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NUCLEAR MAGNETIC RESONANCE STUDIES OF CONFIGURATION AND LIGAND CONFORMATION IN PARAMAGNETIC OCTAHEDRAL COMPLEXES OF NICKEL(II) VI: *Meso*- and *Rac*-2,3-Butane(dinitrilo)-N,N,N',N'-tetraacetate Complexes

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NUCLEAR MAGNETIC RESONANCE STUDIES OF CONFIGURATION AND LIGAND CONFORMATION IN PARAMAGNETIC OCTAHEDRAL COMPLEXES OF NICKEL(II) VI

Meso- and *Rac*-2,3-Butane(dinitrilo)-N,N,N',N'-tetraacetate Complexes

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The effect of ligand stereochemistry upon the rate of intra-molecular interchanges, called *acetate scrambling*, are investigated by proton magnetic resonance. Ni(*rac*-BDTA)²⁻ exhibits slow partial unwrapping followed by nitrogen inversion ($k \approx 1 \times 10^{-5} \text{ sec}^{-1}$ at 72°C). Ni(*meso*-BDTA)²⁻ probably undergoes this process at a similar rate. Because of the great conformational preference of the methyl groups for the pseudo-equatorial position in the chelate ring, the contribution of Δ, Λ -conversion to the acetate scrambling in Ni(*rac*-BDTA)²⁻ is negligible. Ni(*meso*-BDTA)²⁻ undergoes Δ, Λ -conversion rapidly ($k = 1.5 \times 10^3 \text{ sec}^{-1}$) at 72°C. A pseudo-axial methyl group selectively reduces the deuterium exchange rates of one out-of-plane acetate ring by a factor of 3 relative to those observed for the "unhindered" out-of-plane acetate ring. The deuterium exchange on a specific out-of-plane acetate ring is stereospecific with the pseudo-axial proton exchanging three times faster than the pseudo-equatorial proton.

INTRODUCTION

The previous contribution in this series involved nickel(II) complexes of ethylene(dinitrilo)N,N,N',N'-tetraacetate (EDTA), 1,2-propane(dinitrilo)N,N,N',N'-tetraacetate (PDTA), and *trans*-1, 2-cyclohexane(dinitrilo)N,N,N',N'-tetraacetate (CyDTA).¹ In that paper information regarding solution structure, chelate ring conformations, and dynamics of coordination was obtained. Additionally, certain principles concerning the interpretation of pmr spectra of these paramagnetic complexes were established. A major portion of the paper was devoted to elucidating the relative rates of certain *acetate scrambling* processes as shown in Figure 1. By acetate scrambling is meant that acetate chelate rings are allowed to change their relative positions in the complex.

All the previous complexes were found to acetate scramble at some extreme rate relative to the rate of base-catalyzed acetate deuterium exchange. For example, Ni(EDTA)²⁻ exhibited rapid acetate scrambling by both of the processes shown in Figure 1. Ni(CyDTA)²⁻, whose steric requirements forbid acetate scrambling by Δ, Λ -conversion (Figure 1a), was found to be inert to nitrogen inversion as well. Ni(PDTA)²⁻ showed a rapid rate of nitrogen inversion (Figure 1b), but nothing could

be said about the relative rate of Δ, Λ -conversion because of the extreme conformational preference of the propanediamine methyl group for a pseudo-equatorial position in the chelate ring.

This study of nickel(II) 2,3-butane(dinitrilo)

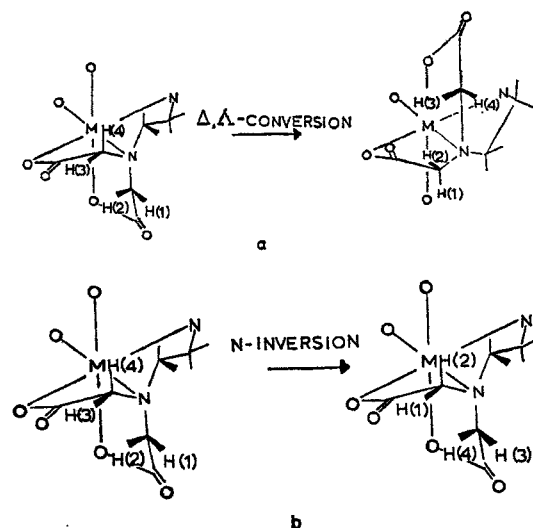


FIGURE 1 Proton interchanges resulting from acetate scrambling processes.

