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MULTINUCLEAR MAGNETIC RESONANCE STUDY OF THE  
BIS-IMINODIACETATE NICKEL(II) COMPLEX  
IN AQUEOUS SOLUTION

K.A. Klotter  
(Ph.D. Thesis)

April 1986

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Multinuclear Magnetic Resonance Study  
of the Bis-iminodiacetate Nickel(II) Complex  
in Aqueous Solution

Kevin Albert Klotter

Submitted for Fulfillment of the Requirements  
of the Degree of Doctor of Philosophy in Chemistry

Lawrence Berkeley Laboratory  
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Berkeley, California 94720

April 1986

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ABSTRACT

Proton, carbon-13, and oxygen-17 NMR spectra of the bis-iminodiacetate nickel (II) complex are reported and interpreted in terms intramolecular cis/trans isomer racemization and carboxylate oxygen interchange. Proton NMR spectra at 60 MHz and 180 MHz are consistent with previously reported spectra. Carbon-13 NMR spectra unambiguously determine the cis/trans isomer ratio. The temperature dependence of the carbon-13 NMR spectra shows no evidence of intermolecular ligand exchange between the complex and the free ligand, in contrast to simple amino acid complexes. Carbon-13 NMR spectra suggest that cis/trans isomer interconversion occurs via a Bailar-twist mechanism.

Oxygen-17 spectra of the bis-iminodiacetate nickel (II) complex are obtained by isotopically enriching the ligand in oxygen-17 and recording spectra in both the continuous wave and Fourier transform modes. The temperature dependence of the linewidth of the non-bonded carboxylate oxygen resonance leads to a determination of the rate of carboxylate oxygen interchange in the complex. Activation parameters for the interchange are determined by fitting the linewidth data to a theoretical equation accounting for interchange and quadrupole coupling relaxation. The results of the computer fitting are  $\Delta H^\ddagger = + 14.6 \pm 0.9$  kcal/mole,  $\Delta S^\ddagger = +0.8 \pm 2.5$  e.u., and  $k(298^\circ\text{K}) = 167 \text{ sec}^{-1}$ . These rate parameters lead to the conclusion that once decoordination of a ligand carboxylate group occurs, on the average 3 or more waters exchange at the decoordinated site before the ligand arm recoordinates. These data indicate that the oxygen interchange rates do not differ greatly for the various carboxylate groups in the cis and trans isomers.

### Dedication

I wish to dedicate this thesis to Bree L. Klotter for the many years spent supporting my efforts in many different arenas. I further wish to give the following quotation as part of that dedication:

"....For three days now we made no expedition of any consequence. The question arises, then, what did we? I have been searching the meagre entries of my journal for an answer, with no satisfactory result. The doctrine that men should be held accountable for their days, or even their hours, is one to which the very young often subscribe as a matter of course, seeing in front of them such a long way to go and so little time: the futility of exact accounts in this sort is apparent among mountains; the span in human life appears so short as hardly to be capable of the usual sub-divisions, and a much longer period than a day may be neglected as easily as a half-penny in current expenditure; and while some hours and days are spent in doing, other pass in simply being or being evolved, a process in the mind not to be measured in terms of time."

George Leigh-Mallory,  
from The Assault on Mt. Everest, 1922

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## I. Introduction

Nuclear magnetic resonance has long been recognized as a valuable tool for probing chemical kinetic and dynamic processes in paramagnetic molecules (1). Oxygen-17 NMR In particular has been extremely useful in the determination of the rate of solvent water exchange from the first coordination sphere of transition metal ions in an aqueous medium (2,3,4). There have been a number of solvent exchange studies in which metal ions are either partially or fully coordinated (4,5,6a,6b), leaving some coordination sites open to solvent exchange at least part of the time. In these cases there may arise inequivalent solvent coordination sites due to the geometry of the chelation (5). Solvent exchange rates from these inequivalent sites may be appreciably different, and NMR has been used as a tool to help determine the rate constants.

NMR has been used in this way to study the cases of iminodiacetate nickel (II),  $\text{Ni}(\text{NH}(\text{CH}_2\text{CO}_2)_2)_2$ , ("NiIDA") (5) and nitrilotriacetate nickel (II),  $\text{Ni}(\text{N}(\text{CH}_2\text{CO}_2)_3)^-$ , ("NiNTA") (6b). The latter species has two coordinated waters of differing geometry and the former three waters, two of which are equivalent but different from the third.

In the course of the study of the NiIDA system it was necessary to consider a correction for the presence of bis-iminodiacetate nickel (II),  $\text{Ni}(\text{IDA})_2^{-2}$ , because

of the strong tendency of IDA to complex Ni (II) under the conditions used. The water line broadening by this species proved to be measurable and was attributed to a first coordination sphere interaction. If none of the coordination sites at the Ni (II) were available for exchange, then there would be only a small broadening contribution due to the second sphere interactions. In fact, the observed broadening was larger than might be reasonably explained by this mechanism. In turn this led to the speculation that some manner of decomplexation occurred, allowing bulk water access to the first coordination sphere.

Presumably the decomplexation is only partial, occurring at an acetate arm of the ligand rather than at the nitrogen. From oxygen-17 linewidth measurements as a function of temperature and from the presence of a chemical exchange controlled region, it was concluded that some one acetate arm of the complex is dissociated approximately 1.5% of the time and that the rate of exchange of water at this site is approximately  $4 \times 10^5 \text{ sec}^{-1}$  at room temperature.

The primary purpose of this thesis is to probe the decomplexation of the carboxylate groups in a direct way via oxygen -17 NMR rather than by inferring it from the solvent exchange data. Specifically, the oxygens of a carboxylate group have two different sites when complexed to the nickel (7). One oxygen is directly bonded to the metal and the other not. Upon dissociation of the group

from the metal and the subsequent return to the complexed form, these two oxygens may interchange their sites. Such exchange is reflected in the chemical shifts and linewidths of the resonances, from which the kinetics of the dissociation may be elucidated, provided that one of the resonances is measurable.

The observation of the oxygen-17 resonances of the acetate group bound to the nickel is seriously limited by the short spin-spin and spin-lattice relaxation times which characterize the NMR of nuclei bound to paramagnetic ions (for example, 3,8). These small values of  $T_1$  and  $T_2$  result from the presence of quadrupolar, dipolar, and scalar coupling mechanisms of relaxation. To estimate the orders of magnitude for the linewidths of the non-bonded oxygen nuclei of  $\text{Ni}(\text{IDA})_2^{-2}$ , one may consider first the linewidth of the first coordination sphere water of  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$  in aqueous solution. Neely and Connick (3) have observed the bound water oxygen-17 resonance directly, and at room temperature the linewidth is approximately  $3 \times 10^4$  Hz. The major relaxation mechanism has been shown to be scalar coupling between the nickel and oxygen interrupted by the electronic relaxation (2,3,8). Using this value as a crude estimate of the bonded acetate oxygen linewidth, ignoring the difference in bonding structure, electronic relaxation times, etc., one estimates that the lifetime of the free induction decay ("FID") signal in the FT-NMR experiment will be 5  $\mu\text{sec}$ . Given the rates of data

acquisition, not nearly enough data may be collected during the FID to determine accurately the  $T_2$  relaxation time. In turn, without accurate measurements of  $T_2$  no kinetic information may be inferred. Hence direct measurement of the bound acetate oxygen is unlikely to be achievable.

However, the scalar coupling interaction leading to the rapid relaxation is known to be attenuated rapidly through sigma bonding systems (9). One might expect that linewidth measurements on the non-bonded carboxylate oxygen nuclei may be possible, since these nuclei are two bonds farther removed from the nickel ion center than the bonded carboxylate nuclei. Pi bonding is a possibility in the coordination of the acetate group to the metal, but the effects of the pi system on the scalar coupling interaction are not well understood. Some attenuation of the effect through the ligand is certain to be present because of the orthogonality of the sigma and pi bonds.

The most important point is that the scalar coupling relaxation depends upon the square of the scalar coupling constant (equation 9), so a decrease by a factor of ten in the value of  $A/h$  results in a factor of 100 decrease in the contribution to the linewidth by scalar coupling. This brings the value of  $1/(2\pi T_2)$  for the non-bonded nuclei closer to 300 Hz, which is only ten times the linewidth of pure water at the same temperature. On this assumption one might expect to observe the non-bonded resonances more

easily than those of the bonded.

In addition to the oxygen-17 measurements, the availability of multinuclear NMR spectrometers operating in the FT mode makes possible the observation of natural abundance proton and carbon resonances from the complex. These observations are attractive because the data for all three nuclei must be self-consistent and because higher field strength magnets provide a larger chemical shift range. Earlier proton NMR work at lower field strengths (10,11) on the  $\text{Ni(IDA)}_2^{-2}$  complex suffered from severe overlapping of the proton resonances, making interpretation difficult.

In the course of applying multinuclear NMR to the problem of determining the kinetics of the carboxylate oxygen interchange, direct measurement of the cis/trans isomer ratio of the  $\text{Ni(IDA)}_2^{-2}$  complex was also accomplished. A mechanism for the racemization between cis and trans isomers has been inferred from the data.

Throughout this thesis, nuclei corresponding to various different functional groups and molecules will be referenced. The system used to designate these nuclei must reference the type of nucleus, the molecule, and the functional group in which it is located. The system developed for this purpose will take the form of:

Nucleus(molecule or isomer, group or position)

where:

Nucleus is proton, carbon-13, or oxygen-17, molecule

or isomer is cis, trans, or uncomplexed, and group or position is amino, methylene, carboxylate, etc.

The following table may be used as a reference:

Designations of the Nuclei  
Possible Entries and Meanings

|                     |                                                   |
|---------------------|---------------------------------------------------|
| Nucleus:            | O: oxygen-17                                      |
|                     | C: carbon-13                                      |
|                     | H: proton                                         |
| Molecule or Isomer: | u: uncomplexed ligand                             |
|                     | c: cis isomer of $\text{Ni}(\text{IDA})_2^{-2}$   |
|                     | t: trans isomer of $\text{Ni}(\text{IDA})_2^{-2}$ |
| Group or Position:  | n: non-bonded to the metal<br>(refers to oxygen)  |
|                     | b: bonded to the metal<br>(refers to oxygen)      |
|                     | c: carboxylate group                              |
|                     | m: methylene group                                |
|                     | e: equatorial position<br>(proton only)           |
|                     | a: axial position<br>(proton only)                |

Note that due to inherent inequivalence of some nuclei in the complex based upon molecular symmetry, a number will be added to further designate the nucleus under discussion.

An example is the carboxylate carbon resonances possible for  $\text{Ni}(\text{IDA})_2^{-2}$ . There are three possible resonances based upon molecular symmetry,  $\text{C}(\text{c}, \text{c1})$ ,  $\text{C}(\text{c}, \text{c2})$ , and  $\text{C}(\text{t}, \text{c})$ , where c1 and c2 designate an a priori inequivalence of the possible carboxylate resonances of the cis isomer.

## II. Theory

Although the instrumentation for the measurement of NMR spectra has become very sophisticated, the theory used to treat NMR shift and relaxation data has been well developed. This is particularly true in the area of the NMR spectra of chemical species in solution. The theory of relaxation mechanisms used in this thesis has been elegantly described in the landmark work of Abragam (12), and equations are reproduced here only for convenience.

Additionally, the chemical systems of interest here are subject to the effects of chemical exchange on the NMR relaxation and chemical shift measurements. This subject has been treated exhaustively in the literature under general (13) and limiting (2) conditions. A short review of the relevant aspects of the theory of chemical exchange is also given.

### 1. Chemical Exchange

The theory of magnetic resonance lineshapes under the condition of chemical exchange has been treated by many authors in a variety of ways and for different limiting conditions (2,14-16). The model used here is applicable to chemical exchange between two sites, a and b, of equal populations. This condition leads to a number of simplifications in the theory. Under the equal population

condition, the average lifetime of a nucleus in either site is the same. Hence  $\tau_{ab} = \tau_{ba} = \tau$  where  $\tau$ 's are the symbols for the average lifetime and are the respective inverses of the first order rate constants for the exchange. Also, in the absence of exchange each site has a resonance centered at a frequency  $\omega_0$  measured in radians per sec. The resonant frequency of site a is then  $\omega_{0a}$ . The difference in resonance frequencies from a to b is written as:

$$\Delta\omega_{ab} = \omega_{0a} - \omega_{0b} \quad (1)$$

In the limit of slow chemical exchange, the difference between the resonances is much larger than the rate of exchange between them. This condition may be expressed as (15):

$$\Delta\omega_{ab} \gg \frac{2}{\tau} \quad (2)$$

where

$$\frac{2}{\tau} = \frac{1}{\tau_{ab}} + \frac{1}{\tau_{ba}}$$

In this case the resulting NMR spectrum consists of two separate resonances centered at  $\omega_{0a}$  and  $\omega_{0b}$  with Lorentzian lineshapes in the absorption mode (15). The linewidths of the observed resonances are broadened by the chemical

exchange such that the effective linewidth of one resonance is the sum of the linewidth in the absence of exchange and the first order rate constant of the chemical exchange from that site to the other. That is,

$$\text{site a: } \frac{1}{T_2}(\text{OBS}) = \frac{1}{T_{2a}} + \frac{1}{\tau_{ba}} \quad (3)$$

and

$$\text{site b: } \frac{1}{T_2}(\text{OBS}) = \frac{1}{T_{2b}} + \frac{1}{\tau_{ab}} \quad (4)$$

Under the conditions of the experiments in this thesis only the slow exchange limit was attainable. For the sake of completeness, the fast exchange limit is now discussed.

As the rate of chemical exchange is increased, for example by raising the temperature, the two resonances continue to broaden and shift toward each other until ultimately they begin to coalesce into a single broad lineshape. The exact form of the lineshape in this transition region is complex (2,13,14,15). As the exchange increases the coalesced lineshape decreases in width and again assumes a simple Lorentzian form with the effective linewidth being the weighted sum of the linewidths from each site, i.e.,

$$\frac{1}{T_2} (\text{OBS}) = \frac{P_a}{T_{2a}} + \frac{P_b}{T_{2b}} \quad (5)$$

where the  $P_a$  and  $P_b$  factors are the fractional populations of the sites. The final resonance frequency is then located at the frequency

$$\omega = P_a \omega_{oa} + P_b \omega_{ob} \quad (6)$$

The first order rate constant is assumed to be temperature dependent and to have the form of the Eyring equation:

$$k(\text{exch}) = \frac{1}{\tau} = \frac{kT}{h} \exp \left[ - \frac{(\Delta H^\ddagger - T\Delta S^\ddagger)}{kT} \right] \quad (7)$$

where

$\Delta H^\ddagger$  = enthalpy of activation, cal/mole

$\Delta S^\ddagger$  = entropy of activation, cal/(mole-°K)

and the  $k$  on the right is the Boltzmann constant.

## 2. Relaxation Mechanisms

The theory of NMR relaxation has been well described by Abragam (12), and the details of the derivations of the equations for the relaxation mechanisms given below are found there. Additionally, as only FT and CW measurements of  $T_2$  were made on the chemical system at hand, only the

equations pertaining to  $T_2$  are given; the equations for the accompanying  $T_1$ 's, or longitudinal relaxation times, are given in Abragam as well.

The understanding of the relaxation mechanisms which operate in these experiments is a central point in interpreting the relaxation data, mainly because of the absence of a good diamagnetic blank for the oxygen-17 data. The lack of a blank resulted in estimating the magnitudes of the contributions of the mechanisms to be observed relaxation rates in order to extract the chemical exchange results.

#### Dipole-dipole Relaxation

This mechanism results from the coupling of the nuclear magnetic moment of the nucleus in question (proton, carbon-13, or oxygen-17) with the strong electronic magnetic moment of the  $\text{Ni}(\text{IDA})_2^{-2}$  complex. The magnitude of this coupling is dependent upon the relative orientation of the electronic moment and the nuclear moment. As the complex tumbles through the solution, this coupling makes a zero net average contribution to the chemical shift, provided the tumbling of the complex is isotropic and the g-tensor has negligible anisotropy. Based upon the crystallographic work on the complex (7) the complex will be assumed to be roughly spherical overall and able to tumble isotropically. Although the g-tensor cannot be exactly isotropic, it seems likely that the anisotropy is small, since the half-filled orbitals

are the two  $e_g$  orbitals which by themselves would be isotropic.

The nuclear relaxation arises by an interruption of the coupling by several possible events, including the tumbling of the complex, electronic relaxation, or chemical exchange (12). In principle this dipolar interaction would exist between any two magnetic moments in the solution, but interactions between nuclei are smaller by ca. three orders of magnitude than the electronic-nuclear interactions. Electronic-nuclear interactions arising from a nucleus in one complex and an electronic moment in another are small on the basis of the strong dependence on the distance between them. Only interactions within one complex will be treated here.

The equation for the transverse relaxation rate for dipolar coupling is:

$$\frac{1}{T_2} (DD) = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6} \left[ 4\tau_1 + \frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2} + \frac{3\tau_1}{1+\omega_I^2\tau_1^2} + \frac{6\tau_2}{1+\omega_I^2\tau_1^2} + \frac{6\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2} \right] \quad (8)$$

where:

$S$  = electronic spin, which is 1 for Ni (II) in octahedral crystal fields

$\gamma_I$  = magnetogyric ratio of the nucleus, radians/sec-Gauss

$\gamma_S$  = magnetogyric ratio for  $Ni(IDA)_2^{-2}$  unpaired electrons, which is given by  $g/\beta\hbar$

$r$  = distance between I and S; S will be assumed to be located effectively at the nickel center.

$\omega_I$  = resonance frequency of the nucleus, radians/sec

$\omega_S$  = resonance frequency of the electronic moment

$$\frac{1}{\tau_1} = \frac{1}{T_{2S}} + \frac{1}{\tau_r} + \frac{1}{\tau}$$

$$\frac{1}{\tau_2} = \frac{1}{T_{1S}} + \frac{1}{\tau_r} + \frac{1}{\tau}$$

$\tau_r$  = rotational correlation time of  $\text{Ni(IDA)}_2^{-2}$  in solution

$\tau$  = exchange lifetime for the nucleus in site a or b

$T_{1S}$  = longitudinal relaxation time of the electrons

$T_{2S}$  = transverse relaxation time of the electrons

### Scalar Coupling

Scalar coupling is an orientation-independent interaction between the nucleus and the unpaired electrons of nickel. It results from mechanisms of delocalization of unpaired spin density or spin polarization (9) so as to yield a non-zero probability of unpaired spin density in an s orbital at the nucleus. The interaction is also the source of paramagnetic shifts (18), which will be described later, as tumbling does not average the interaction to zero. The interaction is interrupted by chemical exchange or electronic relaxation, but not molecular tumbling. The equation for the transverse nuclear relaxation rate is given as (12):

$$\frac{1}{T_2}(\text{SC}) = \frac{S(S+1)}{3} \left( \frac{A}{\hbar} \right)^2 \left[ \tau_{C1} + \frac{\tau_{C2}}{1 + (\omega_I - \omega_S)^2 \tau_{C2}^2} \right] \quad (9)$$

where:

A = Scalar coupling constant, erg; the quantity measured from the chemical shift measurements will be reported as  $A/\hbar$ , radians/sec.

$$\frac{1}{\tau_{C1}} = \frac{1}{T_{2S}} + \frac{1}{\tau}$$

$$\frac{1}{\tau_{C2}} = \frac{1}{T_{1S}} + \frac{1}{\tau}$$

#### Quadrupole Coupling

This interaction arises only for nuclei which have a quadrupole moment, i.e.,  $I > 1/2$ . Proton and carbon-13 nuclei obviously do not experience this mechanism, and generally exhibit sharp lines in diamagnetic solutions as a result. Oxygen-17, with  $I=5/2$ , does experience the coupling, and quadrupole coupling provides a very efficient mechanism of relaxation for this nucleus under even diamagnetic conditions. The nucleus only experiences the coupling in the presence of electronic fields of symmetry lower than cubic, a situation realized in the bonding systems of most molecules. The coupling is dependent upon orientation, and thus, it is interrupted by molecular tumbling. Chemical exchange is also a source of interruption of the interaction. The equation for the transverse relaxation

rate due to quadrupole coupling is given as (12):

$$\frac{1}{T_2}(Q) = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2 q Q}{\hbar}\right) \tau_c \quad (10)$$

where:

$eQ$  = the quadrupole coupling constant of the nucleus

$eq$  = the largest component of the electric field  
gradient tensor, measured in the principle axis  
system of the molecule

$\eta$  = the asymmetry parameter, measuring the asymmetry  
of the electric field gradient at the nucleus  
relative to axial symmetry

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau}$$

and the condition that  $\omega_I^2 \tau_c^2 \ll 1$  is met. For the case of the solutions studied here, where the viscosity is of the order of 0.01 poise (see Experimental section), this condition is easily met.

