^5 \, sec^{-1}$ as compared with $4 \times 10^5 \, sec^{-1}$ from above. These values are similar to the rate measured for the fast site of the NiIDA complex ($2.4 \times 10^5 \, sec^{-1}$) which is not unreasonable. Although the uncertainty in these calculations is large, they serve to give a good idea of the strength of the carboxylate coordination in these complexes and insure that the linewidth correction to the NiIDA data from the $Ni(IDA)_2^{2-}$ complex is negligible.

V.   DISCUSSION

Ligand Labilization Effects

In the past the rates of water exchange from partially complexed
nickel ion have been measured for a number of different complexes and
in particular for those with coordinated nitrogen sites.   A number of
complexes with both coordinated nitrogen and carboxylate oxygen have
also been investigated.   Much of this experimental work has been done
using oxygen-17 NMR and the resulting rates of water exchange and
activation parameters are listed in Table IV for a number of these
complexes.   Also included for comparative purposes are rates of water
replacement from the first sphere of coordination by ammonia for some
of the same nickel complexes, where the temperature jump technique was
employed.[23,24]   Often both the exchange rates and activation parameters,
$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, have been reported and thus the effect of ligand substitutions
may be examined in terms of the effect on these parameters as well as
the exchange rate in general.   It should be remembered in comparing
data for the different chemical systems that the rate constants reported
often have standard deviations of about 10%, with $\Delta H^{\ddagger}$ values reliable
at best to about ± 0.5 kcal and $\Delta S^{\ddagger}$ values to an entropy unit or two.
Differences in sample variables such as ionic strength, pH, and type of
anion present may also result in differing values being reported.
Scalar coupling constants are usually reported for the NMR experiments
and in general are similar for most nickel complexes.   As previously
defined, $k_{298°}$ is the reciprocal of the lifetime of a water molecule

Table IV. Water exchange rates and activation parameters.

Complex	$k_{298°}(\text{sec}^{-1})$	$\Delta H^{\ddagger}$ (kcal)	$\Delta S^{\ddagger}$ (eu)	A/h(Hz)	Ref.	$-H_2O$ $k_{298°}(\text{sec}^{-1})^{\dagger}$	Ref.
	H$_2$O Exchange					NH$_3$ Replacement	
$Ni(H_2O)_6^{2+}$	3.2×10^4	13.9	10	2.7×10^7	1c	2.8×10^4	24
	3.0×10^4	10.8		3.0×10^7	1b		
	2.7×10^4	11.6	0.6	4.3×10^7	1a		
	4.4×10^4	10.3	-5.2	2.2×10^7	25		
	3.4×10^4	12.1	2.9		26		
	3.6×10^4	12.3	3.6	2.3×10^7	27		
$Ni(H_2O)_5(NH_3)^{2+}$	2.5×10^5	10.6	1.8	2.5×10^7	27		
$Ni(H_2O)_4(NH_3)_2^{2+}$	6.1×10^5	7.8	-6.0	1.9×10^7	27		
$Ni(H_2O)_4en^{2+}$	4.4×10^5	10.0	10	2.2×10^7	25	1.8×10^5	24
$Ni(H_2O)_3(NH_3)_3^{2+}$	2.5×10^6	10.2	5.0	2.6×10^7	27		
$Ni(H_2O)_3dien^{2+}$	1.2×10^6	5.5		2.3×10^7	2	8.6×10^5	24
$Ni(H_2O)_2en_2^{2+}$	5.4×10^6	9.1		2.3×10^7	2	2.1×10^8	24
$Ni(H_2O)_2trien^{2+}$	2.9×10^6	7		2.1×10^7	2	3.6×10^6	24

Table IV. Continued.

| Complex	H$_2$O Exchange $k_{298°}$(sec^{-1})	$\Delta H^{\ddagger}$(kcal)	$\Delta S^{\ddagger}$(eu)	A/h(Hz)	Ref.	NH$_3$ Replacement -H$_2$O $k_{298°}$(sec^{-1})[†]	Ref.
Ni(H$_2$O)$_2$tet^{2+}						3.9×10^4	3a
Ni(H$_2$O)(NH$_3$)$_5^{2+}$						4.3×10^6	24
Ni(H$_2$O)$_3$IDA	5.3×10^4	11.8	2.7	1.8×10^7		6.4×10^{4*}	23,24
	2.4×10^5	11.4	4.6	1.9×10^7			
Ni(H$_2$O)$_2$EDDA						1.8×10^{5*}	23,24
Ni(H$_2$O)$_2$NTA$^-$	1.7×10^4	11.3	-0.7	2.9×10^7	32	1.6×10^{5*}	23,24
	1.1×10^6	11.0	5.6	3.2×10^7			
Ni(H$_2$O)$_2$tren^{2+}	8.2×10^5	8.0			28	7.8×10^{6*}	23,24
	9 ×10^6	8.0					
Ni(H$_2$O)EDTA^{2-}	7.0×10^5	8.0	-7.0	2.6×10^7	29	2.6×10^{6*}	23,24

[†] Margerum's experiments gave no evidence of two different exchange rates for any of the complexes studied. In cases where two rates do actually exist, this technique probably reflects the faster rate primarily.