- (a) Δ, Λ -conversion.
(b) Nitrogen inversion.

N,N,N',N'-tetraacetate (BDTA) complexes was initiated in order to further investigate steric effects on acetate scrambling processes. The structures of the complexes are shown in Figure 2.

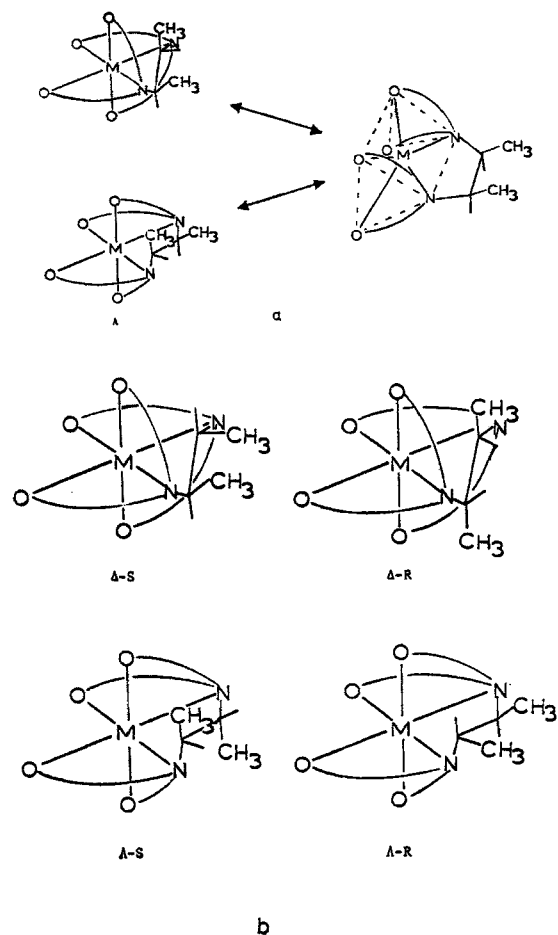


FIGURE 2 Structures of the complexes.
 (a) Δ and Λ forms of a metal-*meso*-BDTA complex showing trigonal intermediate.
 (b) The configurations of a metal-*rac*-BDTA complex.

The ligand BDTA exists in *meso* and *racemic* forms, and complexes of each have different stereochemistries. For example, $\text{Ni}(\textit{meso}\text{-BDTA})^{2-}$ will always require that one methyl group be axial no matter what the optical configuration about the metal. Therefore, the complex will exhibit no intrinsic preference for any of the forms in Figure 1.

In contrast, the complex, $\text{Ni}(\textit{rac}\text{-BDTA})^{2-}$, will always have both methyl groups in the same position—either axial or equatorial—depending upon the optical configuration of the ligand and

the complex. A number of workers have established that, in such a case, the methyl groups will greatly prefer to be in an equatorial position.¹⁻³ Therefore, very small amounts of those complexes with axial methyl groups are expected, but, as has been the case with all complexes studied so far, forms that can be interchanged by nitrogen inversion (Figure 1b) are equally probable.

The butanediamine portion of coordinated *rac*-BDTA is expected to be more rigid than that of coordinated *meso*-BDTA, but both are expected to exhibit less stringent steric requirements than coordinated CyDTA. The extent of methyl substitution on the diamine portion of the ligand has been found to be important in determining the relative rates of acetate scrambling by nitrogen inversion in labile diamagnetic complexes.³ Because these ligands are more highly substituted than PDTA, they are likely candidates to exhibit intermediate behavior with respect to acetate scrambling processes.