### 3. Chemical Shift Mechanisms

#### Contact Shifts

The chemical shifts of greatest interest in this thesis are so-called contact, or scalar, shifts due to the presence of unpaired spin density at the nucleus which is being

observed by the NMR experiment. This scalar coupling mechanism has been discussed above with respect to its effect on nuclear relaxation. The theory of the origins of shifts of this nature have been treated elsewhere (18-22), and only the pertinent aspects of the theory will be presented here.

The scalar coupling interaction is a "through-bond" interaction, and its effect on the nuclear shift was first described by McConnell and Chestnut (20). Bloembergen (19) treated the effect in terms of an isotropic g-tensor and one thermally populated electronic state of a paramagnetic impurity in aqueous solution. Zero-field splitting is ignored. These conditions lead to the following expression, from which the scalar coupling constant can be determined:

$$\frac{\Delta\omega}{\omega_0} = - \frac{g\beta}{\gamma_I} \frac{S(S+1)}{3kT} \cdot \frac{A}{\hbar} \quad (11)$$

where  $g$  = rotationally averaged g-value for the complex

$\beta$  = Bohr magneton

$\gamma_I$  = nuclear magnetogyric ratio

$S$  = electron spin of the complex

$A/\hbar$  = scalar coupling constant in radians/sec

$\Delta\omega$  = contact, or scalar, shift in radians/sec.

The question of a proper chemical shift reference will be considered later.

A more complete theoretical model for the contact shift has been developed (21) which incorporates the effects of zero-field splitting, g-tensor anisotropy, etc., to yield an expression of the following form (assuming  $S = 1$  and an axially symmetric crystal field):

$$\frac{\Delta\omega}{\omega_0} = - \frac{2g\beta}{\gamma_I 3kT} \cdot \frac{A}{\hbar} \cdot \left[ 1 - \frac{g_{\parallel} - g_{\perp}}{9g} \right] \cdot \frac{D}{kT} \quad (12)$$

where  $D$  = zero field splitting constant, in ergs  
 $g_{\parallel}$ ,  $g_{\perp}$  = parallel and perpendicular components of the g-tensor in the axial field.

If  $D \ll kT$ , or if the anisotropy of the g-tensor is small, the expression reduces to that given in equation 11. For nickel in crystal fields of octahedral symmetry,  $D$  is expected to be  $< 5 \text{ cm}^{-1}$  (21). Led and Grant (23) have given a very elaborate, detailed study of the carbon-13 NMR relaxation and shift data for  $\text{Ni}(\text{his})_2$  and found that  $D = 1.05 \text{ cm}^{-1}$ . This value may be considered an approximation to  $D$  in the  $\text{Ni}(\text{IDA})_2^{-2}$  complex. Thus  $D/kT = 5 \times 10^{-3}$ . Using the following relationship for octahedral nickel (21)

$$D = \frac{1}{2} \lambda (g_{\parallel} - g_{\perp}) \quad (13)$$

where  $\lambda$  is the spin-orbit coupling constant, the anisotropy in the g-tensor (strictly only for an axially symmetric crystal field) may be estimated to be on the order of 0.01.

Hence, equation 12 reduces to equation 11, and it is expected that the isotropic contact shift equation may be applied to the data in this thesis without significant error.

Inherent in the justification of the use of the simple contact shift equation is the assumption that the  $\text{Ni}(\text{IDA})_2^{-2}$  species in solution is of essentially cubic symmetry. The crystal structure (7) supports this, as well as the  $\text{Ni}(\text{his})_2$  g-value of 2.13 (23). The predominant form of the  $\text{Ni}(\text{his})_2$  complex has the same molecular symmetry as the cis isomer of  $\text{Ni}(\text{IDA})_2^{-2}$ , and the susceptibility measurements may be expected to be similar. Therefore, as the g-value indicates an octahedral symmetry, it will be assumed that the magnetic symmetry of either isomer of  $\text{Ni}(\text{IDA})_2^{-2}$  in solution is essentially octahedral.

#### Pseudo-contact Shifts

If the g-tensor is anisotropic, as it strictly is in crystal fields of lower than cubic symmetry, a second mechanism of the shift arises, the so-called pseudo-contact shift mechanism (22). It arises when the dipolar interaction between the metal magnetic moment and the nuclear magnetic moment does not average to zero when the complex tumbles isotropically in solution. This residual shift carries the temperature dependence of the magnetic susceptibility. The appropriate equation for the pseudo-contact shift for an  $S = 1$  spin state in an axially

symmetric crystal field is given by (21):

$$\frac{\Delta\omega}{\omega_0} = \frac{2\beta^2(g_u^2 - g_l^2)}{9kT} \cdot \frac{(3\cos^2\Omega - 1)}{R^3} \cdot \left[ 1 - \frac{(g_u^2 + \frac{1}{2}g_l^2)}{3(g_u^2 - g_l^2)} \cdot \frac{D}{kT} \right] \quad (14)$$

$R$  is the metal-nucleus distance, and  $\Omega$  is the angle between  $R$  and the principal magnetic axis of the complex (usually denoted the  $z$  axis). This equation is derived for a complex tumbling in solution. In a formally octahedral crystal field, where the  $g$ -tensor is isotropic, the pseudo-contact shifts vanish identically. The same arguments given earlier for the reduction of the contact shift equation to the isotropic shift equation also lead to a result that the pseudo-contact shifts become unmeasurable. Henceforth, these shifts will be ignored.

#### Diamagnetic Shift Reference

In principle, applying the simple contact shift equation to the data required identifying an appropriate shift reference. In these cases a diamagnetic analogue of  $\text{Ni(IDA)}_2^{-2}$  would be appropriate, perhaps using  $\text{Zn(IDA)}_2^{-2}$ . As mentioned in the Experimental section there were considerable chemical problems making the oxygen-17 shift reference. In all cases treated here the uncomplexed ligand was chosen as the reference, as it was readily available in the solutions studied.

It is expected that the error in using the uncomplexed ligand as the diamagnetic shift reference will be small, perhaps  $<1$  ppm for protons. This is based upon proton NMR spectra taken on the diamagnetic  $\text{Pb}(\text{NTA})^-$  complex (24), where NTA represents the nitrilotriacetate ligand, in which the chemical shift of the protons of the complex were measured relative to the free NTA ligand. In a separate study (25), even smaller relative shifts were observed for  $\text{Zn}(\text{MIDA})_2^{-2}$  and MIDA ligand, where MIDA represents the IDA ligand with a methyl group substituted for the proton at the amino nitrogen. In the case studied here,  $\text{Ni}(\text{IDA})_2^{-2}$ , the chemical exchange of the bulk ligand with the complex is slow, and thus the shift difference between a diamagnetic analogue and the uncomplexed ligand might be expected to be reasonably independent of temperature. An absolute error on the order of 1 ppm does not jeopardize the determination of the scalar coupling constants by the simple contact shift treatment.

### III. Experimental

#### 1. Sample Preparation

A variety of samples was prepared during the course of this work. Although proton and carbon-13 NMR measurements were possible on samples with natural abundance nuclei, oxygen-17 NMR required enriched samples due to the inherently low sensitivity of the nucleus and the limited solubilities of the species of interest.

NMR samples of  $\text{Ni}(\text{IDA})_2^{-2}$  were prepared by weighing out the appropriate amounts of water enriched in oxygen-17, anhydrous  $\text{NiCl}_2$ , dipotassium iminodiacetate ( $\text{K}_2\text{IDA}$ ), and potassium hydrogen iminodiacetate ( $\text{KHIDA}$ ). The amounts which were chosen were calculated on the basis of acid dissociation constants and metal complexation constants given in Sillen and Martell's compilation, Stability Constants of Metal-Ion Complexes (26). The use of anhydrous salts was adopted to avoid isotopic dilution of isotopically enriched water ( $\text{H}_2\text{O}$ -17 35%), which was obtained from the Oak Ridge National Laboratory, Oak Ridge, TN. The oxygen isotopic composition of the water was known; it had a normal proton-deuterium content.

Anhydrous  $\text{NiCl}_2$  was prepared from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (GFS) by treating the hydrated salt with thionyl chloride and drying under vacuum. Although perchlorate salts had been used in

previous studies of  $\text{Ni}(\text{IDA})_2^{-2}$  (5), perchlorate salts in this case would possibly pose a safety hazard and were therefore avoided. Potassium salts of the iminodiacetic acid (Eastman Kodak) were produced by stoichiometric addition of KOH, followed by re-crystallization and drying under vacuum. Composition was checked by elemental analysis. All anhydrous salts were stored in sealed dessicators containing  $\text{P}_2\text{O}_5$  as the dessicant.

In order to observe the  $\text{O}(\text{c},\text{n})$  and  $\text{O}(\text{t},\text{n})$  resonances of  $\text{Ni}(\text{IDA})_2^{-2}$  (collectively labelled  $\text{O}(\text{ct},\text{n})$  in this thesis) the carboxylate group of the IDA ligand had to be enriched with  $\text{O}-17$ , since estimates of scalar coupling constants and other relaxation parameters indicated the resonance to be unmeasurable if  $\text{O}(\text{ct},\text{n})$  were at natural abundance (0.037%). Enrichment was performed on the metal complex in situ at  $\text{pH}=10$  with an excess of ligand and in a sealed Pyrex tube. The tube was heated at ca.  $70^\circ \text{C}$  for 300 hours to promote isotopic oxygen-17 exchange between the carboxylate group of iminodiacetate ligand and water. A small amount of precipitation was noted after the exchange. The pH was checked, and the isotopically depleted solvent water was removed by vacuum distillation. This was replaced with purified natural abundance water. The removal of the enriched water from the sample was necessary as the water oxygen-17 resonance would have been so large as to dominate totally the NMR spectrum of the sample, possibly obscuring

the O(ct,n) resonance of interest. This would have been the case in either FT or CW experiments. Isotopic exchange of oxygens among complex, ligands, and water would obviously continue after redissolving in natural abundance water. However, the bulk of the time would be spent at room temperature, and the isotope exchange rate would be small.

Only one sample of enriched  $\text{Ni(IDA)}_2^{-2}$  was prepared due to the cost of the isotopically enriched water. The concentration of  $\text{Ni(IDA)}_2^{-2}$  was measured spectrophotometrically with a Cary 14 spectrophotometer against carefully prepared calibration standards after the exchange had been done, and oxygen-17 NMR was used to measure the ligand concentration relative to the complex. The composition of this sample is summarized in Appendix I.

As mentioned above, samples studied by proton and carbon-13 NMR did not suffer from the severe constraints of isotope abundance or expense. These were prepared in a much more straightforward manner, although the anhydrous metal and acid salts were used in their preparation as well. Care had to be taken to distill  $\text{H}_2\text{O}$  away from the proton NMR samples and replace it with  $\text{D}_2\text{O}$  to avoid the complications from a large water proton signal and provide a deuterium field locking signal. The samples were either sparged directly with dry nitrogen or prepared with components previously sparged.

Carbon-13 NMR samples were slightly different from the

others in that a small amount of dioxane was added as a chemical shift reference, and the samples contained 20% D<sub>2</sub>O to provide a strong deuterium resonance for magnetic field locking purposes.

## 2. Viscosity Measurements

Viscosities of sample solutions were measured using an Ostwald viscometer thermostatted with a circulating water bath. The viscometer constant was determined with doubly distilled water, and the samples were measured immediately thereafter. As the solutions examined here are relatively dilute, the temperature dependence of the viscosity is assumed to follow the temperature dependence of pure water (27). The uncertainty in the temperature control of the viscometry measurements was estimated to be better than 1° C.

## 3. Fourier Transform NMR Measurements

The oxygen-17, carbon-13, and proton nuclear magnetic resonance measurements were made with a UC Berkeley Department of Chemistry NMR spectrometer, which operates at a field strength of 42 kG and in the Fourier transform (FT) mode. An internal deuterium locking system provides magnetic field strength stability. The NMR system computer, a Nicolet Technology NTC-1180 model, was used in both chemical shift and linewidth measurements, as a number

computing subroutines for peak-picking, baseline adjustment, and lineshape fitting were available. In using these routines care was taken to apply the baseline adjustment program only when the resonances covered a linear (though possibly tilted) baseline region. This was particularly important for spectra with large sweep widths, as baseline problems at times were serious. Care was taken to minimize the phase corrections, as large values for this correction are known to produce lineshape distortion.

The pulse sequence used in these experiments was a simple single pulse sequence, P2-DE-AT-D5, where P2 is the pulse width in microseconds, DE is a delay time in microseconds, AT is the acquisition time for the FID signal (the magnitude of which depends upon the desired sweep width and the size of the memory used for accumulation of the data), and D5 is a wait time of variable length which allows the nuclear magnetization sufficient time to return to its thermal equilibrium value. P2 was chosen such that the pulse power was evenly distributed across the desired spectral width.

Temperature control was effected by flowing heated or cooled dry nitrogen gas through the sample probe. System design allowed temperature regulation via a feedback circuit controlling the fine heating element directly below the probe, while the coarse heating element was crudely adjusted to the approximate desired temperature. This

temperature was monitored with a copper-constantan thermocouple located within 0.5 cm of the bottom of the sample tube as inserted in the probe. The temperature uncertainty was estimated to be within 0.2° C.

Transverse relaxation rates ( $1/T_2$ ) were measured from linewidths by hand or computer fitting subroutines. Although magnet inhomogeneity is known to affect the measurement of  $1/T_2$  (28), the magnitude of such an effect is believed to be less than 0.1% of the total measured linewidth in the cases studied here, based upon the observations and arguments of Earl (17).

Chemical shift measurements were made using the convention that a downfield shift is considered to have a negative shift.

#### 4. Continuous Wave NMR Measurements

The oxygen-17 linewidth measurements were made at the wide-line NMR facility at Washington State University, Pullman, Washington, at a resonance frequency of 13.12 MHz (29). This spectrometer operates in the swept frequency mode, allowing a stable external lock of lithium-7 for signal averaging. The continuous-wave (CW) approach for the O(ct,n) linewidth measurements was favored as a result of serious baseline problems which arose throughout the FT experiments in Berkeley.

A marginal oscillator probe was used for the swept

frequency operation, and the field was modulated at 5.000 kHz. This led to some perplexing, overlapping spectra, but the gain in baseline stability more than compensated for this drawback. In order to extract linewidth data, the non-saturated spectra were fitted to a sum of Lorentzian lineshapes with the Oak Ridge General Least Squares (ORGLS) fitting program (30).

Temperature control for these experiments was accomplished by a continuously circulating, temperature-regulated bath of silicone oil. The temperature was monitored with a copper-constantan thermocouple inserted in the probe body. Temperature stability of this system is excellent and is estimated to be within  $0.1^{\circ}$  C.

## 5. Curve Fitting

Computing and curve fitting were done with the Lawrence Berkeley Laboratory CDC 7600 computer. Both the ORGLS (30) and the Dye and Nicely (31) general least squares computer programs were used. Fitting simultaneous sets of data was done using the appropriate subroutines of these programs.

#### IV. Results and Discussion

##### Characterization of Multinuclear NMR Spectra of



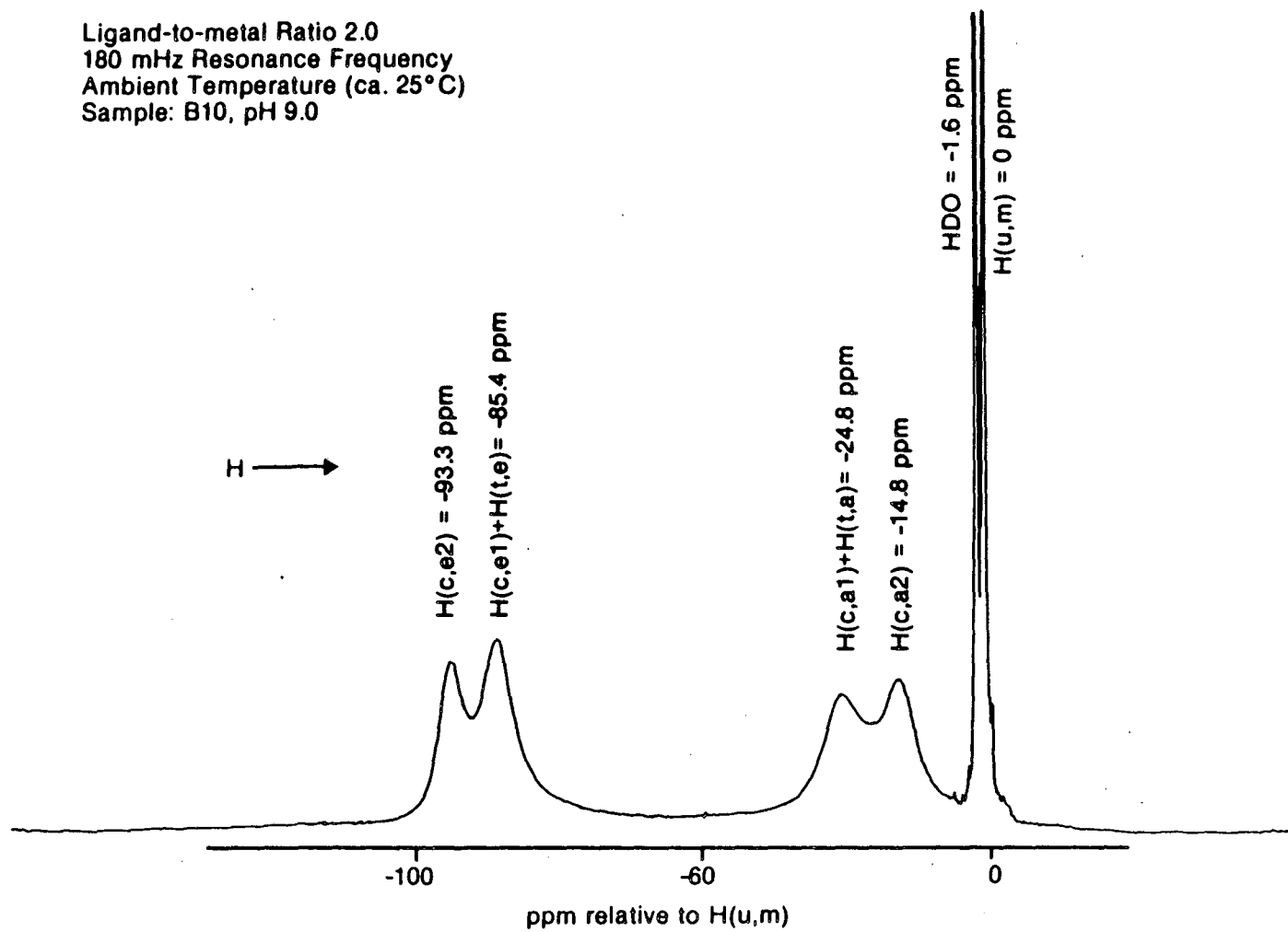
##### 1. Proton NMR Spectra

##### A. Characterization of the Spectra

The proton NMR spectrum of  $\text{Ni(IDA)}_2^{-2}$  has been studied by several groups (10,11,32). Pratt and Smith (10), Erickson, et.al. (11), and Everhart and Evilia (32) have studied this system under continuous wave NMR conditions and have all obtained essentially the same results. The spectrum of  $\text{Ni(IDA)}_2^{-2}$  consists of two pairs of downfield resonances at ca. -20 ppm and -90 ppm at room temperature, relative to uncomplexed ligand resonances. The resonances are due to the methylene protons of the acetate arms coordinated to the nickel ion. An example of the spectrum of  $\text{Ni(IDA)}_2^{-2}$  taken at 180 MHz proton frequency is given in Figure 1. The amino proton of IDA has been reported to be ca. +200 ppm from water (10), and similar results for amino as well as methylene proton resonances have been observed for other amino acid and amine complexes of nickel ion (33-36). All the resonances attributed to the complex are broadened by the strong interaction these nuclei have with the paramagnetic Ni(II), which has electronic spin

**FIGURE 1**  
**Proton NMR Spectrum of  $\text{Ni}(\text{IDA})_2^{3-}$  taken at 180 MHz**

Ligand-to-metal Ratio 2.0  
 180 MHz Resonance Frequency  
 Ambient Temperature (ca. 25°C)  
 Sample: B10, pH 9.0



S=1.