[*] Calculated from the value of k_{12} in reference 24 using Eq. (20) and K_{os} = 0.1 M^{-1}. All other values for $k_{298°}^{-H_2O}$ were calculated by Margerum et al. using the same equation and value for K_{os}.

Abreviations:

IDA   iminodiacetate $NH(CH_2COO^-)_2$

NTA   nitrilotriacetate $N(CH_2COO^-)_3$

EDTA   ethylenediaminetetraacetate $(CH_2COO^-)_2N(CH_2)_2N(CH_2COO^-)_2$

en   ethylenediamine $NH_2(CH_2)_2NH_2$

dien   diethylenetriamine $(NH_2CH_2CH_2)_2NH$

trien   triethylenetetramine $NH_2CH_2(CH_2NHCH_2)_2CH_2NH_2$

tren β,β',β''-triaminotriethylamine $(NH_2CH_2CH_2)_3N$

EDDA   ethylenediamine-N,N'-diacetate $(CH_2COO^-)NHCH_2CH_2NH(CH_2COO^-)$

tet   1,4,8,11-tetraazaundecane $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$

bipy   2,2'-bipyridyl
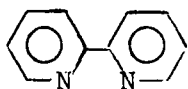
terpy   2,2',2"-terpyridyl
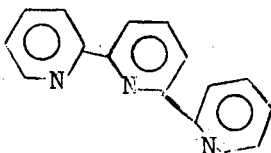
coordinated to the nickel at 25°C. Where more than one type of site exists for the water (e.g. NiIDA with two types of sites), each type of site should have its characteristic value of $k_{298°}$. Where more than one type of water coordination site exists but the separate rate constants could not be resolved from the data (e.g. $Ni(H_2O)_5(NH_3)^{2+}$), the results have been treated as if a single type of site were present. The ammonia substitution rates listed in Table IV as $k_{298°}^{-H_2O}$ are the rate constants for the exchange of water in the inner coordination sphere as defined by the relationship

$$k_{298°}^{-H_2O} = \frac{k_{12}}{K_{os}} \frac{6}{\text{no. of } H_2O} \tag{20}$$

where k_{12} is the forward rate constant for the ammonia substitution reaction and K_{os} is the outer sphere association constant of the amine complex.

Experimental results have tended to support the theory that coordinated aliphatic nitrogens tend to increase the rate of water exchange from the first sphere of hydration. In fact, Hunt[2] has shown in general that for the mono-, di, and tri-amine, en, en_2, dien and trien complexes of nickel, the log of the exchange rate, $k_{298°}$, increases roughly linearly as the number of waters per nickel ion decreases, and this is shown in Fig. 11. The log of the rate of water replacement by ammonia, $k_{298°}^{-H_2O}$, can also be seen in Fig. 11 to increase linearly as the

Fig. 11. The first order rate constant for water exchange from

a particular site, k_{298°, versus the number of coordinated

waters per nickel complex, H_2O/Ni, for:

● - nickel complexes with only aliphatic nitrogen coordinating

ligands as labeled. The solid line is drawn through

these points.

Δ - nickel complexes containing both aliphatic nitrogen

and carboxylate coordinating ligands.