EXPERIMENTAL

2, 3-diaminobutane was synthesized by the method of Dickey *et al.*,⁴ and was also obtained from Wyandotte Chemical Co. The *meso* and *racemic* isomers were separated by an established method⁴ and they were treated separately by the procedure of Dwyer and Garvan⁵ to make the corresponding tetraacetic acids. The acids were found to be very difficult to isolate in a pure state because they seemed to be appreciably soluble in water at high ionic strengths.

Other chemicals were purchased in reagent grade from commercial sources and were used without further purification.

Solutions 0.5*M* solutions of the metal complexes were prepared by weighing out an appropriate amount of ligand, adding about 95% of the aqueous base (KOH) required for neutralization, and adding 20 ml 0.250*M* $\text{Ni}(\text{ClO}_4)_2$ stock solution. The mixture was taken to dryness under reduced pressure; D_2O was added and the potassium perchlorate was removed by centrifugation. The resulting solution was taken to dryness once or twice more with addition of D_2O . Finally the solid was dissolved in D_2O with enough KOD being added so as to provide the desired concentration of OD^- for kinetic runs.

Other solutions were prepared in a similar

manner using smaller amounts of material. The pD of these solutions was adjusted using solutions of KOD or DCI.

The free ligand was released from samples of the complex at various stages of a kinetic run by treatment with excess solid KCN. The solutions eventually turned from blue to yellow-orange indicating the formation of square-planar diamagnetic $Ni(CN)_4^{2-}$.

Kinetic runs Approximately 0.5 ml samples were heated in nmr tubes for varying lengths of time in a water bath at $72 \pm 0.5^\circ C$. The pmr spectra were taken immediately after the reaction was quenched by putting the nmr tube in an ice bath. The free ligand was released subsequent to obtaining the spectra of the paramagnetic complex. Some kinetic runs were done at $100^\circ C$ in a bath of boiling distilled water.

Pmr spectra Pmr spectra were obtained with a Varian HA-100 spectrometer in the manner previously described.² Some spectra were obtained with a JEOL C-60HL using 300 ppm scan width and 12–16 kHz modulation from an external HP-200AB oscillator. Spectra of the free ligand were also obtained on both instruments.

RESULTS

Spectral assignments Schematic spectra of the complexes in D_2O are shown in Figure 3. The shifts are reported relative to the methyl resonance of sodium 3-(trimethylsilyl)-1-propane-sulfonate (TMS*) as internal reference. The residual HOD resonance at -5 ppm is not shown.

$Ni(rac\text{-BDTA})^{2-}$. Three peaks are observed in the spectrum of $Ni(rac\text{-BDTA})^{2-}$ above $pD = 6$. The peaks at -43 ppm and -87 ppm disappear when the solution is made alkaline ($pD = 13$) and is heated. Under these conditions the out-of-plane acetate protons are labile to deuterium exchange, but all acetate protons may exchange if some acetate scrambling process interchanges the in-plane and out-of-plane acetate rings.

All the acetate protons undergo deuterium exchange as could be demonstrated by the following experiment: The complex was heated in base until peaks at -43 ppm and -87 ppm had disappeared; then the solution containing the complex was added to excess solid KCN to form the yellow diamagnetic $Ni(CN)_4^{2-}$ and free $rac\text{-BDTA}$. The

pmr spectrum of this solution revealed that no acetate protons were left on the ligand.

The peak at -87 ppm is about twice as intense as the peak at -43 ppm. By the well-established rule that the more axial protons in a puckered five membered chelate ring will appear at higher field than the corresponding equatorial proton, the peak at -43 ppm was assigned to the out-of-plane axial acetate protons. The peak at -87 ppm was then assigned to both the in-plane and out-of-plane equatorial acetate protons. The in-plane axial acetates are not observed, nor have they been observed in any similar complex studied so far.¹ Their presence will be demonstrated later.

The peak at -18 ppm is assigned to both equatorial methyl groups and to the two axial methine protons on the butanediamine portion of the ligand. The observed shifts are in the typical range of those observed for similar protons in other complexes.¹⁻² Although there is no hint of structure on the peak, area measurements show that the peak is about 25% more intense than it would be if the peak were attributed solely to six methyl protons. The peak positions and assignments for $Ni(rac\text{-BDTA})^{2-}$ are summarized in Table I.