The downfield shifts of the protons of IDA coordinated to nickel have been well characterized by the dependence of the shift upon the dihedral angle created by the Ni-N-C and N-C-H (methylene group) planes in the Ni-N-C-H ligand fragment (1). The extent of spin delocalization to the protons of the methylene group is controlled by this dihedral angle, with equatorial protons relative to the five member ligand/metal ring having greater spin delocalization and downfield shift. Figure 1 has been labelled with the equatorial protons downfield from the axial protons. It is interesting to note that this dihedral angle dependence parallels a similar dependence observed in many other systems, including, for example, proton spin-spin coupling in H-C-C-H fragments (37).

Although the observed spectra (33-36) were essentially identical, they have been interpreted differently. Each group recognized that once the first ligand is attached to the metal ion, the second ligand could complex such that that the nitrogen of the second ligand is either cis or trans to the first ligand nitrogen. Additionally, the ligand might coordinate in a facial or meridional manner, although the meridional isomer can be easily argued to be more strained and thereby unlikely (11).

In fact, this point is resolved by investigating the 1:1 ligand-to-metal complex  $\text{Ni}(\text{IDA})(\text{H}_2\text{O})_3$  (11). In the 1:1

complex the IDA may be coordinated in either the facial or meridional manner. If one acetate arm of the facial isomer moves to the adjacent coordination site, the resulting strain on the acetate arms of the ligand causes axial and equatorial protons to exchange, on the basis of molecular models. The proton NMR of the  $\text{Ni}(\text{IDA})(\text{H}_2\text{O})_3$  complex shows two downfield resonances. As temperature is increased, these resonances sharpen, and the spectrum shows no sign of chemical exchange between the equatorial and axial positions for the protons. Therefore, the observed spectrum must be due to one isomer or the other, but not both, since four resonances would be observed in the slow exchange limit. In the fast limit, axial and equatorial protons would average to give one resonance, which was not observed at any temperature. Therefore, one of the isomers must exist in negligible concentration. Presumably, the facial isomer would be much less strained and thereby favored. The x-ray crystallographic data on  $\text{Ni}(\text{IDA})_2^{-2}$  also shows the ligands to be in the facial configuration (7).

In the trans isomer of  $\text{Ni}(\text{IDA})_2^{-2}$  there are four equivalent equatorial protons labelled  $\text{H}(\text{t},\text{e})$  and four equivalent axial protons labelled  $\text{H}(\text{t},\text{a})$  purely on the basis of symmetry.  $\text{H}(\text{t},\text{e})$  is expected to have a greater downfield shift (1) than  $\text{H}(\text{t},\text{a})$ .

Symmetry, on the other hand, does not allow one to assume that all the equatorial or axial protons of the cis

complex are equivalent. There are four resonances possible:  $H(c,a1)$ ,  $H(c,a2)$ ,  $H(c,e1)$ , and  $H(c,e2)$ . As above, equatorial protons would be shifted downfield relative to the axials. Thus, six resonances are possible for mixtures of cis and trans, but only four are observed in Figure 1. (The amino proton is shifted upfield (10).) Because the areas are not all equal the system cannot be pure cis. Pratt and Smith postulated that  $H(c,a1)$  and  $H(c,a2)$ , as well as  $H(c,e1)$  and  $H(c,e2)$ , are so nearly equivalent that they could not be resolved. These two sets of resonances are located at -20 ppm and -90 ppm relative to the internal standard used in their work, which was t-butanol. Trans resonances were then assigned to be at -19 ppm and -95 ppm, forming a "bracket" around the cis methylene resonances. Integration yielded a cis:trans isomer ratio of ca. 60:40.

Erickson, et.al., (36) reasoned that the  $H(c,a2)$  and  $H(C,a2)$  were not equivalent, based upon the study of the N-methyl substituted analogue,  $Ni(MIDA)_2^{-2}$  (11). The proton spectrum of  $Ni(MIDA)_2^{-2}$  showed clearly sets of four cis resonances and two trans resonances. The authors reasoned that a similar distribution of proton resonances would exist in  $Ni(IDA)_2^{-2}$ , but in that case  $H(c,a2)$  and  $H(C,a2)$  were thought to overlap coincidentally with  $H(t,a)$ . The cis:trans isomer ratio was calculated to be 80:20.

Both explanations are feasible, although arguments based upon  $Ni(MIDA)_2^{-2}$  are more complete and convincing. In

an attempt to utilize the greater resolving power of higher field NMR spectrometers, proton FT-NMR spectra of  $\text{Ni}(\text{IDA})_2^{-2}$  were obtained at 180 MHz frequency as a function of temperature. 60 MHz CW NMR spectra were additionally obtained as a function of temperature. Both sets of data will be discussed below.

#### B. 60 MHz CW-NMR Spectra

CW proton spectra of  $\text{Ni}(\text{IDA})_2^{-2}$  were recorded in the temperature range of 0-100° C at 60 MHz. At ca. 50° C distinct coalescences of both the equatorial and axial protons were observed, consistent with earlier work (32). The sample contained residual free ligand at ca. +2 ppm relative to H<sub>2</sub>O. Neither pair of resonances coalesced with the free ligand methylene resonances in this temperature range.

Since the axial and equatorial protons do not coalesce with each other or with free (uncomplexed) ligand protons, the exchange mechanism at this temperature cannot be due to complete dissociation of the IDA. Dissociation would tend to average axial, equatorial, and uncomplexed proton resonances, which the data do not show. The observation that axial proton sites coalesced together, as did the equatorial, also tends to rule out the significant contribution of a mechanism which depends upon the decomplexation of an acetate arm from the nickel. When an

acetate arm comes off and goes back on again immediately, one would expect the dihedral angle dependence to be lost and partial averaging to occur between the equatorial and axial protons if the arm is off a significant proportion of the time. Some one arm of the complex is decomplexed only 1.5% of the time (5).

On the other hand, an intramolecular rearrangement by a twisting mechanism could explain these data and has been proposed (32). This mechanism would involve the twisting of one ligand of the complex relative to the other ligand about an axis which would be along a  $C_3$  symmetry axis of the  $O_h$  point group, as proposed by Bailar (38). The actual symmetry of the complex studied here is much lower, but the axis can be imagined as running directly through the center of the triangle formed by the three points of complexation of each ligand. The twist occurs around this axis.

Such a mechanism would randomize cis with trans, but not axial with equatorial sites. In fact, if the scalar coupling constants are known for these sites, an estimate could be made of the rate of exchange from one site to the next. Additionally, a carbon-13 NMR experiment would provide an independent measure of the same exchange rate, as well as a measure of the isomer distribution. These experiments were performed and will be described later.

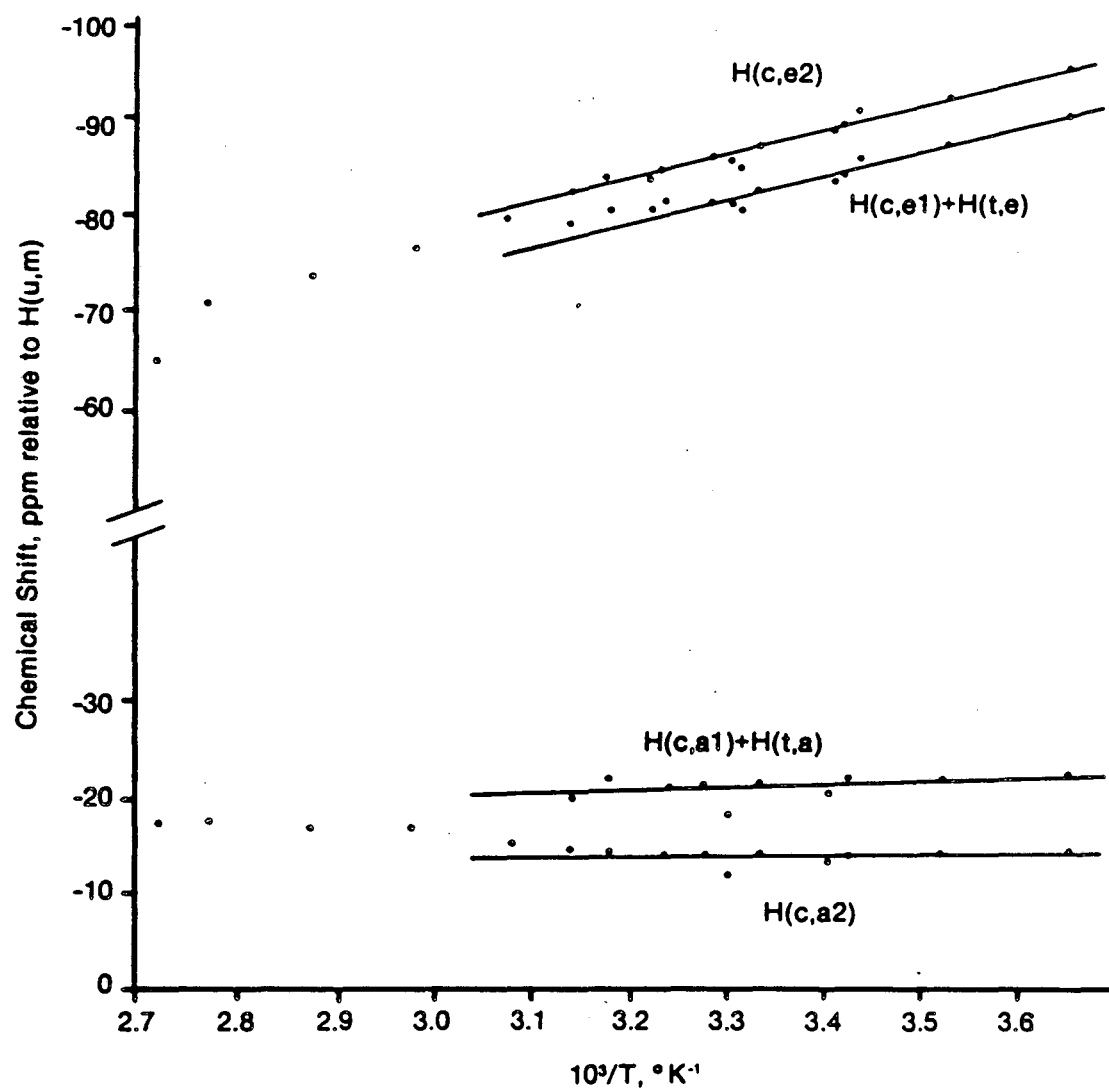
The chemical shifts obtained relative to the free ligand methylene protons, as a function of temperature, are

given in Table I and are plotted versus  $10^3/T$  in Figure 2. In principle, scalar coupling constants can be deduced from these data in the limit of slow chemical exchange, but the figures show that only low temperature points should be used in the analysis of the scalar coupling constants using the Bloembergen equation (equation 11) because of the coalescence.

The Bloembergen equation for the isotropic shift is used to treat the chemical shift data. The equation is accurate in the absence of pseudo-contact contributions to the shift, and this is expected for octahedral nickel complexes. The results of fitting the shift data in Table I, Appendix II, were obtained by choosing data points up to a temperature at which the rate of intramolecular exchange was much slower than the separation of the axial cis and trans proton resonances (as well as the equatorial). The points were then fitted with a linear least squares fitting routine. The linearity of the fit and the deviation of the intercept from zero determined exactly how many data points were to be included. The appropriate upper temperature limit was 30° C. The results of the fitting are as follows:

| Resonance      | Scalar Coupling<br>Constant, $A/\hbar$ , $\text{sec}^{-1}$ | Correlation<br>Coefficient |
|----------------|------------------------------------------------------------|----------------------------|
| H(c,e2)        | $+6.9 \times 10^6$                                         | 0.983                      |
| H(c,e1)+H(t,e) | $+6.7 \times 10^6$                                         | 0.988                      |
| H(c,a1)+H(t,a) | $+1.9 \times 10^6$                                         | 0.877                      |
| H(c,a2)        | $+1.0 \times 10^6$                                         | 0.987                      |

**FIGURE 2**  
**Equatorial and Axial Proton Shifts**  
**of  $\text{Ni}(\text{IDA})_2^{\cdot-}$  vs.  $10^3/T$  at 60 MHz**



The correlation coefficient listed in the last column reflects the degree to which the experimental points are fitted to the a straight line. A perfect fit of the experimental points by the calculated line would yield a correlation coefficient of 1.000. A fair fit of the data is found when the correlation coefficient is less than or equal to 0.9.

### C. 180 MHz FT-NMR Spectra

Proton NMR spectra were additionally recorded in the FT mode at a frequency of 180 MHz. It was hoped that the higher field strength might give some further evidence of the nature of the spectral assignments. Spectra were again recorded as a function of temperature, but in this case 50° C was the upper limit of the temperature range.

The spectra exhibit the same general pattern as those obtained at 60MHz. Although the chemical shifts of the protons were readily measured from the spectra, linewidth data were difficult to extract. Chemical shifts were determined using computer programs available for the FT-NMR which fit the spectra to a sum of Lorentzian lineshapes. Chemical shift data are given in Table II. The linewidth data are given in Table III, Appendix II, but due to the uncertainty in the measurements, no analysis is presented

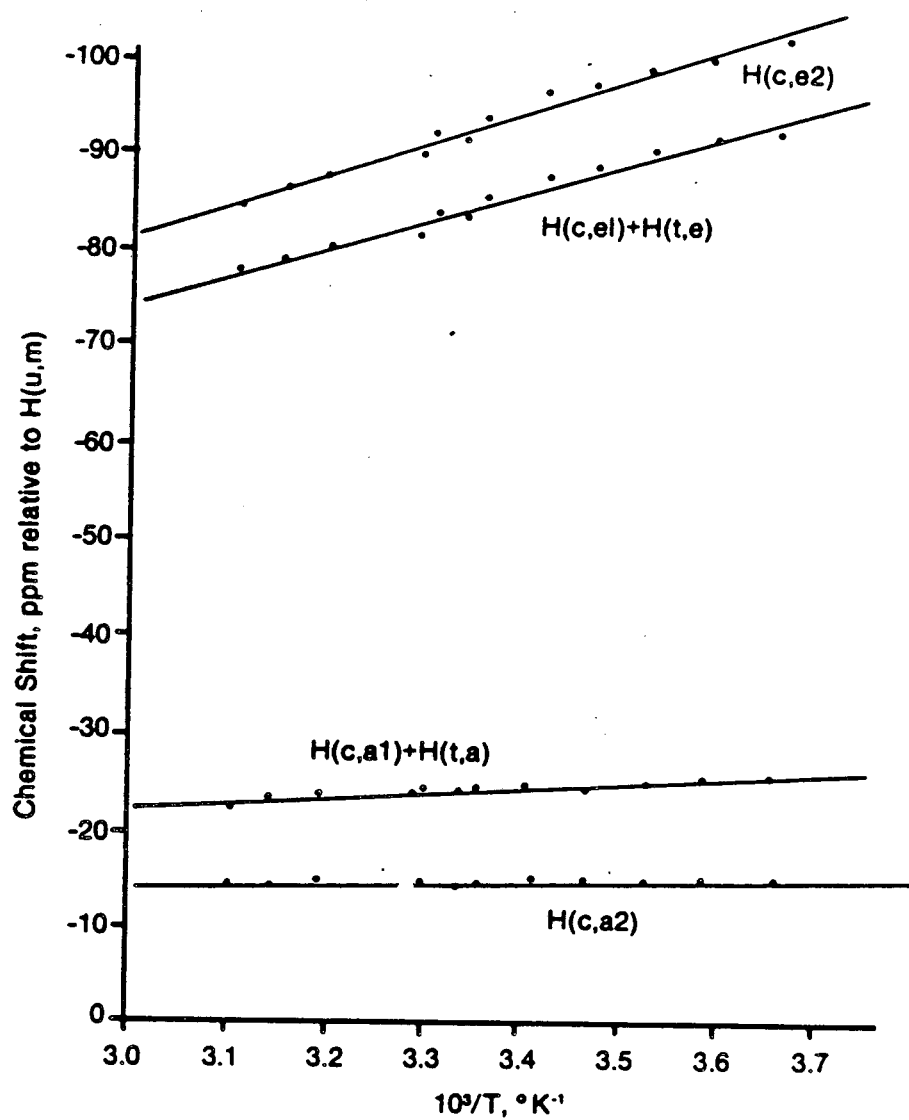
here.

It is interesting to note that no distinct coalescence of resonances was observed. Based on the 60 MHz data above, in which coalescence was observed at ca. 50° C, one might predict that at 180 MHz the rate of intramolecular exchange would have to be three-fold higher in order to observe a similar coalescence. For an activation energy of 10 kcal/mole for the rearrangement, as 10 degree rise would approximately double the rate of rearrangement. Therefore, if spectra had been recorded at 60 or 70° C, similar coalescence might have been observed. It is unfortunate that this could not be done at the time.