O - The first order rate constant for water replacement by

ammonia for a particular site, $k_{298^\circ}^{-H_2O}$, for nickel

complexes as labeled. The dashed line is drawn through

the points containing only aliphatic nitrogen co-

ordinating positions.
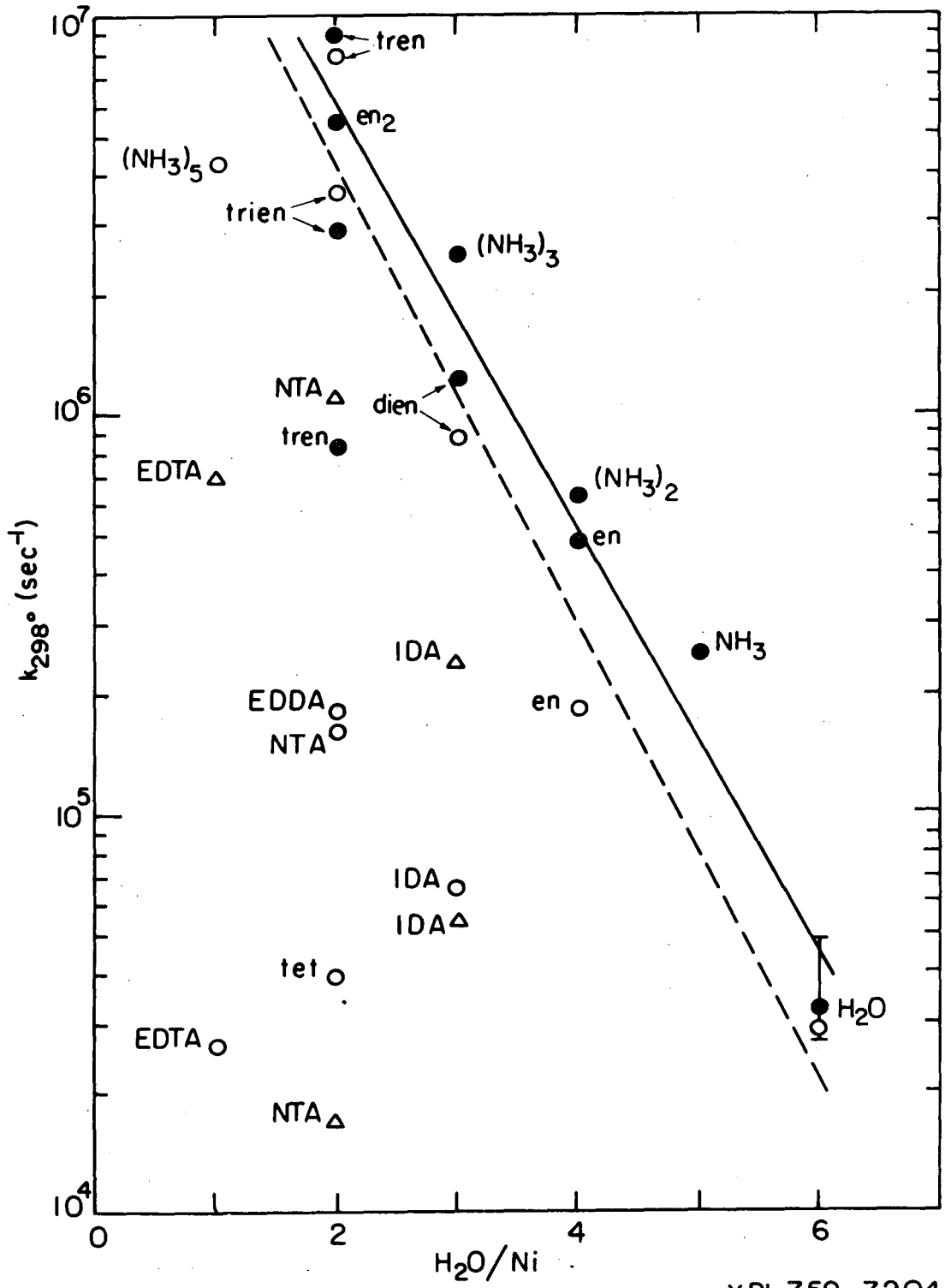
XBL 759-7204

Fig. 11

number of waters per nickel ion decreases for the en, dien, trien and pentamine complexes. Only the en_2 and tet complexes are in gross disagreement with both the linear trend and the value expected from the water exchange rate determined by the NMR method. For the rates determined by NMR there does not appear to be any well defined trend in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values as the number of coordinated nitrogens increases (no activation parameters given for the ammonia substitution reactions). Whereas there is a $\Delta H^{\ddagger}$ increase in going from the en to the en_2 complex, the mono-, di-, and tri-amine complexes give irregular values. The same holds true for $\Delta S^{\ddagger}$ values although they are most commonly small and positive. The same rate enhancement factors are not found for ligands coordinated at unsaturated nitrogen sites such as bipy, terpy, $bipy_2$, or NCS^-, although again for the first three complexes the logarithm of the exchange rates increase roughly linearly as the number of water coordinating positions decreases, but with a much smaller slope than for the aliphatic nitrogen complex.

These trends may be satisfactorily explained based on the electron donating/withdrawing ability of the complexing ligand. Aliphatic nitrogens, which are good electron donors, increase the electron density at the metal center, thereby weakening the remaining coordinated water bonds as is manifested by increased exchange rates. However for unsaturated or aromatic nitrogens, the electron donor properties are to some degree neutralized by π backbonding and thus labilization is greatly diminished from the value expected from aliphatic nitrogen coordination. Certainly this is an overly simplified view of the

problem as ligand geometry and configuration have not been taken into

account. In view of this fact, the degree of correlation between

$\log k_{298°}$ and H_2O/Ni is somewhat surprising.