$Ni(meso\text{-BDTA})^{2-}$. Six peaks are observed. Those at -40 ppm, -80 ppm, and -85 ppm vanish upon deuterium exchange; therefore, they

TABLE I
Spectral assignments for $Ni(meso\text{-BDTA})^{2-}$ and $Ni(rac\text{-BDTA})^{2-}$ at 30° and $pH \approx 10$

Complex	Contact shift ^a	Assignment ^b
$Ni(meso\text{-BDTA})^{2-}$	- 2	3 axial methyl
	- 16	3 equatorial methyl, 1 axial en
	- 40	2 axial out-of-plane ac
	- 80	1 equatorial in-plane ac
	- 85	1 equatorial in-plane ac, 2 equatorial out-of-plane ac
$Ni(rac\text{-BDTA})^{2-}$	-109	1 equatorial en
	- 18	6 equatorial methyl, 2 axial en
	- 43	2 axial out-of-plane ac
	- 87	2 equatorial out-of-plane ac 2 equatorial in-plane ac

^aShifts are given in ppm relative to internal sodium 3-trimethylsilyl-1-propane-sulfonate.

^bNumerical values refer to number of protons of the designated type.

are assigned to acetate protons. As was the case in $\text{Ni}(\text{rac-BDTA})^{2-}$ the upfield peak (-40 ppm) is assigned to the out-of-plane axial protons. The two out-of-plane axial protons could, in principle, have different contact shifts because they are in spatially non-equivalent environments relative to the methyl groups. However, only one resonance is observed for these protons.

The peaks at -80 ppm and -85 ppm are assigned to the out-of-plane and in-plane equatorial acetate protons. The combined area of the two peaks corresponds to four protons, and the peak at -85 ppm is about three times more intense than the peak at -80 ppm. The peak at -80 ppm is ascribed to the in-plane equatorial proton designated as H(3) in Figure 3. The peak at -85 ppm

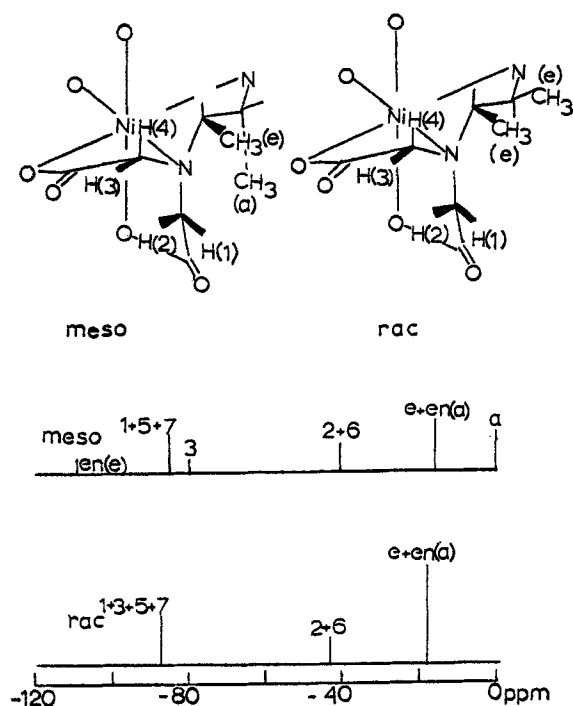


FIGURE 3 Schematic spectra of $\text{Ni}(\text{BDTA})^{2-}$ complexes. Numbers correspond to those in Table III. Residual HOD resonance is not shown.

is then assigned to the other in-plane and out-of-plane equatorial protons. Justification of the assignments is based on deuterium exchange experiments to be discussed.

No other peaks in the spectrum may be ascribed to acetate protons. Therefore, in keeping with the behavior of other complexes of this type, we are

led to propose that the in-plane axial acetate proton resonances are not observed.

The peak at -109 ppm is assigned to the equatorial methine proton on the butanediamine "backbone" of the complex; its axial counterpart contributes to the area of the peak at -16 ppm.