The shift data at 180 MHz are plotted in Figure 3. As mentioned above in the 60 MHz section, 30° C was chosen as the temperature above which no data would be included in the calculation of the scalar coupling constant using equation 11. Following this approach, and using the same linear least squares fitting routine as above, the following scalar coupling constants were computed.

| Resonance      | Calculated Scalar Coupling<br>Constant, $A/\hbar$ , $\text{sec}^{-1}$ | Correlation<br>Coefficient |
|----------------|-----------------------------------------------------------------------|----------------------------|
| H(c,e2)        | $+7.46 \times 10^6$                                                   | 0.991                      |
| H(c,e1)+H(t,e) | $+6.89 \times 10^6$                                                   | 0.991                      |
| H(c,a2)+H(t,a) | $+1.03 \times 10^6$                                                   | 0.973                      |
| H(c,a2)        | $+0.49 \times 10^6$                                                   | 0.900                      |

**FIGURE 3**  
Equatorial and Axial Proton Shifts  
of  $\text{Ni}(\text{IDA})_2^{\cdot-}$  vs.  $10^3/T$  at 180 MHz



The first two results agree with the 60 MHz constants to within 10%. The two final values are different by a factor of two, which may have been due to the poor resolution of the resonance at 60 MHz. The 180 MHz spectra were somewhat clearer, and the shift data were more easily extracted with greater accuracy. The chemical shift data were also fitted using the ORGLS program, and the results were essentially identical to those above. Equatorial proton data were fitted with a smaller residual and better fit than the axial proton data. The fit was better by a factor of three or less, and the scalar coupling constant agreed with the results above to less than 6% for equatorial protons and 16% for axial protons.

Finally, spectra were obtained of  $\text{Ni}(\text{IDA})_2^{-2}$  as a function of metal-to-ligand ratio. The purpose there was to look for changes in the spectra for  $L/M \geq 2.0$ , which would be the maximum expected coordination of the nickel. Essentially no change in the spectrum occurred, as expected. This result was further verified by repeating similar experiments using carbon-13 NMR. These data lead one to argue that no more than two ligands per nickel chelate in the excess of ligand.

## 2. Carbon-13 NMR Spectra

There has been considerable interest in using proton NMR spectra to characterize structure and dynamic processes occurring in transition metal/amino acid complexes in aqueous solution, as discussed in the preceeding section of this thesis. Although proton NMR has enhanced our understanding of electron spin delocalization and polarization processes, these spectra tend to give resonances which cover only a small chemical shift range. Any given proton does not contribute much to the overall molecular orbital bonding system, and the proton shift range is narrow. In diamagnetic compounds this range is well known to be <20 ppm. The range is ca. 200 ppm for the carbon-13 resonances under the same conditions, since this nucleus has up to four atoms bonded to it, each influencing its chemical shift to a large degree. Resolution of carbon resonances is greatly improved relative to proton resonances, allowing better identification and characterization. In comparison, even in paramagnetic complexes like  $\text{Ni}(\text{IDA})_2^{-2}$ , where the bound proton chemical shifts are between -100 and -20 ppm relative to the uncomplexed ligand, these shifts are relatively small compared to carbon. Proton resonances likely overlap leaving uncertainties in structural identification.

One of these uncertainties in the characterization of the  $\text{Ni}(\text{IDA})_2^{-2}$  complex is the cis/trans isomer distribution.

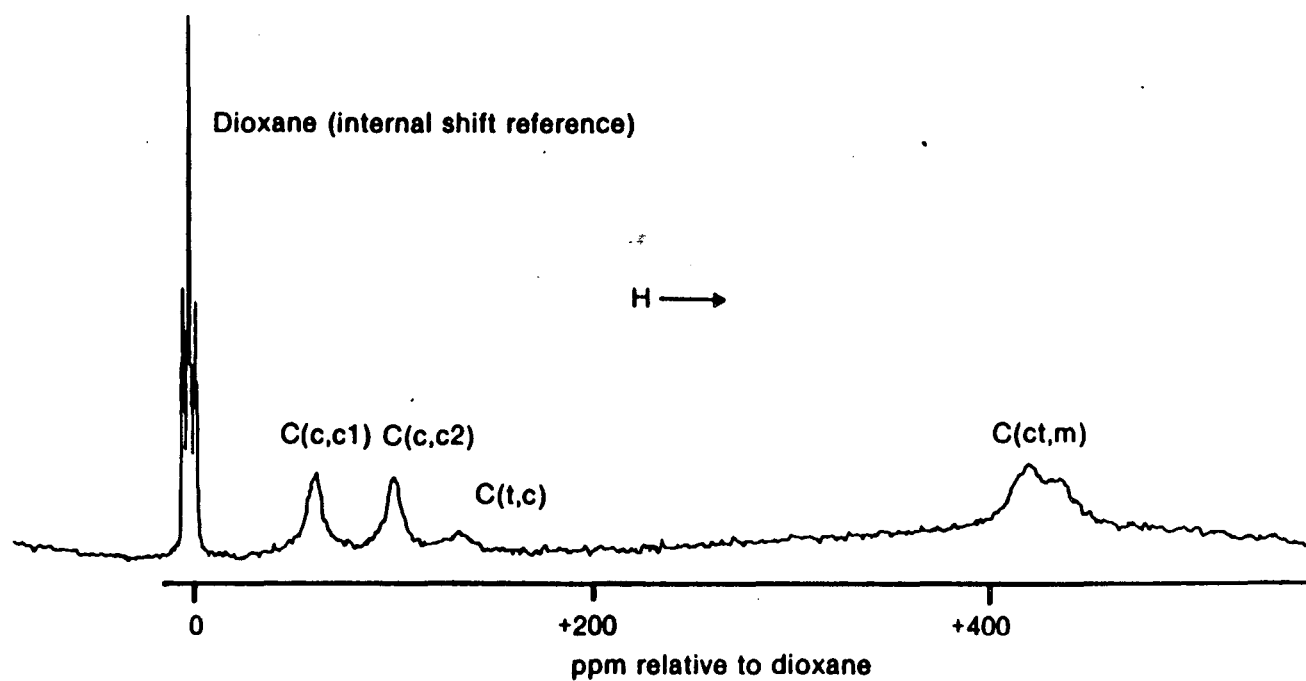
Although the analogies and indirect arguments used by Erickson, et.al., (11) can be persuasive, direct measurement of the cis/trans ratio is convincing. The large shift range of carbon NMR increases the likelihood that resonances will not overlap. Carbon-13 NMR spectra were obtained from the  $\text{Ni(IDA)}_2^{-2}$  complex in an attempt to measure directly this isomer ratio, as well as to obtain a second set of NMR data as a function of temperature which can be used both to characterize and to quantitate scalar coupling constants and relaxation mechanisms of the complex in aqueous solution.

A. Characterization of the Spectra at 25° C and the cis/trans Isomer Ratio

The recorded carbon-13 FT-NMR spectra, an example of which is given in Figure 4, may be compared with the CW-NMR spectra of  $\text{Ni(EDTA)}^{-2}$  recorded by Matwiyoff (39). The  $\text{Ni(IDA)}_2^{-2}$  spectra seem to fit well the pattern of resonances established for  $\text{Ni(EDTA)}^{-2}$ . Carbon-13 chemical shifts in the  $\text{Ni(EDTA)}^{-2}$  complex measured relative to the corresponding resonances in the uncomplexed ligand in the same solution are compared below with the analogous shifts in  $\text{Ni(IDA)}_2^{-2}$ .

**FIGURE 4**  
**Carbon-13 NMR Spectrum of  $\text{Ni(IDA)}_2^+$  in Aqueous Solution**

Ligand-to-metal Ratio 2.0  
45.29 MHz Resonance Frequency  
Temperature: 25.5°C  
Sample: C15, pH 8.0  
Undecoupled



| Nucleus                             | Approximate Chemical Shift,<br>ppm relative to uncomplexed ligand |                                    |
|-------------------------------------|-------------------------------------------------------------------|------------------------------------|
|                                     | Ni(EDTA) <sup>-2</sup>                                            | Ni(IDA) <sub>2</sub> <sup>-2</sup> |
| Carboxylate Carbon<br>C(ct,c)       | +100                                                              | +190                               |
| Acetate Methylene Carbon<br>C(ct,m) | +400                                                              | +425                               |
| Ethylenediamine Carbon              | +450                                                              | N/A                                |

As seen in Figure 4, resonances for Ni(IDA)<sub>2</sub><sup>-2</sup> fall in approximately these same regions, with the carboxylate carbons well resolved and the methylene carbons not. On the basis of the possible structures of Ni(IDA)<sub>2</sub><sup>-2</sup> the integrated intensities of the C(c,c1) and C(c,c2) resonances are theoretically equal. Direct integration of the two least upfield carboxylate resonances shows them to have equal populations. One of these two resonances corresponds to a carboxylate carbon nucleus located in an acetate arm which is located trans to another acetate coordination, while the other corresponds to an acetate located trans to an amino nitrogen. The assignment of the resonances is arbitrary, as there is no direct way to ascertain a priori which nucleus is shifted farther upfield. Henceforth, the less upfield resonance will be designated C(c,c1), and the more upfield resonance will be designated C(c,c2).

The third carbon resonance in the carboxylate region

may be assigned to the trans isomer, in which the four carboxylate carbon nuclei,  $C(t,c)$ , are equivalent on the basis of symmetry. When these  $C(c,c1)$ , and  $C(c,c2)$ , and  $C(t,c)$  resonances are all taken together, the resonances are distributed 80% cis isomer/20% trans isomer. This 80/20 cis/trans ratio supports earlier reasoning (11) which has already been described.

The methylene carbon resonances on the other hand were not fully resolved, and thus they are not useful for a second measurement of the cis/trans ratio. In fact, the severe overlap prohibited even semi-quantitative measurements. Because these resonances (of which there are again three possible) are severely overlapping, it may indicate that there are greater differences in spin delocalization mechanisms among the carboxylate nuclei than among the methylene carbon nuclei. This difference in the carbon resonances may indicate that the predominant contact interaction for the methylene carbons is through the amino nitrogen, whereas for the carboxylate carbons it is through the acetate oxygen, which in turn may be by direct delocalization or spin polarization arising from correlation effects. This would be consistent with carbon-13 NMR work on nickel complexes of amino acids (39,40).

#### B. 45.29 MHz NMR Spectra

##### Carbon-13 Chemical Shifts

Chemical shifts of the carbon resonances were obtained

by FT-NMR spectra at 45.29 Mhz resonance frequency. Three experiments were performed. The first experiment was a study of the carbon spectrum of  $\text{Ni(IDA)}_2^{-2}$  as a function of ligand-to-metal ratio in sample solutions. This was done to obtain shifts of both the complexed and uncomplexed ligand carbon nuclei while looking for distinct spectral changes as L/M increased. The L/M study was performed at ambient probe temperature, which was measured by thermocouple to be 24.5-25.5° C. Spectra were generally obtained without decoupling the proton resonances from the carbons to avoid excess heating of the probe due to the decoupling rf power. Results for this experiment are given in Table IV, Appendix II.

As the L/M ratio varied the observed chemical shifts (Table IV, Appendix II) remained constant. If one assumes that the chemical shifts for the bound carboxylate resonances should be the same regardless of the L/M ratio, then the uncertainty of the measurement of the shift is based on the repeatability of the observations. The C(u,c)-C(t,c) shift varied from 243.9 to 248.8 ppm, and the standard deviation of the series of measurements indicates a reproducibility of ca.  $\pm 3$  ppm, or  $\pm 1\%$ , sample-to-sample, in the worst case.

Second, a fourth resonance arose in the bound carboxylate carbon region of the spectrum in the L/M=1.5 sample. This sample was expected to have an appreciable amount of

Ni(IDA) species is found to be directly between C(c,c1) and C(c,c2). Methylene carbon resonances severely overlapped with those of  $\text{Ni(IDA)}_2^{-2}$ .

No changes occur in the spectrum above L/M=2.0. This confirms that the presence of species like  $\text{Ni(IDA)}_3^{-4}$  and higher species is unlikely.

The second experiment was a study of the unbound ligand resonances in the presence of dilute Ni(II) as a function of temperature to look for chemical exchange broadening of the carbon resonances. No exchange phenomena were evident in these experiments. Chemical shifts are given in Table V, Appendix II. The unbound ligand spectrum appears to be only weakly temperature dependent. In fact, the C(u,c)-C(u,m) shift over the 20° C range changed only by ca. 0.5 ppm, which is well within the accuracy of those measurements.

Over the same temperature range the resonant frequency of the dioxane standard shifted by -8.7 Hz absolute, or ca. -0.2 ppm. From this information one might estimate the temperature dependence of the dioxane shift to be -0.01 ppm/° C. The estimate does not take into account the temperature dependence of the deuterium resonance. The temperature dependence of the deuterium resonance is estimated to be +0.01 ppm/° C, so that the D<sub>2</sub>O resonance shifted ca. 0.2 ppm during the temperature study. If the lock signal shifts upfield by 0.2 ppm, the carbon resonances shift 0.2 ppm downfield. Hence one can expect that the

temperature dependence of the dioxane resonance is very weak, and measurement of the chemical shifts of  $C(c,c1)$  and  $C(c,c2)$  relative to it would be predicted to be accurate to  $\pm 1$  ppm, well within the observed reproducibility of the measurements given in Table IV, Appendix II.

Finally, the  $C(u,c)$ -IS chemical shift is constant over this temperature range to the accuracy of  $\pm 1$  ppm. This will be important when discussing temperature dependence of the bound carboxylate shifts and the application of the contact shift equation (equation 11).

The third experiment was the careful measurement of the  $C(c,c1)$ ,  $C(c,c2)$ , and  $C(t,c)$  chemical shifts and linewidths as a function of temperature relative to the dioxane internal standard. A solution containing an  $L/M = 2.0$  was used as the test sample (sample C15, Appendix 1). Three separate attempts were made to make these measurements, and the combined results are given in Table VI, Appendix II.

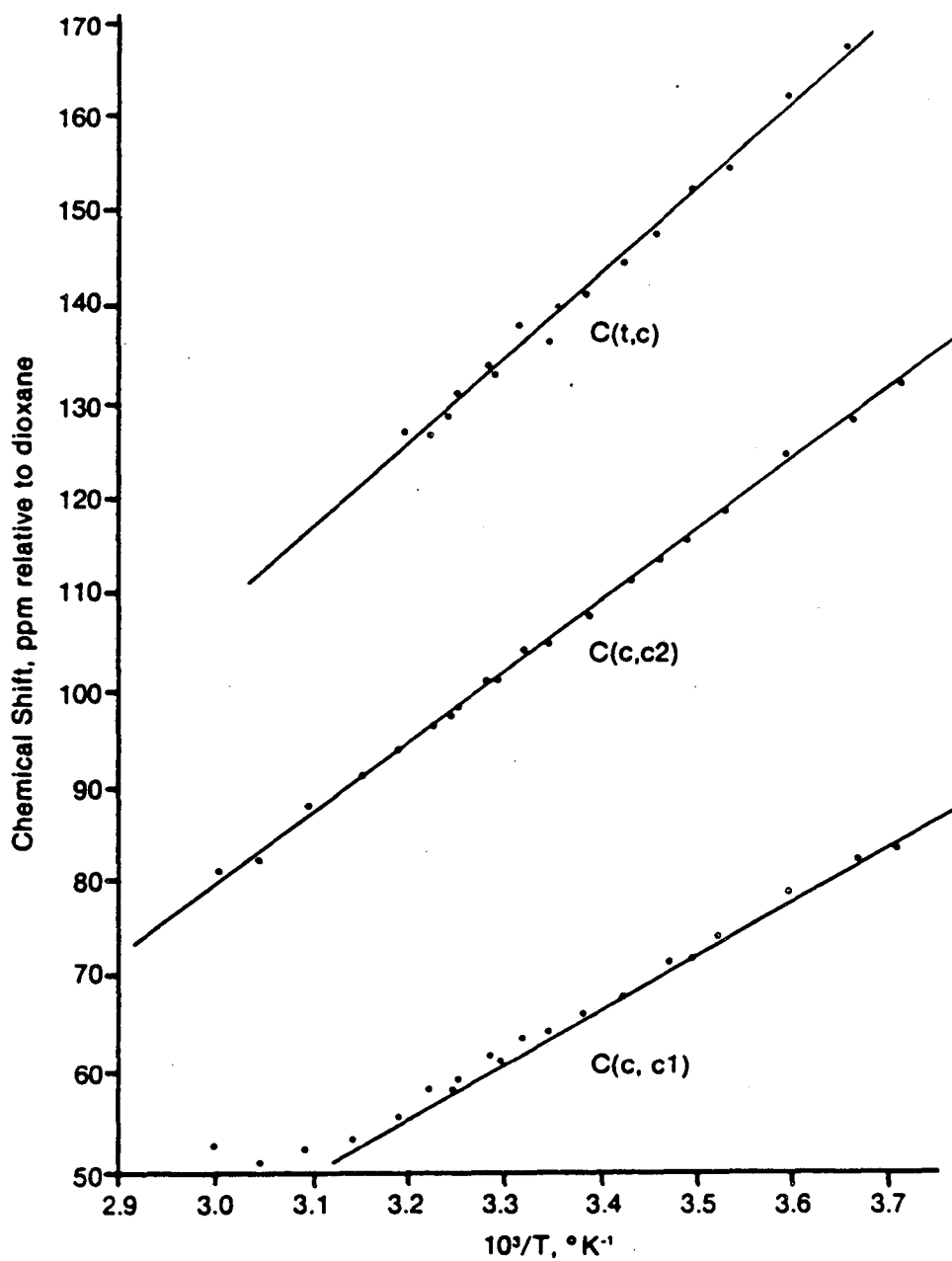
Data collected from the NMR spectra were interpreted in terms of the contact shift equation (equation 11). An important point to bear in mind when interpreting paramagnetic shifts in these terms is that the measurement of the shift should be made relative to a suitable diamagnetic analogue of the species under study. For the case of  $Ni(IDA)_2^{-2}$  a suitable analogue might be the  $Zn(II)$  complex. This particular analogue was not used; rather,

as in the case of the proton shifts discussed earlier, the uncomplexed ligand was taken as the diamagnetic blank.

Rather than measure shifts relative to the unbound ligand, shifts in Table VI, Appendix II, are measured relative to dioxane. This approach is acceptable for several reasons. It has been shown above that the dioxane resonance is expected to be only weakly dependent upon temperature. Thus, the C(u,c)-IS shift is only weakly dependent on temperature. Also, the parameter of real interest here is the scalar coupling constant, which is nearly independent of the shift standard, provided the shift standard chemical shift is not strongly temperature dependent. The scalar coupling constant is the key parameter in estimating the contribution of the scalar coupling relaxation mechanism to the bound carboxylate transverse relaxation rates.

The scalar coupling constants for the three bound carboxylate carbon nuclei were determined by a best linear least squares fit of the shift data vs.  $1/T$ , plotted in Figure 5. The intercept of this best line should correspond to the shift of those nuclei in the diamagnetic analogue of the complex at infinite temperature. One can see from the table below that three separate intercepts are calculated, possibly indicating that the unbound ligand carboxylate resonance, C(u,c), may not be altogether appropriate as the diamagnetic analogue.