The effect of configuration is immediately evident in a direct

comparison of the nickel tren and trien exchange rates and this will be

discussed along with the EDTA, IDA, and NTA complexes later. Margerum[24]

has reported the effects of N-alkyl substitution in diamine ligands on

the rate of water replacement by ammonia. For example, the addition

of an ethyl group to one nitrogen of en produced a 2 1/2 fold increase

in the rate of ammonia substitution. Also based on a study of the rate

of water replacement by ammonia, Cobb and Hague have concluded that the

labilizing influence on the remaining water molecules is larger for

trans- than for cis-nitrogen molecules.[3a] They have reached this

conclusion by comparing the data for the nickel en_2, trien, and tren

complexes which are all thought to have two remaining waters trans to

coordinated nitrogens[30a,b,c,d] with that for the nickel tet complex,

where the two waters are opposite each other. Whereas the first three

complexes have drastically labilized waters, water replacement by

ammonia on the tet complex occurs barely faster than for the hexaquo

nickel ion. However there appears to be no other evidence at this time

to establish this trend; indeed, with such a drastic cis-trans

labilization effect as claimed, one might have expected to measure two

water exchange rates for complexes such as $Ni(H_2O)_4 en^{2+}$, where two remaining

waters are cis and two are trans to coordinated nitrogens. Thus,

although the number of coordinated nitrogen sites is indeed extremely

important, other factors may also greatly affect the degree of labilization

produced by the ligand.

Carboxylate coordination labilization trends have not been as well

determined, with cases of both slight rate enhancement and more often

small decreases being reported.[24] It is difficult to determine directly

the effect of the carboxylate coordination since the ligands most often

also contain one or two coordinated nitrogens. EDTA (five coordinate)

gives a slightly faster exchange rate for its remaining water than does

its precursor en. Again, this may be more a configurational effect

rather than an enhancement due to the three carboxylate groups and will

be treated as such later. Unfortunately, there are no NMR water exchange

data on either the N, N'-EDDA or the N,N-EDDA complexes to compare with

those of the nickel en system. The N,N'-EDDA system in particular

should yield straightforward information on the effects of carboxylate

coordination with minimal configurational considerations, while a

comparison of the two EDDA complexes would yield configurational

information. Margerum[24] has measured a rate of 1.8×10^5 sec^{-1} for water

replacement by ammonia in the nickel en complex and from data given in

this same reference an identical rate of 1.8×10^5 sec^{-1} can be calculated

for the N,N'-EDDA complex, suggesting that the carboxylate groups have

little labilizing effect. It is not surprising that the carboxylate

group does not provide a large labilization of the remaining coordinated

waters, as it is not nearly the electron donor that nitrogen is. In fact,

the carboxylate oxygen may not differ drastically from the water oxygen

in its static electronic (point dipole) properties, and thus would not
be expected to have a much different effect from that of water itself
on the remaining coordinated water molecules.

For the complexes of nickel with IDA, NTA and tren a different
approach is necessary in order to explain the observance of two different
water exchange rates. The results for the EDTA complex will also be
considered here since this complex is to some degree structurally similar
to these three ligands. In both the $NiNTA^-$ and $Ni(tren)^{2+}$ complexes
the two remaining waters are located at structurally nonequivalent
positions and similarly for NiIDA the cis and trans to nitrogen water
sites are structurally quite different. Since in the NiIDA study it
has been determined that the slower exchanging site is trans to the
nitrogen group, it is assumed here that the same should hold true for the
$NiNTA^-$ complex (as postulated by Vriesenga on the basis of proton NMR^{5b}),
and for the Ni(tren) complex the equivalent position will be that site
trans to the tertiary nitrogen. The $NiNTA^-$ and NiIDA trans site
exchange rates generally fit the expected trend with a labilizing effect
due to nitrogen being partially balanced by a small delabilizing effect
from each carboxylate coordinating position. Although slightly slower
than would be predicted from the $Ni(trien)^{2+}$ and $Ni(en)_2^{2+}$ results, the
trans site rate for $Ni(tren)^{2+}$ is considerably faster than for the NTA
or IDA complexes as is expected due to the four nitrogen coordination
sites.

The water exchange site on the five coordinate EDTA complex may

either be cis to one nitrogen and trans to the other, or cis to both

nitrogens. A structural study of the solid nickel EDTA complex by

Smith and Hoard has shown that one of the cis/trans positions remains

uncoordinated by the EDTA ligand.[32] This isomer appears to provide

a water exchange site similar to the fast IDA site in terms of the

effects of bond strain about the coordinated nitrogens, while the latter

provides a site similar to the fast NTA site. Since the EDTA complex

has one more coordinated nitrogen than the NTA complex, should the

cis/trans isomer prevail, an exchange rate enhanced by about a factor

of three might be predicted along with an additional enhancement of about

a factor of four and a half due to the IDA type strain thought to be

present. This procedure yields an exchange rate or about 2×10^5 sec^{-1}

compared with the reported value of 7×10^5. For the cis/cis isomer the

strain enhancement factor would be expected to be considerably greater

as with the NTA complex (enhancement factor of about 70), and thus

including the enhancement of the additional coordinated nitrogen a rate

of about 3×10^6 sec^{-1} would be predicted. Although the strain produced

in each of these isomers may not be exactly like that of either the IDA

or NTA complexes due to the steric interactions of the ethylene link

in the ligand, it seems reasonable that the observed value falls some-

where between the two predicted values.