FIGURE 5  
Carbon-13 Chemical Shifts of C(ct,c)  
Nuclei of  $\text{Ni}(\text{IDA})_2^{\cdot-}$  vs.  $10^3/T$



Only data up to 45° C from Table VI were used for the linear fit because above that temperature it is clear that C(t,c) is undergoing chemical exchange with C(c,c1) and C(c,c2) due to a coalescence. For C(t,c) data up to only 25° C were used. The results of the fitting are:

| Resonance | Scalar Coupling<br>Constant, A/h, sec | Intercept,<br>ppm | Corr.<br>Coeff. |
|-----------|---------------------------------------|-------------------|-----------------|
| C(c,c1)   | $-3.7 \times 10^6$                    | -123              | 0.9969          |
| C(c,c2)   | $-4.9 \times 10^6$                    | -142              | 0.9987          |
| C(t,c)    | $-6.1 \times 10^6$                    | -170              | 0.9984          |

Other methods for fitting the carbon shift data were also used. Methods included constraining the intercept of the shift vs. 1/T linear plot to the shift of the C(u,c) resonance, measured from a sample of the free ligand in aqueous solution, simultaneous fitting of both linewidth and chemical shift data for one nucleus, and simultaneous fitting of linewidth and chemical shift data for two nuclei. (Simultaneous linewidth and shift fitting will be discussed later.)

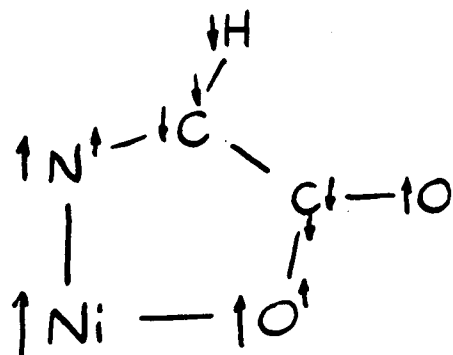
The results of these various methods gave the same value of the scalar coupling constant to an accuracy of  $\pm 4\%$ , with the exception of the "constrained intercept" fit. The result there deviated by 10% from the average of all the others; the quality of the fit was also worse by a

factor of two to seven, depending on the nucleus.

On the basis of the data in Table V one might expect that the intercept would be +107 ppm, and indeed the calculated intercept is not grossly inappropriate. It is interesting to note that there are three distinct intercepts rather than an approximate convergence to one value. It suggests that a diamagnetic analogue like  $\text{Zn}(\text{IDA})_2^{-2}$  might have three measurable chemical shifts for the bound ligand carboxylate carbons.

It is interesting to compare the scalar coupling constants calculated above with those calculated for the proton bound to the methylene carbon of the bound ligand. First, the two groups are of opposite sign, as one group is shifted downfield (negative scalar coupling constant) while the other is shifted upfield (positive scalar coupling constant).

The observation has been made before (39,40), and the upfield shift of the methylene carbon has been attributed to a spin polarization mechanism, whereas the downfield proton shifts have been argued to be due to direct delocalization of electron spin through the sigma bonding system of the ligand. A spin polarization mechanism also gives rise to downfield methylene proton shifts as well as upfield amino proton shifts which have also been observed (10). The following diagram illustrates the spin polarization mechanism (9):



If the predominant interaction for the methylene proton resonances is transferred through the amino nitrogen, then the spin polarization mechanism would yield a downfield shift for the protons, as observed. The same mechanism for the carboxylate carbon would tend to give an upfield shift, if the effect is predominantly transferred through the bonded oxygen of the acetate arm.

The magnitudes of the carbon and proton sets of coupling constants are similar. If proton shift is dominated by spin polarization, and delocalization contributes in a positive way to the carboxylate shift, one would expect the effective field strength at the carboxylate carbons to be larger than that at the proton, as the carboxylate carbon nucleus is two bonds removed from the metal while the protons are three bonds removed. The effective field is proportional to  $A/\gamma_I$ , and the value of  $\gamma_I$  for carbon-13 is four-fold smaller than that of the proton for similar values of  $A$ .

It would be interesting to measure the carbon-13 NMR spectrum of the  $\text{Zn}(\text{IDA})_2^{-2}$  complex under the same conditions

in order to verify the values of the shifts predicted by the fitting of the  $\text{Ni}(\text{IDA})_2^{-2}$  carbon data. With that measurement one might be able to determine the cis/trans ratio for the Zn complex if the shifts predicted correlate well enough with the observed, since a priori there is no reason to expect that the zinc complex would have the same isomer ratio.

### Carbon-13 Linewidth Measurements

Instrumental sensitivity was high enough and the resonance resolution large enough to allow linewidth measurements of the carboxylate resonances. The sweep widths used in obtaining the spectra were large enough that there was significant transmitter power present in the probe during the FID acquisition. In principle, transmitter power is to have fully dissipated before data acquisition from the pulse occurs. When this does not happen, there is said to be "feed-through" of the pulse into the acquisition. This can be a severe interference in the detection of the FID. The problem was encountered here as well as in the oxygen-17 spectra; this will be discussed in a later section.

Nonetheless, linewidth measurements were possible as a function of temperature for the carboxylate nuclei. Carboxylate NMR spectra could be corrected over a desired range using available computer routines to flatten baselines and fit the spectra to a sum of Lorentzian

lineshapes, from which transverse relaxation rates were determined.

Linewidth data were taken from the same spectra as the chemical shift data for the carboxylate carbon nuclei given in Table VI, Appendix II. The linewidth data for these spectra are given in Table VII, Appendix II. One notices immediately that there seems to be significant uncertainty in the data; this is due to the facts that the spectra were noisy, the peaks were broad, and the baseline often needed correction. This was especially true at higher temperatures. The uncertainty in the measurements was estimated to be ca. +6%, and the computer fitting of the data was weighted accordingly.

The model chosen to describe the carbon relaxation rates observed for C(c,c1), C(c,c2), and C(t,c) nuclei included contributions from only the dipolar and scalar coupling mechanisms. Both contributions may be estimated from a combination of x-ray structural data (7), published electronic relaxation times for Ni(II) complexes in aqueous solution (5), viscosity measurements, and the scalar coupling constants measured above. By these estimates, the dipolar contribution accounts for >80% of the observed relaxation rate. Scalar coupling accounts for the remainder, keeping in mind that other relaxation mechanisms either do not apply (e.g., quadrupolar mechanism) or are likely too small to be significant. A study of the Ni(II)/acetate

system by carbon-13 NMR has resulted in similar values for the relative contributions of these relaxation mechanisms for the carboxylate carbon of the coordinated acetate (45).

As the relaxation data for the C(t,c) resonance were somewhat more variable than those for the other two resonances, fitting of the relaxation data was only attempted on the two cis resonances. In applying the dipolar mechanism equation to  $\text{Ni}(\text{IDA})_2^{-2}$  the distance between the Ni (II) and the carboxylate carbon nuclei was needed. Using the law of the cosines, the x-ray data (7) give an inter-nuclear distance of 2.50 Å. Also, chemical exchange was assumed to make a negligible contribution to the rate of interruption. The correlation times in the dipole-dipole relaxation rate equation then take the form:

$$\frac{1}{\tau_1} = \frac{1}{T_{2S}} + \frac{1}{\tau_r} \qquad \frac{1}{\tau_2} = \frac{1}{T_{2S}} + \frac{1}{\tau_r}$$

For Ni (II) in approximately octahedral symmetry electronic relaxation is very short. It is assumed that  $T_{1S} = T_{2S} = \tau_S$  and that  $\tau_S = \tau_S(0)\exp(V/RT)$  for computer fitting purposes.

The rotational or tumbling correlation time,  $\tau_r$ , is often estimated from viscosity and structural data. The viscosity of solutions used for NMR study was measured at 21.1° C by an Ostwald viscometer to be ca. 1.185 cp. From Ref. 7, one can estimate O(t,n)-Ni internuclear distance

to be ca. 3.7 Å, which added to the Van der Waals radius of oxygen gives 5.1 Å. The effective radius of the complex as it tumbles through solution is probably appreciably larger, due to water coordination. If the radius is taken at 5 Å as a crude estimate, the rotational rate of interruption is calculated to be ca. 4% of the electronic. Henceforeth it will be ingnored as a significant contribution, and only electronic relaxation will be used to fit the relaxation rate data for carboxylate carbons.

Under these assumptions the dipolar mechanism equation for  $1/T_2$  reduces to the following form:

$$\frac{1}{T_2}(\text{DD}) = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6} \left[ 7\tau_1 + \frac{13\tau_2}{1 + \omega_S^2\omega_2^2} \right]$$

where

$$r = 2.5 \times 10^{-8} \text{ cm}$$

$S = 1$  for Ni (II) in octahedral symmetry

$$\gamma_I = 6.73 \times 10^3 \text{ sec}^{-1} \text{ G}^{-1} \text{ for carbon-13 (15)}$$

$$\gamma_S = 2.0 \times 10^7 \text{ sec}^{-1} \text{ G}^{-1} \text{ for Ni(IDA)}_2^{-2}, \text{ assumed to be approximately equal to Ni(H}_2\text{O)}_6^{+2} \text{ (5,43)}$$

and  $\omega_I \ll \omega_S, \omega_I\tau \ll 1$ .

The equation for scalar coupling relaxation is given in the theory section also. The scalar coupling constants given in the shift section for the appropriate nuclei were used as initial values in the data fitting process.

The results of the computer fitting of the carbon data are given in the tables below. The first gives the results of attempting to fit the  $C(c,c1)$  and  $C(c,c2)$  relaxation rate data simultaneously in order to generate values for the electronic relaxation time with greater certainty. Also shown is the fit for relaxation rate and chemical shift. One can see that the electronic relaxation parameters are relatively insensitive to the values of the scalar coupling constants, the initial (starting) values of which are given in the preceding chemical shift section.

The quality of the fit was better for simultaneous rate and shift data for the two nuclei than the rate data alone, as measured by the sum of the squares of the residuals. This may have been an artifact of the greater number of easily-fitted shift points used in the former case.

Results of Simultaneous Computer Fitting of Carbon  
C(c,c1) Linewidth, Carbon C(c,c2) Linewidth, and their  
Chemical Shift Data by ORGLS Fitting Program (30)

|                                                         | Simultaneous $1/T_2$       | Simultaneous $1/T_2$      |
|---------------------------------------------------------|----------------------------|---------------------------|
|                                                         | Fit                        | and Shift Fit             |
|                                                         | <u>C(c,c1) and C(c,c2)</u> | <u>C(c,c1 and C(c,c2)</u> |
| A/h $\times 10^{-6}$<br>(sec <sup>-1</sup> )<br>C(c,c1) | -3.6                       | -3.8                      |
| A/h $\times 10^{-6}$<br>(sec <sup>-1</sup> )<br>C(c,c2) | -4.8                       | -4.6                      |
| $\tau_s(0) \times 10^{12}$                              | 3.9                        | 3.9                       |
| V (cal/mole)                                            | 1150                       | 1150                      |

The results of independent fits of the rate and shift data for the individual nuclei fell on either side of the simultaneous fittings results. This is expected since the simultaneous fit by definition will find values of parameters based on constraints of both data sets. Results are given below.

Results of Computer Fitting Carbon Relaxation Rate  
and Chemical Shift Data Separately for Carbon C(c,c1)  
and Carbon C(c,c2) Nuclei using ORGLS Fitting Program

|                                              | Simultaneous $1/T_2$<br>and Shift Fit<br><u>C(c,c1)</u> | Simultaneous $1/T_2$<br>and Shift Fit<br><u>C(c,c2)</u> |
|----------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| A/h x $10^{-6}$<br>(sec $^{-1}$ )<br>C(c,c1) | -3.6                                                    | ----                                                    |
| A/h x $10^{-6}$<br>(sec $^{-1}$ )<br>C(c,c2) | ----                                                    | -4.8                                                    |
| $\tau_s(0)$ x $10^{12}$<br>(sec)             | 4.5                                                     | 3.5                                                     |
| V (cal/mole)                                 | 1100                                                    | 1200                                                    |

One further attempt at simultaneous fitting was made by trying to fit the H(c,e2), H(c,e1)/H(t,e), C(c,c1), and C(c,c2) rate and shift data to the same values of the electronic relaxation parameters. The quality of the fit clearly suffered relative to the "carbon only" fits discussed above by a factor of two. Nominal values for the electronic relaxation parameters generated were:

$$\tau_s(0) \times 10^{12} \text{ (sec)} = 1.3$$

$$V \text{ (cal/mole)} = 1800$$

These are somewhat similar to the results of Rowland (5).

The quality of the fit was probably poorer because of the greater uncertainty in the linewidth measurement for the proton resonances. Recall that the proton resonances overlapped severely, and thus the data were less certain.

In conclusion, the electronic relaxation parameters generated in the carbon-only fit of shift and rate data will be used in the following section dealing with the oxygen-17 data obtained from this chemical system. These parameters are:

$$\tau_S(0) = 3.9 \times 10^{-12} \text{ sec}$$
$$V = 11.50 \text{ cal/mole}$$

### 3. Oxygen-17 NMR Spectra

To complete the multinuclear NMR characterization of the  $\text{Ni}(\text{IDA})_2^{-2}$  complex in solution, oxygen-17 NMR spectra were recorded using both CW and FT techniques. CW spectra were recorded at 13.21 MHz, while the FT spectra were recorded at 24.42 MHz. The two different experiments gave essentially identical spectra, although the CW spectra were recorded at high rf power, leading to saturation of some of the resonances. A representative FT spectrum of the  $\text{Ni}(\text{IDA})_2^{-2}$  complex in the presence of excess ligand is given in Figure 6.

### A. Characterization of the Spectra

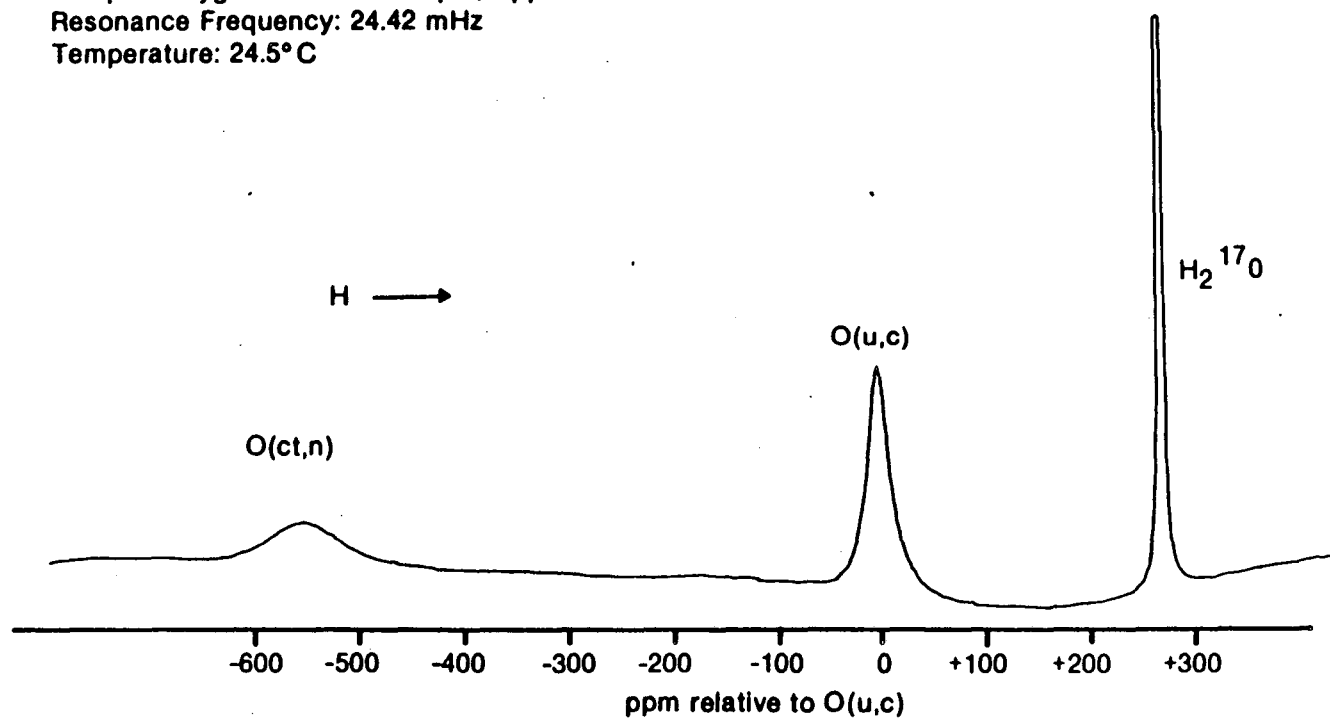
Resonances attributable to water, uncomplexed excess ligand, and non-bonded carboxylate oxygen of  $\text{Ni}(\text{IDA})_2^{-2}$  were observed in the oxygen-17 NMR spectrum.

The non-bonded carboxylate oxygen resonances is assigned collectively to the averaged  $\text{O}(\text{c},\text{n}1)$ ,  $\text{O}(\text{c},\text{n}2)$ , and  $\text{O}(\text{t},\text{n})$  resonances, and is designated  $\text{O}(\text{ct},\text{n})$ . No resonance corresponding to the bonded oxygen was observed. The bonded carboxylate oxygen is expected to have a linewidth so large so as to make detection unlikely.

It is possible to estimate the linewidth of the bonded oxygen based upon the work of Neely and Connick (3), the x-ray data (7), and the electronic relaxation times determined in the preceeding section of this work, assuming that scalar coupling and dipole-dipole mechanisms interrupted by electronic relaxation control the nuclear relaxation. Using the scalar coupling constant from Neely, one estimates that the linewidth of the bonded carboxylate oxygen would be approx.  $10^5$  Hz, which is too large to be detected readily by either the CW or FT techniques. Therefore the third resonance in Figure 6 may be assigned to  $\text{O}(\text{ct},\text{n})$  since the chemical shift for that resonance would be expected to exhibit Curie law temperature dependence common to contact shifts, and this behaviour was observed. Contact shift results for  $\text{O}(\text{ct},\text{n})$  will be discussed in the following section.

**FIGURE 6**  
**Oxygen-17 Fourier Transform NMR**  
**Spectrum of  $\text{Ni}(\text{IDA})_2^{\cdot-}$  In Aqueous Solution**

Sample: Oxygen-17 NMR Sample, Appendix I  
Resonance Frequency: 24.42 MHz  
Temperature: 24.5°C



Both linewidth and chemical shift data were collected as a function of temperature, although the linewidth data were only readily measureable from the CW spectra, due to baseline distortion of the FT spectra. However, obtaining linewidth measurements from the CW spectra did require spectral simulation techniques, since the field modulation used in the CW apparatus at 5 kHz gives rise to modulation sidebands (41), which were often overlapping. The ORGLS fitting program used earlier to fit carbon shift and relaxation data was used to fit the spectra to appropriate sums of Lorentzian lineshapes.

High rf power was used in these CW experiments, and thus resonances which were fairly narrow, like O(u,c) and H<sub>2</sub>O-17, may not have been strictly Lorentzian due to saturation. The O(c,n1), O(c,n2), and O(t,n) resonances were determined to be in a non-saturation mode, and therefore could be fitted to extract the relaxation rate.

The O(u,c) resonance linewidth and shift were on the other hand most easily measured from the FT spectra. The observations at 25° C were compared with those of Hunston, et.al., (42), in which oxygen-17 NMR spectra are recorded for a series of amino acids dissolved in buffer solutions. Their data are compared with the results of this study below

Comparison of Chemical Shifts and Linewidths of Amino  
Acids with IDA

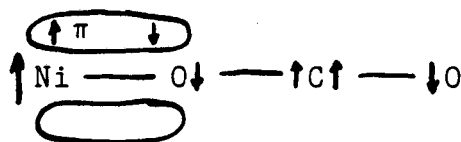
| Compound | Measured Chemical Shift,<br>ppm, relative to H <sub>2</sub> O-17 | Measured Linewidth,           |
|----------|------------------------------------------------------------------|-------------------------------|
|          |                                                                  | 1/2 width @ 1/2<br>Height, Hz |
| IDA      | -268                                                             | 280                           |
| Glycine  | -170                                                             | 201                           |
| Alanine  | -226                                                             | 277                           |

It is important to note that the published values of the linewidths (42) are sensitive to the buffer solution in which they are measured. Additionally, the glycine and alanine data were taken at a pH=6, whereas the IDA measurement made here was made at pH 9.5. The authors of the glycine/alanine work used the opposite sign convention in reporting results, and all data above are presented with consistent conventions.

It is interesting to note that both the O(ct,n) resonance and bound water resonance of hexaaquonickel(II) are shifted downfield from the water oxygen resonance (3). Either direct delocalization or the spin polarization mechanism predicts that O(ct,n), O(ct,b), and Ni(H<sub>2</sub>O-17)<sub>6</sub><sup>+2</sup> will be shifted in the same direction (9). However, the simple application of the spin polarization mechanism to the carboxylate group coordinated to nickel predicts that

both the protons of the methylene group and the O(ct,n) nucleus should have net parallel spin. This leads to a downfield shift for the proton, but because the nuclear magnetic moment of oxygen-17 is of opposite sign its shift is predicted to be upfield. This is contrary to observation, as seen in Figure 6. The correct mechanism must lead to net residual parallel spin at H(ct,m) and net antiparallel spin at O(ct,n).

The spin polarization mechanism is illustrated below.



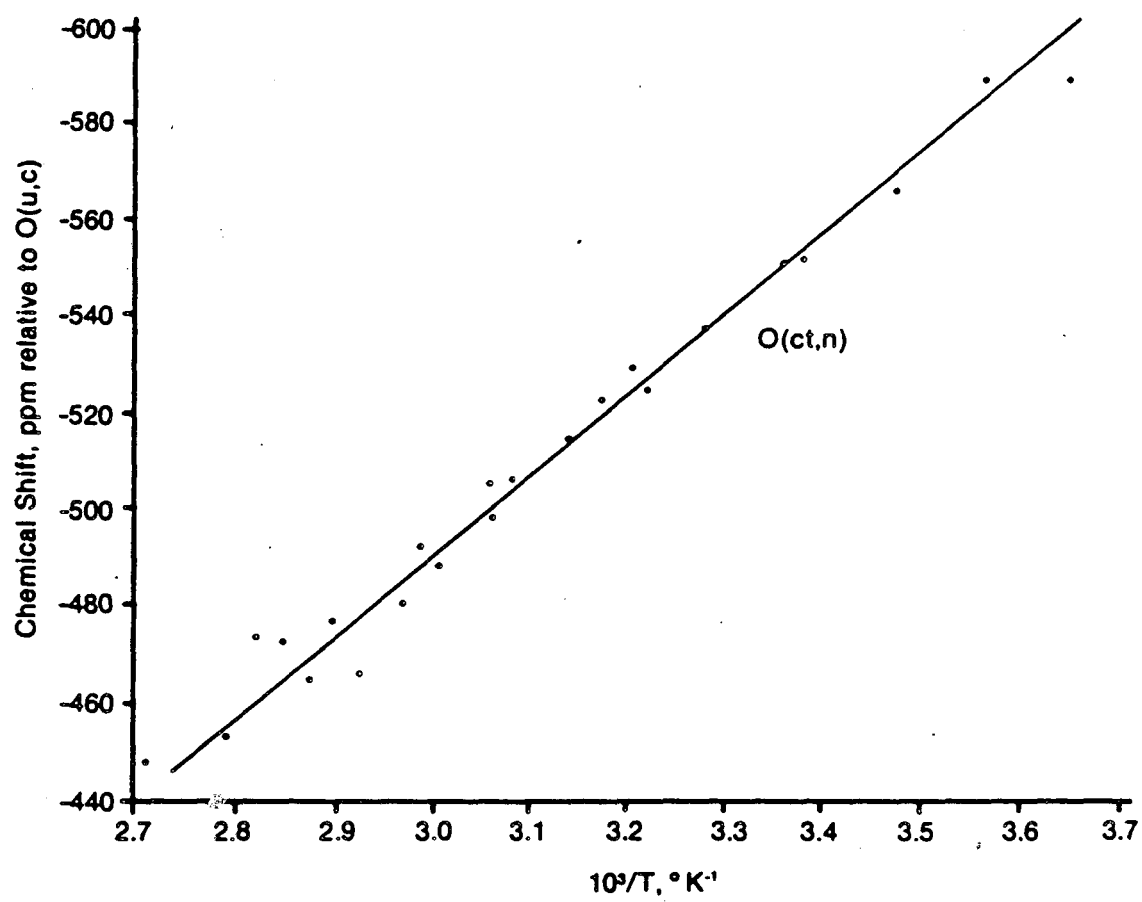
#### B. 13.21 mHz NMR Spectra

##### Oxygen-17 Chemical Shifts

As mentioned above, the downfield chemical shift of the non-bonded carboxylate oxygens was measured as a function of temperature using both CW and FT-NMR spectra. The data obtained from the CW experiments are given in Table VIII, Appendix II. The shift reference was taken to be the uncomplexed ligand resonance, O(u,c). The shift data at 13.21 mHz are also given in Figure 7.

Using the same linear least squares fitting program used for both carbon and proton data the following results were obtained for the oxygen 13.21 mHz chemical shift data;

**FIGURE 7**  
**Oxygen-17 Chemical Shift of O(ct,n)**  
**Nucleus vs.  $10^3/T$  at 13.21 MHz**



| Frequency | Scalar Coupling Constant    | Correlation |
|-----------|-----------------------------|-------------|
|           | $A/\hbar, \text{ sec}^{-1}$ | Coefficient |
| 13.21     | $-5.7 \times 10^6$          | 0.9940      |

The temperature dependence of the resonance shift is good evidence that the Fermi contact interaction is the origin of the shift. No pseudo-contact contributions are to be expected, as mentioned in the Theory section of this thesis.

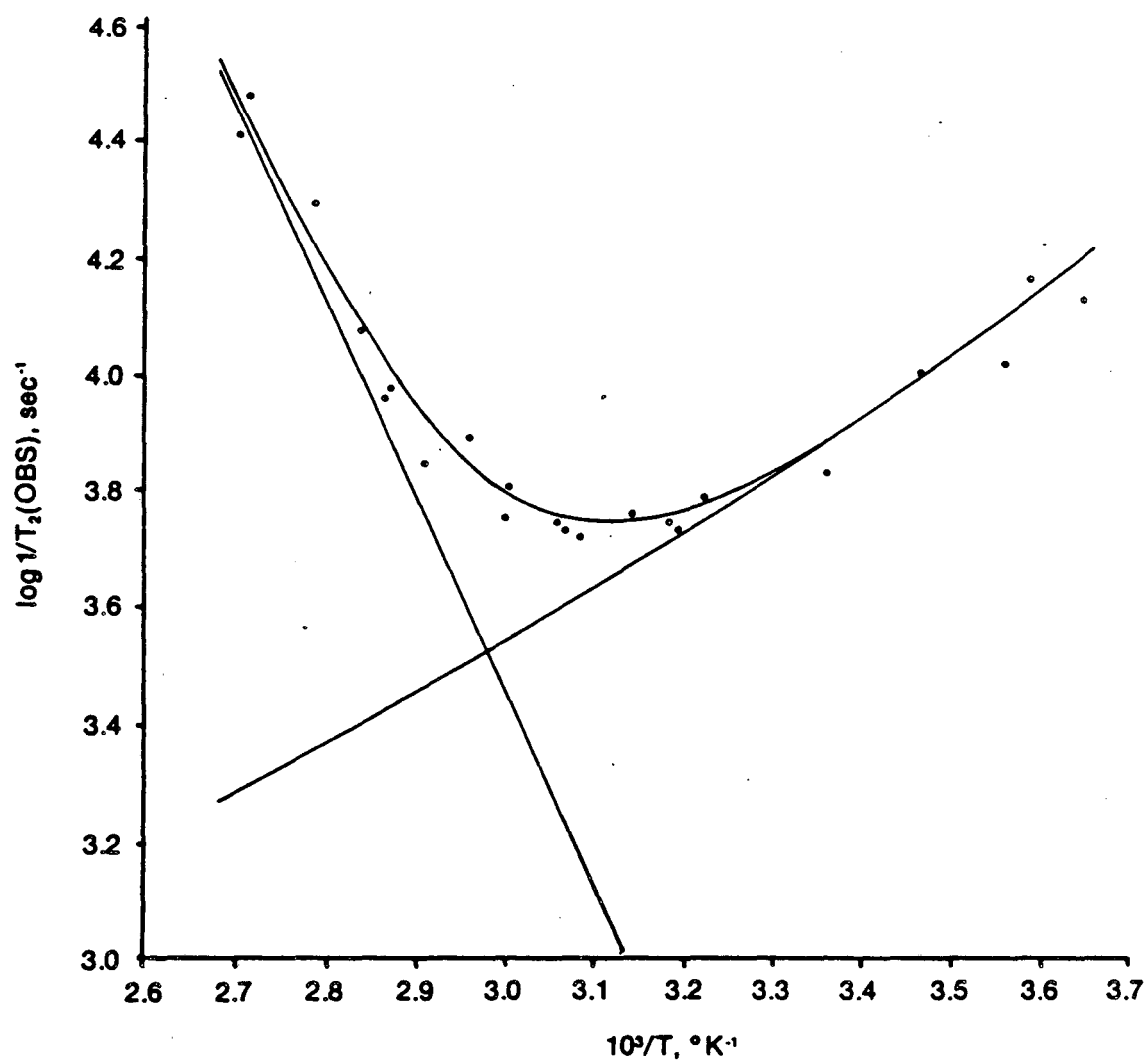
#### Oxygen-17 Linewidth Measurements

As these spectra were recorded in the CW mode using amplitude modulation, sidebands resulted and required the use of computer fitting to extract the  $1/T_2$  values. The ORGLS fitting program (30) was used to fit the spectra to the necessary sum of Lorentzian lineshapes. The lineshapes of the  $O(u,c)$  and  $H_2O-17$  resonances were not necessarily truly Lorentzian, as high strength rf fields were used to maximize the  $O(ct,n)$  signal. Further details of the equipment is given in the Experimental section.

Although not strictly Lorentzian, the  $O(u,c)$  and  $H_2O-17$  sideband resonances were fitted well enough so as to extract the  $1/T_2$  value from the  $O(ct,n)$  resonance to an accuracy of  $\pm 8\%$ . The accumulated data of three independent series of measurements are given in Table IX, Appendix II, and are plotted in Figure 8.

Figure 8 shows that as temperature is increased up to

**FIGURE 8**  
**Oxygen-17 Linewidth of O(ct,n)**  
**Nucleus of Ni(IDA)<sub>2</sub> vs.  $10^3/T$  at 13.21 MHz**



room temperature ( $10^3/T = 3.36^\circ\text{K}^{-1}$ ) the linewidth decreases. This is the behaviour expected in the absence of chemical exchange due to the decrease in rotational correlation time attributable to a decrease in bulk viscosity of solution. As the temperature is further increased above ca.  $50^\circ\text{C}$ , broadening of the resonance occurs. This broadening is attributed to the chemical exchange of  $\text{O}(\text{ct},\text{n})$  with  $\text{O}(\text{ct},\text{b})$  in the  $\text{Ni}(\text{IDA})_2^{-2}$  complex. Data were recorded up to a temperature of ca.  $100^\circ\text{C}$ , and it is evident that the spectrum may be characterized as being in the chemical exchange controlled region (2).

To determine the kinetic parameters of the exchange (equation 7), the following model was used to fit the linewidth data. As no diamagnetic blank was available for correcting the data, as has been used in earlier work (5), the contributions to the relaxation mechanism of the  $\text{O}(\text{ct},\text{n})$  resonance in the absence of exchange has to be estimated. The relaxation mechanisms were assumed to be dipole-dipole, scalar coupling, and quadrupole coupling interrupted predominantly by electronic relaxation and molecular tumbling. As the data show the presence of only a chemical exchange controlled region, the following equation was used for the computer fitting:

$$\frac{1}{T_2}(\text{OBS}) = \frac{1}{T_2}(\text{DD}) + \frac{1}{T_2}(\text{Q}) + \frac{1}{T_2}(\text{SC}) + \frac{1}{\tau}$$

Calculation of the contribution of each relaxation mechanism to the relaxation was made at 21° C, which was the temperature at which the viscosity of the oxygen-17  $\text{Ni}(\text{IDA})_2^{-2}$  sample was measured. The dipole-dipole coupling mechanism contribution was estimated using crystal structure data (7), molecular reorientation correlation time based upon the Stokes-Einstein relationship, a value of  $g(\text{eff})=2.27$  for  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$  (43), and the electronic relaxation time  $T_{2S}$  calculated previously in section III of this thesis. The contribution of this mechanism to the total relaxation rate was calculated to be  $5 \text{ sec}^{-1}$ .

The scalar coupling mechanism contribution was estimated using the average value of the scalar coupling constant calculated from the shift data at 13.21 and 24.42 MHz, and the correlation times identified above. This contribution was estimated to be  $44 \text{ sec}^{-1}$ .

Using a value of the quadrupole coupling constant for  $\text{O}(\text{ct},\text{n})$  estimated from nuclear quadrupole resonance studies of carboxylic acids (44) and other parameters given above, the quadrupole coupling mechanism contributes  $9700 \text{ sec}^{-1}$ . This calculated value is in fair agreement with the observed value of  $8000 \text{ sec}^{-1}$ .

Comparing these three contributions, the quadrupole coupling is seen to dominate, the others contributing perhaps 1% or less to the relaxation. Thus, the linewidth data were fitted to the empirical equation:

$$\frac{1}{T_2}(\text{CALC}) = \frac{1}{T_{2a}} + \frac{1}{\tau_{ba}}$$

where:

$$\frac{1}{T_{2a}} = \frac{1}{T_2}(Q) \text{ for quadrupole coupling, equation 10}$$

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau}$$

$$\tau_{ba} = \tau_{ab} = \tau$$

$$\tau_r = \frac{\eta}{T} \cdot \beta \quad (\text{Stokes-Einstein relationship})$$

$\eta$  = viscosity of water

$\beta$  = constant dependent on the molecular volume

The rate constant was given the form of the Eyring equation, given in equation 7 in the Theory section.

The viscosity of water was chosen because the sample 01 was fairly dilute, and the viscosity which was measured did not differ greatly from that of water. The temperature dependence of the viscosity of water was taken to be the empirical relationship given in the CRC Handbook of Chemistry and Physics (27).

The temperature independent constants were given the following values:

$$I = 5/2 \text{ for oxygen-17}$$

$$\eta = 0.1, \text{ an estimate of the asymmetry parameter}$$

The parameters which were determined by the fit of the data were  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $(e^2qQ/\hbar) B$ . The least square fitting routine used to fit the data minimized the square of the residual computed by the difference between the calculated relaxation rate and the observed relaxation rate. The result of the fitting was:

$$\begin{aligned}\Delta H^\ddagger &= 14600 \pm 900 \text{ cal/mole} \\ \Delta S^\ddagger &= 0.8 \pm 2.5 \text{ e.u.} \\ e^2qQB/\hbar &= 31 \pm 1\end{aligned}$$

The uncertainties reflect the effects of random error, but in no way account for systematic error.

If  $e^2qQ/\hbar$  is assumed to be  $8.0 \times 10^6$  and the resulting value of  $B$  is used to calculate a molecular radius using the Stokes-Einstein relationship, a value of  $r = 5.06 \times 10^{-8}$  cm is calculated. This value agrees fortuitously well with the value used in the preceeding section of this thesis in which a value of  $5 \times 10^{-8}$  cm was proposed as an estimate to the molecular radius.

### C. 24.42 MHz NMR Spectra

#### Oxygen-17 Chemical Shifts

Chemical shifts of the O(ct,n) resonance observed in these spectra were treated in essentially the same manner

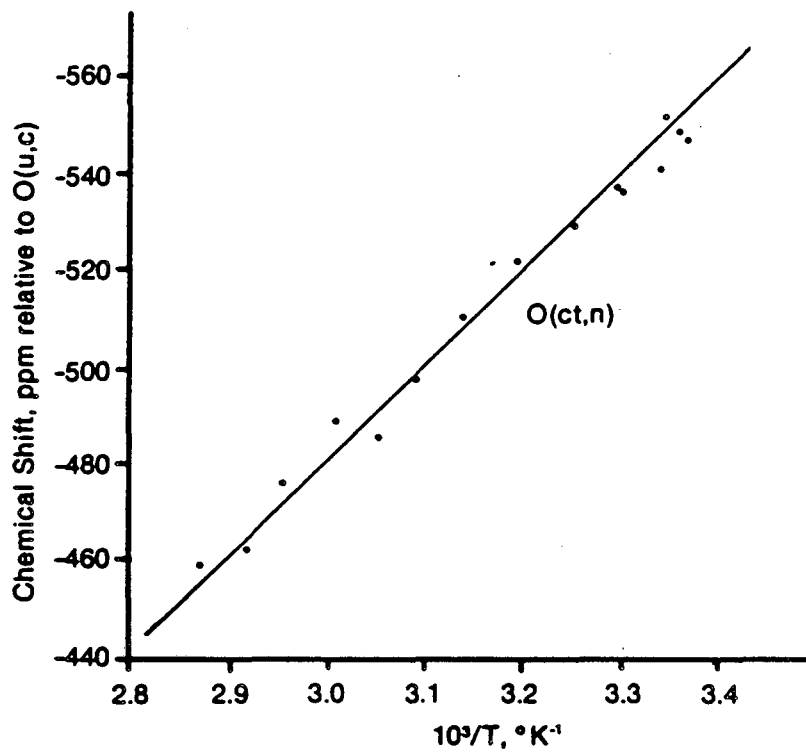
as those at 13.21 MHz. The data are given in Table X, Appendix II, and are plotted in Figure 9. The results of the least square fitting are given below:

| Frequency | Scalar Coupling Constant    | Correlation |
|-----------|-----------------------------|-------------|
|           | $A/\hbar, \text{ sec}^{-1}$ | Coefficient |
| 24.42 MHz | $-6.6 \times 10^6$          | 0.9931      |

The scalar coupling constants computed for the data at the two frequencies agree to  $\pm 7\%$ . The average of the two has been used to estimate contributions of scalar coupling to  $O(ct,n)$  linewidths.

Due to measurement difficulties, linewidth data at this frequency were not taken.

FIGURE 9  
Oxygen-17 Chemical Shift of O(ct,n)  
Nucleus vs.  $10^3/T$  at 24.42 MHz



## V. Interpretation

### 1. Spin Delocalization Mechanisms

Contact shifts for protons, carbon-13, and oxygen-17 nuclei have been measured for the  $\text{Ni}(\text{IDA})_2^{-2}$  complex. The results are summarized in the following table.