The fast exchanging sites on the NTA and tren complexes are both

cis to a tertiary nitrogen and the two fast IDA sites are cis to a

secondary nitrogen. Fisher-Hirshfelder models of the complexes show a

large degree of bond strain about the tertiary or secondary nitrogens,

making it hard to fasten all of the remaining coordinating positions simultaneously. This strain about the nitrogen would of course operate to push the complex into such a configuration as to allow tetrahedral bonding to the central nitrogen. This can be achieved if the complex becomes trigonal bipyramidal in shape, eliminating one cis coordinating position. A number of similar Ni^{2+} complexes such as nickel tris (2- methylaminoethyl)amine, where the aliphatic substitution to the tren ligand has sterically increased the strain in the octahedral configuration, are known to have trigonal bipyramidal structure in the solid state and are thought to retain this structure in solution.[31a,b] For the nickel IDA, NTA, tren, and EDTA complexes a tendency toward such a configurational intermediate would explain the unusually high rates of water exchange from the cis water sites. One would expect the greater strain in the tren and NTA tertiary nitrogens to produce a faster water exchange rate than the strain in the secondary nitrogen of the IDA complex, as is observed, NTA's fast rate being approximately five times that of IDA. Additionally, the faster exchange rate for the tren complex relative to the NTA is in line with the fourfold increase in coordinated nitrogens. The $Ni(IDA)_2^{2-}$ where exchange is occurring at a dissociated carboxylate group also appears to fit the general pattern described above, giving a rate somewhat faster than for the fast site of the mono complex, as would be expected due to the addition of both a nitrogen and a carboxylate coordinating group.

The above observations lead to a set of conclusions which establish
or reinforce a number of ligand labilization trends. First, coordinated
aliphatic nitrogen labilizes the remaining water molecules present
in the complex, although the degree of labilization may be affected
by substitution on the coordinating nitrogen group. Secondly,
coordinated carboxylate groups have a small delabilizing effect.
Third, the strain produced by certain ligand configurations may cause
a large degree of labilization. In particular, tertiary nitrogen bond
strain can produce a water exchange rate enhancement as great as that
expected from the coordination of three aliphatic nitrogens. Secondary
nitrogens appear to have a similar but diminished effect. Fourth,
conformation of the ligand causes measureable ligand labilization effects
which are yet of an unclear nature. However, based on the currently
available data, one or more exceptions can be found to any one of these
trends, which illustrate, in general, the complexity of predicting ligand
labilization trends where the effects of ligand electron donor ability
of the particular ligand involved, configurational strain, and conformation
may all have roles of nearly equal importance in determining the degree
of labilization of the remaining coordinated water molecules. Due to
the limited number of systems which have been studied to this date and
due to the complexity of these systems, no numerical treatment of either
the carboxylate labilization or the nitrogen bond strain effects can be
given.

ACKNOWLEDGMENTS

APPENDIX I. EXPERIMENTAL DATA

Table Ia. Oxygen-17 bulk water linewidth data as a function of temperature (below 40°C) and pH using 0.10 M NH_4ClO_4 adjusted to the desired pH with NaOH.[*]

Temp(°C)	$10^3/T(°K^{-1})$	$T_{2H_2O} \times 10^3$(sec)
Sample 1: pH 8.42 at 26°C		
40.36	3.190	8.73
36.07	3.234	7.97
28.85	3.311	6.96
Sample 2: pH 8.53 at 16°C		
20.07	3.410	5.60
15.75	3.461	4.92
11.26	3.516	4.20
Sample 3: pH 8.61 at 5°C		
8.56	3.550	3.88
4.32	3.604	3.17
1.41	3.642	2.81

[*]The change in pH of the 0.10 M NH_4ClO_4 solution as a function of temperature was similar to, but slightly larger than the 0.025 M NiIDA samples.

Table 1b. The pH of a 0.025 M NiIDA sample as a function of temperature.

Temp(°C)	pH
31.2	8.37
21.4	8.45
17.6	8.49
9.2	8.60
1.4	8.65

Table IIa. Linewidth data for a 0.0249 M NiIDA sample adjusted to pH 8.4 at 25°C. Sample also contains 0.0249 M Ni(IDA)$_2^{2-}$ and 2.99×10^{-4} M Ni^{2+} and was made by adding 32.6 mg Ni(ClO$_4$)$_2$·6H$_2$O, 17.8 mg NH(CH$_2$COOH), and 1.1 mg NH$_4$ClO4 to 1.8474 g of 12% H$_2$O^{17} (~24% H$_2$O^{18}). P$_m$(Ni^{2+})=3.232×10-5; P$_m$(NiIDA)**=1.346×10^{-3}