#### Contact Shifts for Nuclei of $\text{Ni}(\text{IDA})_2^{-2}$

| Nucleus | Shift Direction<br>relative to un-<br>complexed ligand | Scalar Coupling<br>Constant, $A/\hbar$ , $\text{sec}^{-1}$ |
|---------|--------------------------------------------------------|------------------------------------------------------------|
| O(ct,n) | Downfield                                              | $-6.2 \times 10^6$                                         |
| C(c,c1) | Upfield                                                | $-3.7 \times 10^6$                                         |
| C(c,c2) | Upfield                                                | $-4.9 \times 10^6$                                         |
| C(t,c)  | Upfield                                                | $-6.1 \times 10^6$                                         |
| C(ct,m) | Upfield                                                | $-10 \times 10^6$ (est.)                                   |
| H(c,e2) | Downfield                                              | $+7.2 \times 10^6$                                         |
| H(c,e1) | Downfield                                              | $+6.8 \times 10^6$                                         |
| H(t,e)  | Downfield                                              | $+6.8 \times 10^6$                                         |
| H(t,a)  | Downfield                                              | $+1.0 \times 10^6$                                         |
| H(c,a1) | Downfield                                              | $+1.0 \times 10^6$                                         |
| H(c,a2) | Downfield                                              | $+0.8 \times 10^6$                                         |

The proton resonances above have a well-known dihedral

angle dependence (11) which makes them very sensitive to acetate arm conformation when coordinated to metal ions. The source of this dependence is the ability to delocalize residual unpaired spin density directly by the hyperfine interaction between, in this case, the nitrogen orbital containing residual unpaired spin and the proton's orbital. La Mar (9) has shown that when a filled ligand orbital coordinates to a partially filled  $e_g$  orbital, as in  $d^8$  Ni (II), residual parallel spin is delocalized onto the nitrogen. There results a charge transfer from ligand to metal, but a net spin transfer from metal to ligand. The dihedral angle dependence controls the coupling of this parallel spin to the methylene protons, giving the observed downfield shift and a positive value of the scalar coupling constant.

The methylene carbon behaves very differently (39,40). Its shift is upfield, presumably because of the presence of antiparallel spin density arising from an electron polarization effect. Both the delocalized spin density and polarization are certainly present at the C(ct,m) nucleus, but as it is adjacent to the donor atom, nitrogen polarization apparently dominates. Carbon-13 spectra alpha-aminobutyric acid coordinated to nickel (40) shows that the polarization mechanism decreases very rapidly. The decrease is so rapid that the beta carbon in the molecule is affected little by this mechanism, its main source of

spin coming from delocalization directly. This leads one to the conclusion that  $C(ct,c)$  will be affected by spin polarization arising from the carboxylate coordination, not from the amino. Hence,  $C(ct,c)$  nuclei show upfield shifts similar to published results (39,40).

The oxygen results are very puzzling. Water bound to nickel is known to have a strong downfield oxygen-17 shift (3), indicating a net residual antiparallel spin density from the nickel. The negative magnetic moment of oxygen-17 and antiparallel spin results in a downfield shift, following equation 11. Spin polarization through the sigma bonding system attenuates too rapidly to affect the  $O(ct,n)$  resonance strongly. Direct delocalization of the parallel spin density is apparently weaker than the polarization when close to the donor atoms of the ligand, but does not attenuate as rapidly. A direct delocalization of parallel spin density would lead to an upfield shift for the  $O(ct,n)$ , which is not observed.

La Mar has also pointed out that when empty ligand orbitals interact with filled metal orbitals a net transfer of antiparallel spin results in the ligand M.O. In the case of the carboxylate coordination, it is possible that  $\pi^*$  M.O.'s carry this antiparallel spin, which results in net antiparallel spin at  $O(ct,n)$ .

Although some qualitative arguments can be made about simple contact shifts, cases arise which are not easily

interpreted by a simple model.

## 2. Intramolecular Rearrangements

The intramolecular rearrangement of cis/trans isomers of  $\text{Ni}(\text{IDA})_2^{-2}$  via the so-called Bailar twist has already been mentioned in this thesis. Coalescence of both  $\text{H}(\text{ct}, \text{m})$  resonances provides strong evidence of a twist mechanism.

Carrington and McLachlan have pointed out that for a simple two site exchange process the rate of exchange can be estimated from the separation of the two resonances and the temperature at which the coalescence occurred (15). They had considered the case of temperature-independent shifts, but in principle the technique can be applied here.

The approximate relationship they gave for the exchange rate is given as:

$$\frac{1}{\tau} \approx \frac{\Delta\omega_a - \Delta\omega_b}{2\sqrt{2}} \quad (15)$$

where:  $\frac{1}{\tau}$  = exchange rate (equation 7)

$\Delta\omega_a$  = expected contact shift of the "a" nucleus in the absence chemical exchange

$\Delta\omega_b$  = expected contact shift of the "b" nucleus in the absence of chemical exchange

From Figure 2, the coalescence temperature of the

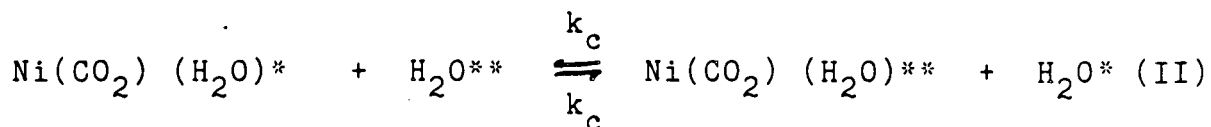
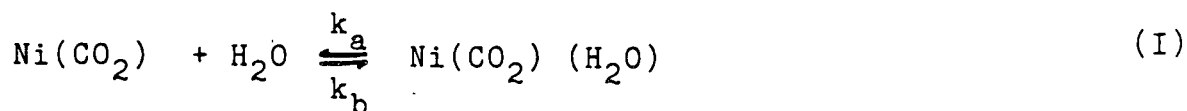
equatorial and axial groups is given as ca. 50° C. Using the values of the scalar coupling constants listed above the chemical shift difference between the two resonances can be calculated. This is a good approximation to the two site condition, as the equatorial protons gave a pattern of two resonances. By this approximation, the rate of intramolecular exchange at ca. 50° C is 300 sec<sup>-1</sup>.

This value of the rate corresponds to a  $\Delta G^\ddagger = \underline{\text{ca.}} \text{ 15 kcal/mole}$ , in agreement with Everhart and Evilia (32).

### 3. Kinetics of Carboxylate Exchange

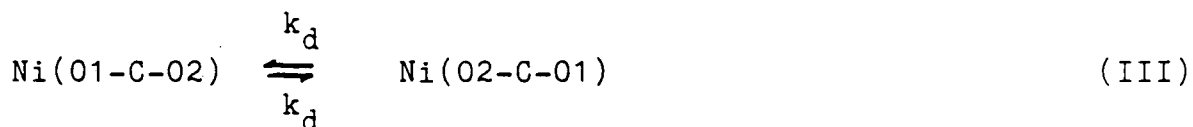
Ultimately the intent of this study was to determine the rate of carboxylate oxygen interchange in  $\text{Ni(IDA)}_2^{-2}$  and infer a possible mechanism for the interchange. The results of the NMR study are given in the preceeding section.

There are two mechanisms by which the carboxylate oxygens of a glycinate arm of the ligand may be interchanged. The first allows for the carboxylate to become decoordinated, followed by water exchange at the site, allowing time for the carboxylate group to become randomized. This may be represented by the following equations.



where  $\text{Ni}(\text{CO}_2)$  refers to a particular ligand arm.  $\text{Ni}(\text{CO}_2)$  ( $\text{H}_2\text{O}$ ) refers to an arm which is decoordinated from the nickel and where there is a water replacing the arm in the first coordination sphere. The asterisks identify different waters.

The second mechanism for interchanging the two oxygens of the carboxylate group does not involve water coordination, i.e., the carboxylate group does not become fully decoordinated but merely rotates in place. This can be represented by the equation



where the two oxygens in a particular carboxylate group have been interchanged, as indicated by the labelling.

The overall rate of carboxylate oxygen interchange was determined in Section IV, and that rate may be associated with the rate constants in the equations above by the following relationship:

$$k(\text{obs}, 298) = k_d + k_a/2 = 167 \text{ sec}^{-1}$$

The factor of two arises because once a carboxylate group decoordinates, there is equal probability that either oxygen of the group will return for coordination. Obviously, if the same oxygen which was coordinated returns to be coordin-

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ated again no exchange has occurred. It is reasonable to assume that during the time a water molecule is coordinated to the nickel and the carboxylate group is uncoordinated that there is equal probability of either oxygen of the group to return. The lifetime of a water molecule in the first coordination sphere has been measured to be ca.  $10^{-5}$   $\text{sec}^{-1}$  (5), during which time it is likely that the group will be totally randomized by intermolecular collisions.

It is also known that some one arm of a  $\text{Ni}(\text{IDA})_2^{-2}$  is uncoordinated some 1.5% of the time (5). This results in the following expression written for a particular arm of the four in the complex:

$$\frac{k_a}{k_b} = \frac{\text{Ni}(\text{CO}_2) (\text{H}_2\text{O})}{\text{Ni}(\text{CO}_2)} = \frac{0.015}{4}$$

Finally, the rate of water displacement has been measured (5), and is represented by

$$k_b + k_c = 4 \times 10^5 \text{ sec}^{-1} \quad (T=298^\circ \text{ K})$$

There are now three equations in four unknowns, and the values of  $k_a$ ,  $k_b$ , and  $k_c$  may be solved in terms of the fourth unknown,  $k_d$ . These values are:

$$k_a = 334 - 2k_d$$

$$k_b = (8.9 \times 10^4) - (5.3 \times 10^2) k_d$$

$$k_c = (3.1 \times 10^5) + (5.3 \times 10^2) k_d$$

The significance of these values is that  $k_c > k_b$  for any value of  $k_d$ , i.e.,  $k_c/k_b > 1$ . The first order rate constant  $k_b$  is a measure of the rate of replacement of water by carboxylate, and the first order rate constant  $k_c$  is a measure of the rate of replacement of water with another water. Hence, it is probably, on the average, that a water of coordination will undergo at least three subsequent replacements by another water before the glycinate ligand arm recoordinates.

In fact, if one assumes  $k_d = 0$ , then the exchange occurs only through the water exchange mechanism ( (I) and (II) ), and ca.3 waters exchange at a given decoordinated site before the arm recoordinates. This result seems entirely reasonable, since the decoordinated glycinate arm could move rather far away from the coordination site, providing ample time for the exchange of several waters before the carboxylate group recoordinates.

Inherent in the above discussion is the assumption that all carboxylate groups are equivalent with respect to the decoordination and recoordination. It is clear that three different types of carboxylate groups exist in the cis and trans isomers of  $\text{Ni}(\text{IDA})_2^{-2}$  solely on the basis of molecular

symmetry. In Section IV the non-bonded oxygen resonances have been designated  $O(c,n1)$ ,  $O(c,n2)$ , and  $O(t,n)$ , corresponding to these three types. It may be true that decoordination is favored for one type of group over another, and it is important to explore the consequences of such a possibility.

If one assumes, for example, that two of the four cis isomer carboxylate groups and none of the trans groups undergo decoordination, then carboxylate oxygen interchange occurs at only 40% of the total possible sites. This figure assumes a cis/trans isomer ratio of 80/20, as Section IV. The equation for  $k_a/k_b$  needs to be adjusted as follows:

$$\frac{k_a}{k_b} = \frac{\text{Ni}(\text{CO}_2)(\text{H}_2\text{O})}{\text{Ni}(\text{CO}_2)} = \frac{0.015}{4 \times 0.40}$$

This leads to the following changes in the values of  $k_b$  and  $k_c$ :

$$k_b = (3.6 \times 10^4) - (2.1 \times 10^2) k_d$$

$$k_c = (3.6 \times 10^5) + (2.1 \times 10^2) k_d$$

If  $k_d = 0$ , then  $k_c/k_b = 10$ , which changes the average number of replacements by water from ca. 3 to ca. 10. It does not fundamentally change the observation that water tends to replace water before recoordination occurs.

If it were true that only 40% of the carboxylate groups are available for exchange, then the observed  $O(ct,n)$  resonance (Figure 6) could give a peculiar peak shape as temperature is increased. Assuming the rate of intramolecular rearrangement via the Bailar twist mechanism is negligibly slow, and that  $O(c,n1)$ ,  $O(c,n2)$ , and  $O(t,n)$  resonate at the same frequency, then some 40% of the nuclei in the resonance undergo exchange, and 60% do not. As temperature is increased 60% of the resonance should narrow, and 40% should broaden. Based upon the curve fitting of Figure 8, the linewidth of the broadened part of the resonance would be ca. 4000 Hz, whereas the narrowed part would be ca. 300 Hz at the highest temperature achieved (ca. 97° C). This effect would be striking, but it was not observed. The fitting of the line-shapes gave no indication of two overlapping resonances, as a single Lorentzian was able to define the lineshape adequately. This suggests that if a percentage of the carboxylate groups is really not available for water exchange, this percentage must be small, perhaps less than 15%. No computer modeling was done to give an upper limit to this value. In any case, the existence of a portion of unavailable sites does not invalidate the conclusion that there are multiple water exchanges prior to recoordination.

It was assumed above that the resonance frequencies of the non-bonded oxygens were all equal and that the rate of intramolecular rearrangement through the Bailar twist only needs to be fast enough to average the three possible

resonances. The rate of the Bailar twist can be estimated from the free energy of activation,  $\Delta G^\ddagger$ , and equation 15. Assuming that  $\Delta H^\ddagger$  is approximately equal to  $\Delta G^\ddagger$  and  $\Delta S^\ddagger \approx 0$  then at 25° C the twist rate can be estimated to be ca. 60  $\text{sec}^{-1}$ . If  $\Delta\omega_a - \Delta\omega_b$  in equation 15 can be associated with the difference in resonance frequencies between the highest and lowest non-bonded carboxylate oxygen resonances, then the range of chemical shifts averaged by a twist rate of this magnitude is ca. 13 ppm. In other words, the group of non-bonded carboxylate oxygen resonances must fall in a range of 13 ppm in order to be effectively averaged by the twist at this temperature. The 13 ppm range for the non-bonded carboxylate oxygen resonances corresponds to ca. 1000  $\text{sec}^{-1}$  frequency range. The measured linewidths at 25° C are on the order of 14,000  $\text{sec}^{-1}$ , so that the resonances fall in a range which is only ca. 7% of the measured linewidth. An error in the linewidth due to assuming there are no overlapping resonances is lost in the 5-10% uncertainty in the linewidth data. Therefore it is impossible to say if the resonances are being averaged by the twist or if they are just seriously overlapping.

The estimated value of the twist rate is not sufficient to collapse the carbon-13 carboxylate resonances from which the cis/trans isomer ratio was determined. The spread of these resonances at 298°K is ca. 70 ppm. It is impossible to predict from the data at hand just what the spread of resonances could be for the non-bonded oxygen resonances in

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the absence of the Bailar twist, but the fact that the nuclei are one bond farther from the nickel than are the carbon nuclei and that these non-bonded nuclei do not participate in the actual 5-membered chelate ring structure may make them much less dependent on the geometry. Hence, one might well expect to see little chemical shift difference in the resonances.

The Bailar twist is actually not negligibly slow, since at 50° C the Bailar twist is observed to be ca.  $300 \text{ sec}^{-1}$ , whereas the rate of non-bonded carboxylate oxygen interchange is ca.  $1380 \text{ sec}^{-1}$ , from Figure 8. The two are different by a factor of only 4.6, and no longer is the Bailar twist negligibly small, as assumed above. The problem of the description of the non-bonded linewidth is more complex, as there are three sites which the twist tends to average, with only one of those sites available for carboxylate oxygen interchange in our hypothetical model. If the non-interchanging sites (60%) are being transferred into the interchanging sites (40%) via the Bailar twist, the problem becomes a four-site exchange problem, with only certain exchanges allowed among the nuclei, and unequal populations of the sites.

The three of the four sites are  $O(c,n1)$ ,  $O(c,n2)$ , and  $O(t,n)$  which are exchanged by the twist. The fourth site is  $O(c,b1)$ , which is the site in the same carboxylate group as  $O(c,n1)$  and which is assumed to be the only one which

undergoes carboxylate oxygen interchange. The relaxation rate of  $O(c,n1)$  has been measured in Figure 8. The broadening of the  $O(c,n2)$  and  $O(t,n)$  resonances will be only ca.  $1/5$  as much as that of  $O(c,n1)$ , since it is the exchange arising from the twist which leads to their broadening. If one assumes that  $\Delta H^\ddagger$  for the twist is approximately the same as that for the oxygen interchange, the rate of interchange will be approximately 5 times the rate of twist at higher temperatures as well. At  $50^\circ \text{C}$  one would expect to see the combined oxygen resonance as roughly the sum of two Lorentzian lineshapes in which the peak width of 60% of the non-bonded nuclei is eight-tenths of the width of the remaining 40% of the nuclei which undergo the carboxylate oxygen interchange. At  $80^\circ \text{C}$ , 60% of the nuclei in the resonance would have a linewidth which is only ca.  $1/2$  that of the 40% of the nuclei which undergo the carboxylate oxygen interchange. This is due to the 60% being broadened by only the twist while the 40% are broadened by the twist and oxygen interchange. At the highest temperature achieved, 60% would have a linewidth of ca.  $1/4$  that of the interchanging 40%.

Nonetheless, this example again leads to an expected resonance lineshape composed of the sum of two Lorentzian lineshapes of widths which are different by a factor of ca. 4 at  $97^\circ \text{C}$ . The observed resonance did not show this behavior, which would have been readily apparent. Therefore

one can conclude that a mechanism involving selective sites at which carboxylate oxygen interchange occurs may be unlikely. It is reasonable to state that carboxylate oxygen interchange can occur at all three non-bonded sites at rates which are not too dissimilar, and likely within a factor of five. This factor of five arises since the interchange at any non-bonded site must compete with the averaging of three non-bonded carboxylate sites by the Bailar twist, which in turn is five times slower than the measured interchange rate. The original assumption that the rates of interchange at the non-bonded sites are approximately equal is therefore reasonably accurate.

This conclusion can be compared with the results which Rowland found for the water exchange from  $\text{Ni}(\text{IDA})_2^{-2}$  (5). There the water exchange rates from the two inequivalent water sites were different by a factor of ca. 4.5 at 25° C, with sites cis to the ligand nitrogen exchanging faster than that site trans to the ligand nitrogen. Based on the examples and arguments above the rates of carboxylate oxygen interchange are probably equal to within a factor of five. This would be consistent with the bond strain arguments of Rowland, but there is no way to predict easily what the ligand labilization effects would be in the bis complex relative to the mono complex.

Appendix I  
NMR Sample Data

Proton NMR  $= +2.675 \times 10^4 \text{ sec}^{-1} \text{ G}^{-1}$   
(ref. 15)

| Sample Number | Ni(IDA) <sub>2</sub> <sup>-2</sup><br>Concentration | L/M* | pH   | Viscosity |
|---------------|-----------------------------------------------------|------|------|-----------|
| B9            | (Ni <sup>+2</sup> )=0.50 M                          | 1.0  | 8.1  | -----     |
| B10           | 0.50 M                                              | 2.0  | 10.6 | -----     |
| B11           | 0.50 M                                              | 2.5  | 11.0 | -----     |
| B12           | 0.50 M                                              | 3.0  | 11.1 | -----     |
| B13           | 0.50 M                                              | 4.0  | 11.3 | -----     |

Carbon-13 NMR  $= +6.728 \times 10^3 \text{ sec}^{-1} \text{ G}^{-1}$   
(ref. 15)

| Sample Number | Ni(IDA) <sub>2</sub> <sup>-2</sup><br>Concentration | L/M   | pH   | Viscosity             |
|---------------|-----------------------------------------------------|-------|------|-----------------------|
| C10           | 0.50 M                                              | 2.0   | 9.5  | ---                   |
| C11           | 0.50 M                                              | 2.5   | 9.5  | ---                   |
| C12           | 0.50 M                                              | 3.0   | 10.1 | ---                   |
| C14           | (Ni <sup>+2</sup> )=0.50 M                          | 1.5   | 7.9  | ---                   |
| C15           | 0.50 M                                              | 2.0   | 8.0  | 1.185 cp<br>(21.1° C) |
| C17           | 0.015 M                                             | 180.0 | 9.8  | -----                 |

Oxygen-17 NMR  $= -3.628 \times 10^3 \text{ sec}^{-1} \text{ G}^{-1}$   
(ref.15)

|    | Ni(IDA) <sub>2</sub> <sup>-2</sup><br>Concentration | L/M  | pH  | Viscosity           |
|----|-----------------------------------------------------|------|-----|---------------------|
| O1 | 0.41 M                                              | 2.95 | 9.5 | 1.5 cp<br>(21.1° C) |

\*L/M denotes ligand-to-metal ratio.

## Appendix II

## Chemical Shift and Relaxation Data

- Table I.....Chemical Shifts of Methylene Protons of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 60 MHz
- Table II.....Chemical Shifts of Methylene Protons of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 180 MHz
- Table III....Transverse Relaxation Rates of Methylene  
 Protons of  $\text{Ni}(\text{IDA})_2^{-2}$  at 180 MHz
- Table IV.....Chemical Shifts of the C(ct,c) Resonances of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 45.29 MHz as a Function of Ligand-  
 to-Metal Ratio (l/M)
- Table V.....Chemical Shifts of C(u,c) and C(u,m) Resonances  
 in the Presence of Dilute Amounts of Ni(II) as  
 a Function of Temperature
- Table VI.....Chemical Shifts of the C(ct,c) Resonances of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 45.29 MHz
- Table VII....Transverse Relaxation Rates of the C(ct,c)  
 Resonances of  $\text{Ni}(\text{IDA})_2^{-2}$  at 45.29 MHz
- Table VIII...Chemical Shifts of the O(ct,n) Resonance of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 13.21 MHz
- Table IX.....Transverse Relaxation Rate of the O(ct,n)  
 Resonance of  $\text{Ni}(\text{IDA})_2^{-2}$  at 13.21 MHz
- Table X.....Chemical Shifts of the O(ct,n) Resonance of  
 $\text{Ni}(\text{IDA})_2^{-2}$  at 24.4 MHz

TABLE I  
CHEMICAL SHIFTS OF METHYLENE PROTONS OF  $\text{Ni(IDA)}_2^{-2}$   
AT 60 Mhz

| Temperature<br>°C | Chemical Shift, ppm relative to H(u,m) |         |                   |                   |         |
|-------------------|----------------------------------------|---------|-------------------|-------------------|---------|
|                   | $10^3/T, ^\circ\text{K}^{-1}$          | H(c,e2) | H(c,e1)<br>H(t,e) | H(c,a1)<br>H(t,a) | H(c,a2) |
| -2.0              | 3.690                                  | -95.8   | -90.9             | ----              | ---     |
| 0.9               | 3.651                                  | -95.0   | -89.9             | -22.3             | -15.1   |
| 10.3              | 3.530                                  | -92.2   | -87.5             | -22.0             | -14.5   |
| 18.2              | 3.434                                  | -90.8   | -85.6             | -21.5             | -14.2   |
| 19.5              | 3.419                                  | -89.5   | -84.3             | ----              | ---     |
| 21.0              | 3.410                                  | -88.8   | -83.6             | -20.9             | -14.0   |
| 26.4              | 3.340                                  | -87.4   | -82.6             | -21.3             | -13.9   |
| 28.7              | 3.315                                  | -85.0   | -80.5             | ----              | ---     |
| 29.1              | 3.310                                  | -85.6   | -81.1             | -19.1             | -12.3   |
| 31.0              | 3.289                                  | -86.0   | -81.3             | -21.1             | -14.1   |
| 35.9              | 3.237                                  | -84.7   | -91.1             | -20.9             | -14.2   |
| 37.5              | 3.221                                  | -84.2   | -80.2             | ----              | ---     |
| 41.0              | 3.185                                  | -83.6   | -80.3             | -20.2             | -14.3   |
| 45.0              | 3.145                                  | -82.1   | -79.5             | -20.1             | -14.6   |

AFTER COALESCENCE

|      |       | Equatorial | Axial |
|------|-------|------------|-------|
| 51.0 | 3.086 | -79.6      | -15.2 |
| 63.0 | 2.976 | -76.4      | -17.0 |
| 75.1 | 2.873 | -73.5      | -17.0 |
| 87.2 | 2.776 | -70.8      | -16.8 |
| 95.2 | 2.716 | -66.0      | -16.9 |

Note: The labelling of the resonances is based upon the over-lapping of the H(t,e) with the H(c,e1) resonance. This assignment is discussed in the carbon-13 NMR section of this thesis.

Sample: B7, Appendix I

TABLE II  
CHEMICAL SHIFTS OF METHYLENE PROTONS OF  $\text{Ni(IDA)}_2^{-2}$   
AT 180 Mhz

| Temperature<br>°C | $10^3/T, \text{ }^\circ\text{K}^{-1}$ | Chemical Shift, ppm relative to H(u,m) |                   |                   |         |
|-------------------|---------------------------------------|----------------------------------------|-------------------|-------------------|---------|
|                   |                                       | H(c,e2)                                | H(c,e1)<br>H(t,e) | H(c,a1)<br>H(t,a) | H(c,a2) |
| 0.0               | 3.661                                 | -101.3                                 | -93.1             | -26.1             | -15.3   |
| 5.0               | 3.595                                 | -99.9                                  | -91.4             | -25.8             | -15.3   |
| 10.0              | 3.532                                 | -98.3                                  | -90.1             | -25.4             | -15.3   |
| 15.0              | 3.472                                 | -96.7                                  | -88.5             | -25.0             | -15.1   |
| 20.0              | 3.413                                 | -95.3                                  | -87.4             | -25.0             | -15.1   |
| 25.0              | 3.354                                 | -93.3                                  | -85.4             | -24.8             | -14.8   |
| 27.0              | 3.332                                 | -91.4                                  | -83.7             | -24.7             | -14.6   |
| 30.0              | 3.298                                 | -91.5                                  | -84.0             | -24.7             | -14.8   |
| 35.0              | 3.285                                 | -89.9                                  | -82.3             | -24.3             | -14.8   |
| 40.0              | 3.193                                 | -87.8                                  | -80.6             | -23.9             | -14.7   |
| 45.0              | 3.145                                 | -86.4                                  | -79.4             | -23.8             | -14.7   |
| 50.0              | 3.096                                 | -84.5                                  | -78.1             | -23.0             | -14.7   |

Note: The labelling of the resonances is based upon the over-lapping of the H(t,e) with the H(c,e1) resonance. This assignment, and likewise the axial assignment, are discussed in the carbon-13 NMR section of this thesis.

Sample: B10, Appendix I

TABLE III  
TRANSVERSE RELAXATION RATES OF METHYLENE PROTONS OF  
 $\text{Ni}(\text{IDA})_2^{-2}$  AT 180 MHz

| Temperature<br>° C | $10^3/T, ^\circ\text{K}^{-1}$ | H(c,e2) | $1/T_2, \text{sec}^{-1}$ |                    | H(c,a2) |
|--------------------|-------------------------------|---------|--------------------------|--------------------|---------|
|                    |                               |         | H(t,e)+<br>H(c,e1)       | H(t,a)+<br>H(c,a1) |         |
| 0.0                | 3.661                         | 3600    | 5500                     | 6500               | 5900    |
| 5.0                | 3.595                         | 3800    | 5200                     | 6100               | 5700    |
| 10.0               | 3.532                         | 3400    | 4600                     | 6000               | 5200    |
| 15.0               | 3.472                         | 3700    | 4000                     | 5600               | 5000    |
| 20.0               | 3.413                         | 3700    | 3900                     | 5200               | 4900    |
| 25.0               | 3.354                         | 3400    | 3600                     | 4700               | 4200    |
| 27.0               | 3.332                         | 3400    | 3300                     | 4800               | 4300    |
| 30.0               | 3.298                         | 3100    | 3300                     | 3700               | 4000    |
| 35.0               | 3.285                         | 2700    | 3600                     | 3400               | 3800    |

Sample: B10, Appendix I

Note: Linewidths determined by curve fitting using 180 MHz NMR program.

TABLE IV

CHEMICAL SHIFTS OF THE C(ct,c) RESONANCES OF  $\text{Ni}(\text{IDA})_2^{-2}$   
AT 45.29 MHz AS A FUNCTION OF LIGAND-TO-METAL RATIO (L/M)

| Temperature,<br>° C | L/M | Chemical Shift, ppm |                |            |
|---------------------|-----|---------------------|----------------|------------|
|                     |     | C(u,c)-IS           | C(u,c)-C(c,c2) | IS-C(c,c1) |
| 25.5                | 1.5 | ----                | 169.9          | ----       |
| 24.5                | 2.0 | 107.0               | 171.6          | 64.7       |
| 25.0                | 2.5 | 107.0               | 171.6          | 64.7       |
| 24.5                | 3.0 | 109.1               | 173.8          | 64.7       |

| Chemical Shift, ppm |            |               |           |
|---------------------|------------|---------------|-----------|
| C(u,c)-C(c,c2)      | IS-C(c,c2) | C(u,c)-C(t,c) | IS-C(t,c) |
| 210.8               | ----       | 243.9         | ----      |
| 211.7               | 104.8      | 245.4         | 138.4     |
| 211.7               | 104.8      | 245.4         | 138.4     |
| 213.9               | 104.8      | 248.8         | 139.7     |

Samples: C10, C11, C12, C14; Appendix I

TABLE V

CHEMICAL SHIFTS OF C(u,c) and C(u,m) RESONANCES  
IN THE PRESENCE OF DILUTE AMOUNTS OF Ni (II)  
AS A FUNCTION OF TEMPERATURE

| Temperature,<br>° C | Chemical Shift (ppm) |           |           |
|---------------------|----------------------|-----------|-----------|
|                     | C(u,c)-C(u,m)        | C(u,c)-IS | IS-C(u,m) |
| 30.0                | 123.1                | 106.1     | 16.9      |
| 40.0                | 122.8                | 106.0     | 16.8      |
| 50.0                | 122.6                | 105.9     | 16.7      |

Note: Dioxane was used as the internal shift standard, IS.

Sample: C17, Appendix I

TABLE VI  
CHEMICAL SHIFTS OF C(ct,c) RESONANCES OF Ni(IDA)<sub>2</sub><sup>-2</sup>  
AT 45.29 Mhz

| Temperature,<br>° C | Chemical Shift, ppm relative to p-dioxane<br>10 <sup>3</sup> /T. °K <sup>-1</sup> internal standard |         |         |        |
|---------------------|-----------------------------------------------------------------------------------------------------|---------|---------|--------|
|                     |                                                                                                     | C(c,c1) | C(c,c2) | C(t,c) |
| -3.0                | 3.702                                                                                               | 84.3    | 131.7   | 169.6  |
| 0.0                 | 3.661                                                                                               | 82.5    | 128.2   | 167.7  |
| 5.0                 | 3.595                                                                                               | 79.4    | 124.5   | 162.0  |
| 10.0                | 3.532                                                                                               | 74.9    | 119.1   | 155.2  |
| 13.0                | 3.495                                                                                               | 72.5    | 116.3   | 152.2  |
| 16.0                | 3.458                                                                                               | 71.2    | 113.7   | 148.6  |
| 19.0                | 3.423                                                                                               | 68.3    | 111.1   | 145.1  |
| 22.0                | 3.388                                                                                               | 66.6    | 108.5   | 142.4  |
| 24.9                | 3.357                                                                                               | 64.0    | 105.8   | 138.5  |
| 25.0                | 3.354                                                                                               | 65.0    | 106.2   | 138.6  |
| 25.2                | 3.353                                                                                               | 63.4    | 104.5   | 138.1  |
| 25.4                | 3.351                                                                                               | 64.1    | 104.8   | 138.5  |
| 25.5                | 3.350                                                                                               | 64.7    | 105.2   | 137.2  |
| 28.0                | 3.321                                                                                               | 64.0    | 104.2   | 138.2  |
| 30.0                | 3.299                                                                                               | 61.4    | 101.9   | 133.3  |
| 31.1                | 3.288                                                                                               | 62.1    | 101.9   | 134.6  |
| 34.0                | 3.256                                                                                               | 59.8    | 99.0    | 130.7  |
| 35.0                | 3.246                                                                                               | 58.5    | 97.7    | 129.1  |
| 37.0                | 3.224                                                                                               | 58.5    | 96.4    | 126.8  |
| 40.0                | 3.193                                                                                               | 56.2    | 94.1    | 126.8  |
| 45.0                | 3.145                                                                                               | 53.6    | 90.8    | -----  |
| 50.0                | 3.096                                                                                               | 52.9    | 88.2    | -----  |
| 55.0                | 3.048                                                                                               | 51.0    | 83.0    | -----  |
| 60.0                | 3.002                                                                                               | 52.9    | 81.0    | -----  |

Sample: C15, Appendix I

TABLE VII  
 TRANSVERSE RELAXATION RATES OF THE  $C(ct,c)$   
 RESONANCES OF  $Ni(IDA)_2^{-2}$  AT 45.29 Mhz

| Temperature,<br>° C | $1/T_2, \text{ sec}^{-1}$ |           | $C(t,c)$ |
|---------------------|---------------------------|-----------|----------|
|                     | $C(c,c1)$                 | $C(c,c2)$ |          |
| -3.0                | 1730                      | 1800      | 2270     |
| 0.0                 | 1700                      | 1860      | 2170     |
| 5.0                 | 1390                      | 1600      | 1740     |
| 10.0                | 1510                      | 1420      | 1860     |
| 13.0                | 1210                      | 1320      | 1350     |
| 16.0                | 1280                      | 1560      | 1810     |
| 19.0                | 1210                      | 1390      | 1790     |
| 22.0                | 1280                      | 1440      | 1460     |
| 25.0                | 1160                      | 1370      | 2160     |
| 28.0                | 1120                      | 1400      | 1460     |
| 31.0                | 1180                      | 1250      | 1980     |
| 34.0                | 1280                      | 1400      | 1720     |
| 37.0                | 1350                      | 1400      | 2090     |
| 40.0                | 1250                      | 1350      | 2180     |

Sample: C15, Appendix I

TABLE VIII  
CHEMICAL SHIFTS OF THE O(ct,n) RESONANCE OF  
Ni(IDA)<sub>2</sub><sup>-2</sup> AT 13.2 Mhz

| Temperature,<br>° C | 10 <sup>3</sup> /T, °K <sup>-1</sup> | Chemical Shift, ppm relative<br>to O(u,c) |
|---------------------|--------------------------------------|-------------------------------------------|
| 0.9                 | 3.650                                | -587.4                                    |
| 7.8                 | 3.560                                | -587.4                                    |
| 15.3                | 3.467                                | -566.2                                    |
| 23.4                | 3.372                                | -551.8                                    |
| 23.9                | 3.367                                | -551.1                                    |
| 30.9                | 3.289                                | -538.2                                    |
| 37.4                | 3.221                                | -523.8                                    |
| 38.9                | 3.205                                | -526.6                                    |
| 41.1                | 3.183                                | -522.3                                    |
| 45.0                | 3.144                                | -514.8                                    |
| 50.9                | 3.086                                | -505.8                                    |
| 52.7                | 3.069                                | -499.6                                    |
| 53.5                | 3.062                                | -503.4                                    |
| 60.0                | 3.002                                | -487.5                                    |
| 61.4                | 2.990                                | -490.3                                    |
| 64.6                | 2.961                                | -480.7                                    |
| 70.1                | 2.914                                | -466.3                                    |
| 71.7                | 2.900                                | -475.2                                    |
| 75.0                | 2.873                                | -465.6                                    |
| 77.8                | 2.850                                | -471.2                                    |
| 81.2                | 2.811                                | -473.2                                    |
| 85.5                | 2.789                                | -454.2                                    |
| 96.9                | 2.703                                | -448.5                                    |

Sample: 01, Appendix I

TABLE IX  
 TRANSVERSE RELAXATION RATE OF THE O(ct,n)  
 RESONANCE OF Ni(IDA)<sub>2</sub><sup>-2</sup> AT 13.21 Mhz

| Temperature,<br>°C | 10 <sup>3</sup> /T, °K <sup>-1</sup> | 1/T <sub>2</sub> , sec <sup>-1</sup> |
|--------------------|--------------------------------------|--------------------------------------|
| 0.9                | 3.649                                | 13699                                |
| 5.5                | 3.589                                | 14600                                |
| 7.8                | 3.559                                | 10600                                |
| 15.3               | 3.467                                | 10100                                |
| 23.9               | 3.366                                | 7800                                 |
| 24.5               | 3.360                                | 6810                                 |
| 30.9               | 3.289                                | 6720                                 |
| 37.4               | 3.220                                | 6280                                 |
| 39.6               | 3.197                                | 5400                                 |
| 41.1               | 3.182                                | 5650                                 |
| 45.0               | 3.143                                | 5780                                 |
| 51.0               | 3.085                                | 5320                                 |
| 52.7               | 3.069                                | 5530                                 |
| 53.5               | 3.061                                | 5650                                 |
| 60.0               | 3.002                                | 6530                                 |
| 60.5               | 2.997                                | 5700                                 |
| 64.6               | 2.961                                | 7850                                 |
| 70.4               | 2.911                                | 7100                                 |
| 75.0               | 2.872                                | 9420                                 |
| 75.8               | 2.866                                | 9160                                 |
| 79.3               | 2.837                                | 12200                                |
| 85.5               | 2.788                                | 19800                                |
| 88.6               | 2.764                                | 19600                                |
| 95.4               | 2.713                                | 30100                                |
| 96.9               | 2.701                                | 26100                                |

Sample: 01, Appendix I

TABLE X  
 CHEMICAL SHIFTS OF THE O(ct,n) RESONANCE OF  
 $\text{Ni}(\text{IDA})_2^{-2}$  AT 24.4 Mhz

| Temperature,<br>°C | $10^3/T, ^\circ\text{K}^{-1}$ | Chemical Shift, ppm relative<br>to O(u,c) |
|--------------------|-------------------------------|-------------------------------------------|
| 24.5               | 3.360                         | -547.5                                    |
| 25.3               | 3.351                         | -549.6                                    |
| 26.0               | 3.342                         | -552.0                                    |
| 26.5               | 3.337                         | -541.4                                    |
| 29.8               | 3.301                         | -537.3                                    |
| 30.0               | 3.299                         | -538.5                                    |
| 35.0               | 3.245                         | -529.5                                    |
| 40.0               | 3.193                         | -520.9                                    |
| 45.0               | 3.143                         | -511.9                                    |
| 50.0               | 3.095                         | -499.6                                    |
| 55.0               | 3.047                         | -486.1                                    |
| 60.0               | 3.002                         | -489.4                                    |
| 65.0               | 2.957                         | -475.8                                    |
| 70.0               | 2.914                         | -461.9                                    |
| 75.0               | 2.873                         | -458.6                                    |

Sample: 01, Appendix I

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