Temp.(°C)	$10^3/T(°K^{-1})$	$T_{2H_2O}×10^3$(sec)[*]	$T_{2p}(Ni^{2+})$(sec)	T_{2p}(NiIDA)×10^3 (sec)
3.93	3.609	3.10	7.18	17.80
6.79	3.572	3.62	4.55	13.05
11.49	3.513	4.27	2.99	9.59
15.18	3.468	4.80	2.16	7.72
19.10	3.422	5.38	1.57	6.18
23.54	3.370	6.03	1.08	4.92
28.24	3.318	6.81	0.743	4.01
28.39	3.316	6.86	0.733	3.97
28.80	3.312	6.91	0.712	3.98
34.80	3.247	7.91	0.446	3.44
39.05	3.203	8.60	0.325	3.34
45.02	3.143	9.67	0.217	3.51
51.40	3.081	10.8	0.154	3.70
58.72	3.013	12.3	0.112	4.19
66.39	2.945	14.0	0.0938	5.28
70.84	2.907	15.0	0.0913	6.14
78.24	2.846	16.7	0.0962	7.64
84.27	2.798	18.4	0.106	9.57
91.02	2.746	20.2	0.119	12.3
96.28	2.707	21.8	0.130	13.8
104.38	2.649	24.4	0.148	15.6
113.98	2.583	27.1	0.166	17.5
115.15	2.575	28.0	0.168	18.02
132.24	2.467	34.3	0.191	20.5
142.88	2.404	38.7	0.199	21.3

[*]Values for T_{2H_2O} taken from Fig. 3. [**]where P$_m$(NiIDA) = P$_{m_1}$+P$_{m_2}$.

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Table IIb. Linewidth data for a 0.0147 M NiIDA sample adjusted to pH 3.1 at 25°C. Sample also contains 3.04×10^{-3} M $Ni(IDA)_2^{2-}$ and 8.57×10^{-4} M Ni^{2+} and was made by adding 9.5 mg $Ni(ClO_4)_2\cdot6H_2O$, and 20.7 mg $NH(CH_2COOH)$ to 1.4220 g of 6% H_2O^{17} (12% H_2O^{18}). $P_m(Ni^{2+}) = 9.265\ 10^{-5}$; $P_m(NiIDA)^* = 7.946\times10^{-4}$.

Temp.(°C)	$10^3/T(°K^{-1})$	$T_{2H_2O}\times10^3$(sec)**	$T_{2p}(Ni^{2+})$ (sec)	$T_{2p}(NiIDA)\times10^3$ (sec)
27.02	3.339	6.81	0.287	6.74
40.21	3.191	8.87	0.105	5.11
59.57	3.005	12.55	3.78×10^{-2}	6.34

*where $P_m(NiIDA) = P_{m_1} + P_{m_2}$.

**normal acidic water blank data used.

Table III. Chemical shift data for a 0.0259 M NiIDA sample adjusted to pH 8.4 at 25°C. Sample also contains 0.0222 M $Ni(IDA)_2^{2-}$ and 3.63×10^{-4} M Ni^{2+} and was made by adding 31.4 mg $Ni(ClO_4)_2 \cdot 6H_2O$, 16.9 mg $NH(CH_2COOH)$, and 1.2 mg NH_4ClO_4 to 1.8312 g of 10% H_2O^{17} (~20% H_2O^{18}). γH_K is the magnetic susceptibility correction. All measured shifts were downfield shifts. $P_m(Ni^{2+}) = 3.922 \times 10^{-5}$; $P_m(NiIDA)^* = 1.400 \times 10^{-3}$.

$10^3/T(°K^{-1})$	$-\Delta\omega_{H_2O}^{Ni^{2+}}(sec^{-1})$	$\gamma H_K(sec^{-1})$	$-\Delta\omega_{H_2O}(sec^{-1})$	$-\Delta\omega_{H_2O}+C^{**}(sec^{-1})$
3.446	0.01	25.1	-42.8	0.7
3.404	0.05	24.8	-0.17	43.3
3.305	0.11	24.1	56.8	100
3.258	0.22	23.7	113	157
3.236	0.28	23.6	148	191
3.220	0.39	23.4	178	222
3.207	0.45	23.3	248	291
3.183	0.67	23.1	281	325
3.167	0.82	23.0	286	329
3.159	0.86	22.9	293	336
3.131	1.33	22.7	352	396
3.095	2.00	22.4	410	454
3.060	2.86	22.2	480	524
3.010	4.71	21.7	537	581
2.962	7.26	21.4	590	634
2.894	11.9	20.8	582	626

*where $P_m(NiIDA) = P_{m_1} + P_{m_2}$.

**$C = 44 (sec^{-1})$.

Table III. Continued.

$10^3/T(°K^{-1})$	$-\Delta\omega_{H_2O}^{Ni^{2+}}(sec^{-1})$	$\gamma H_K(sec^{-1})$	$-\Delta\omega_{H_2O}(sec^{-1})$	$-\Delta\omega_{H_2O}+C^{**}(sec^{-1})$
2.850	14.9	20.4	628	672
2.819	16.5	20.2	620	664
2.747	19.4	19.6	636	680
2.706	20.0	19.2	616	660
2.642	20.6	18.8	562	606
2.617	20.8	18.5	585	629

Table IVa. Linewidth data for a 0.497 M $Ni(IDA)_2^{2-}$ sample adjusted to pH 9.2 at 25°C. The sample was made by adding 328.8 mg $Ni(ClO_4)_2 \cdot 6H_2O$, 264.0 mg $NH(CH_2COOH)$, and 10.7 mg NH_4ClO_4 to 1.8080 g of 7% H_2O^{17} (~14% H_2O^{18}).

Temp.(°C)	$10^3/T(°K^{-1})$	$T_{2H_2O}* \times 10^3$(sec)	$T_{2p} \times 10^2$(sec)
10.80	3.522	3.12	6.62
15.60	3.463	3.66	4.98
19.78	3.414	4.13	4.48
24.54	3.359	4.70	3.98
29.39	3.305	5.38	3.43
34.29	3.253	6.06	3.60
38.64	3.207	6.66	3.80
40.93	3.184	7.00	4.29
44.26	3.150	7.51	5.10
48.74	3.107	8.19	5.18
55.02	3.047	9.26	5.81
61.20	2.991	10.3	6.21
65.61	2.952	11.2	6.21
73.42	2.885	12.6	8.02
84.33	2.797	14.8	8.05
94.13	2.723	16.7	7.95
103.94	2.652	18.9	8.83

*T_{2H_2O} determined by measuring T_2 of a 0.515 M $Zn(IDA)_2^{2-}$ sample.

Table IVb. Linewidth data for a 0.515 M $Zn(IDA)_2^{2-}$ sample
adjusted to pH 9.2 at 25°C. The sample was made by
adding 334.3 mg $Zn(ClO_4)_2 \cdot 6H_2O$, 263.7 mg $NH(CH_2COOH)$,
and 11.3 mg NH_4ClO_4 to 1.7740 g of 7% H_2O^{17} (14% H_2O^{18}).

Temp.(°C)	$10^3/T(°K^{-1})$	$T_{2H_2O} \times 10^3 = T_2(Zn(IDA)_2^{2-})$ (sec)
1.46	3.641	2.27
3.74	3.611	2.46
7.35	3.565	2.75
10.58	3.524	3.11
14.88	3.472	3.57
18.88	3.424	4.00
23.59	3.370	4.57
28.24	3.318	5.20
34.10	3.255	6.07
39.69	3.196	6.82
47.07	3.123	7.94
53.88	3.058	9.05
60.39	2.998	10.2
68.73	2.925	11.7
76.20	2.862	13.2
84.40	2.797	14.7
93.39	2.728	16.7
101.60	2.668	18.9

APPENDIX II.

Computer Programs

An example of a computer subroutine for the Dye and Nicely General
Purpose Curve Fitting Program[16] for fitting two equations (linewidth
and chemical shift) simultaneously:

```
C**********SIMULTANEOUS CHEMICAL SHIFT AND LINEWIDTH SUBROUTINE***************
      SUBROUTINE EQN
      COMMON KOUNT,ITAPE,JTAPE,I,T,LAP,AINCR,NOPT,NUVAR,NOUNK,A,U,ITMAX,
     1WIX,IEST,I,AV,RESID,IAR,EPS,ITYP,AX,RXTYP,DAII,FOP,FU,FU,P,ZL,TO,
     2EIGVAL,XST,T,DT,EM,JJJ,Y,DY,VECT,NCST,CONST,LOG,JJ
      DIMENSION X(4,100), U(20), WIX(4,100), AX(4), FOP(100), FU(100),
     1FU(100), P(20,21), VECT(20,21), ZL(100), TO(20), EIGVAL(20),
     2AST(100), Y(10), DY(10), CONST(16), CMUKH7(4), CMUKI(4), PH25(4),
     3TL(4), TL(4), TA(4), ZH(100), ZK7(100), ZKH(100), EM(100),ZKI(100)
      GO TO (3,4,5,6,1,7,8), ITYP
    1 CONTINUE
      ITAPE = 5
      JTAPE = 6
      LOG = 0
      WRITE (JTAPE,2)
    2 FORMAT (1H ,'CHEMICAL SHIFT AND LINEWIDTH DATA')
      NOUNK = 6
      NOVAR = 2
      CC = 0.0249
      CA = 0.0259
      TE = 1.24E-12
C     PROGRAM WRITTEN SO THAT
C          CC IS CONCENTRATION OF NI(L) FOR LINEWIDTH DATA
C          CA IS CONCENTRATION OF NI(L) FOR CHEMICAL SHIFT DATA
C          TE IS ELECTRONIC CORR. TIME TAU E 0
C          U(*) IS SCALAR COUPLING CONSTANT OF THE FAST SITE
C          U(2) IS SCALAR COUPLING CONSTANT OF THE SLOW SITE
C          U(3) IS DELTA H FOR FAST SITE
C          U(4) IS DELTA H FOR SLOW SITE
C          U(5) IS DELTA S FOR FAST SITE
C          U(6) IS DELTA S FOR SLOW SITE
C          AX(1) IS I/T TIMES 1.0E3
C          AX(2) IS DELTA OMEGA OR 1/T2P
      RETURN
    3 CONTINUE
      IF (JJ .LE. 20) GO TO 100
      W = (CC*(((2.699E119)*(U(1)**4)*TE*TE*EXP((-U(3)*AX(1)*0.5032E-3)
     1+0.5032*U(5))+(AX(1)*6.038E-1))/AX(1))+((9.38E78)*(U(1)**2)*TE*
     1EXP((-U(3)*AX(1)*1.0064E-3)+1.0064*U(5)) +(AX(1)*3.019E-1))/
     2AX(1)**2)+(1.362E60)*(U(1)**2)*AX(1)*EXP((-U(3)*AX(1)*0.5032E-3)
     3+0.5032*U(5)))/((3.394E107)*(U(1)**4)*TE*TE*EXP(AX(1)*6.038E-1)
     4+((2.498E67)*(U(1)**2)*TE*EXP((-U(3)*AX(1)*0.5032E-3)+0.5032*U(5)+
```

```
     5(XX(1)*3.019E-1))/XX(1))+((4.343E26)*EXP((-U(3)*XX(1)*1.0064E-3)
     6+1.0064*U(5))/XX(1)**2)+(1.8133E48)*(U(1)**2)*(XX(1)**2)))
     7+(CC*(((1.350E119)*(U(2)**4)*TE*TE*EXP((-U(4)*XX(1)*0.5032E-3)
     8+0.5032*U(6)+(XX(1)*6.038E-1))/XX(1))+((4.69UE76)*(U(2)**2)*TE*
     9EXP((-U(4)(XX(1))*1.0064E-3)+1.0064*U(6) +(XX(1)*3.019E-1))/
     AXX(1)**2)+(6.809E59)*(U(2)**2)*XX(1)*EXP((-U(4)*XX(1)*0.5032E-3)
     B+0.5032*U(6)))/((3.594L107)*(U(2)**4)*TE*TE*EXP(XX(1)*6.038E-1)
     C+((2.498E67)*(U(2)**2)*TE*EXP((-U(4)*XX(1)*0.5032E-3)+0.5032*U(6)+
     D(XX(1)*3.019E-1))/XX(1))+((4.343E26)*EXP((-U(4)*XX(1)*1.0064E-3)
     E+1.0064*U(6))/XX(1)**2)+(1.8133E48)*(U(2)**2)*(XX(1)**2)))
      GO TO 101
 100  W = (((2.1075E49)*CA*U(1)*EXP((-U(3)*XX(1)*1.0064E-3)+1.0064*U(5))
     1/XX(1)))/((3.5945E107)*(U(1)**4)*(TE**2)*EXP(XX(1)*6.038E-1)
     2+((2.4988E67)*(U(1)**2)*TE*EXP((-U(3)*XX(1)*0.5032E-3)+0.5032*U(5)
     3+(XX(1)*3.019E-1))/XX(1))+((4.343E26)*EXP((-U(3)*XX(1)*1.0064E-3)+
     41.0064*U(5))/(XX(1)**2)+(1.8133E48)*(U(1)**2)*(XX(1)**2)))
     5+((((1.0538E49)*CA*U(2)*EXP((-U(4)*XX(1)*1.0064E-3)+1.0064*U(6))/
     6XX(1))/((3.5945E107)*(U(2)**4)*(TE**2)*EXP(XX(1)*6.038E-1)
     7+((2.4988E67)*(U(2)**2)*TE*EXP((-U(4)*XX(1)*0.5032E-3)+0.5032*U(6)
     8+(XX(1)*3.019E-1))/XX(1))+((4.343E26)*EXP((-U(4)*XX(1)*1.0064E-3)+
     91.0064*U(6))/(XX(1)**2))+(1.8133E48)*(U(2)**2)*(XX(1)**2)))
 101  RESID = W - XX(2)
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      RETURN
    6 CONTINUE
      RETURN
    7 CONTINUE
      DO 300 J = 1,NOPT
      READ (5,61) X(1,J), X(2,J), WTX(2,J)
   61 FORMAT (3E12.4)
  300 WTX(1,J) = 0.005
      RETURN
    8 CONTINUE
      RETURN
      END
```

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