Because the two methyl groups are always in non-equivalent environments, two methyl peaks are expected unless some exchange process averages their resonance positions; two are observed. The peak at -16 ppm is attributed to the equatorial methyl group, and the axial methyl is at -2 ppm. Integration of the two methyl peaks indicates that the equatorial peak (-16 ppm) is slightly more intense than the axial methyl peak (-2 ppm). This is taken as evidence that the axial methine proton contributes to the area of the equatorial methyl peak even though no shoulder can be observed.

A summary of peak positions and assignments for $\text{Ni}(\text{meso-BDTA})^{2-}$ is given in Table I.

Deuterium exchange experiments The rate and stereospecificity of acetate proton deuteration of both complexes in $0.1N$ KOD/ D_2O were investigated. Spectra of both paramagnetic complexes and of the corresponding diamagnetic free ligand (released from the complex by treatment with excess KCN) were recorded after samples had been heated for varying times. Spectra of the complexes and of the liberated ligands at selected stages of deuterium exchange are given in Figures 4-7.

Pseudo-first order rate constants for the disappearance of the acetate peaks were determined by plotting $\ln(\text{peak-height})$ vs. time to obtain a half life, $t_{1/2}$, and calculating k from $k = 0.693/t_{1/2}$. The rate constants determined are given in Table II.

TABLE II

Pseudo-first order rate constants for Acetate Deuterium exchange in $\text{Ni}(\text{BDTA})^{2-}$ complexes, $[\text{OD}^-] = 0.1M$, temperature = 72°C .

Complex	Chemical Shifts of Observed Peak, ppm	k_{obs} , sec^{-1}
$\text{Ni}(\text{meso-BDTA})^{2-}$	-40	2.2×10^{-4}
	-80	1.7×10^{-4}
	-85	1.1×10^{-4}
$\text{Ni}(\text{rac-BDTA})^{2-}$	-43	9.2×10^{-4}
	-87	3.1×10^{-4a}
	-87	1.2×10^{-5b}

^aRate constant for decrease of out-of-plane equatorial acetate protons.

^bRate constant for decrease of in-plane equatorial acetate protons.

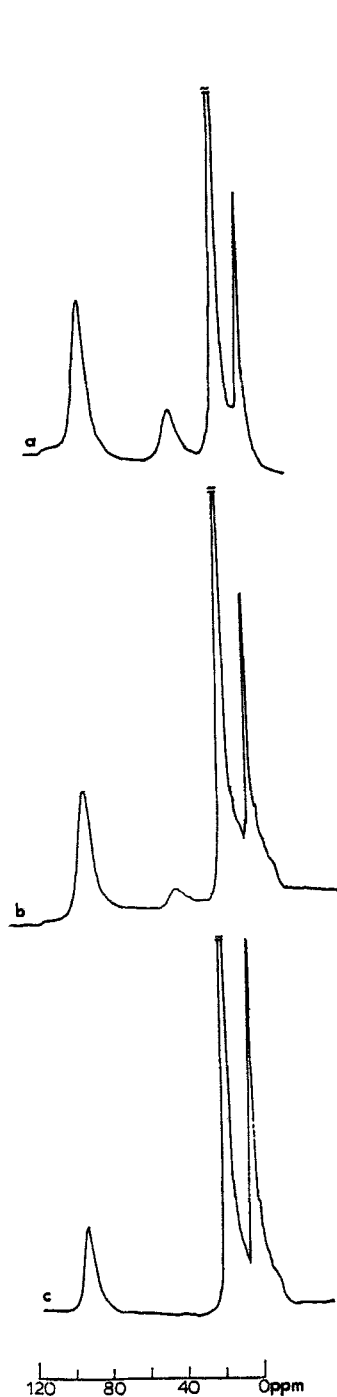


FIGURE 4 Proton exchange in $\text{Ni}(\text{rac-BDTA})_2^{2-}$ at $T = 72^\circ\text{C}$ and $\text{KOD} = 0.1M$.

- (a) $t = 0$.
 (b) $t = 20$ min.
 (c) $t = 240$ min.

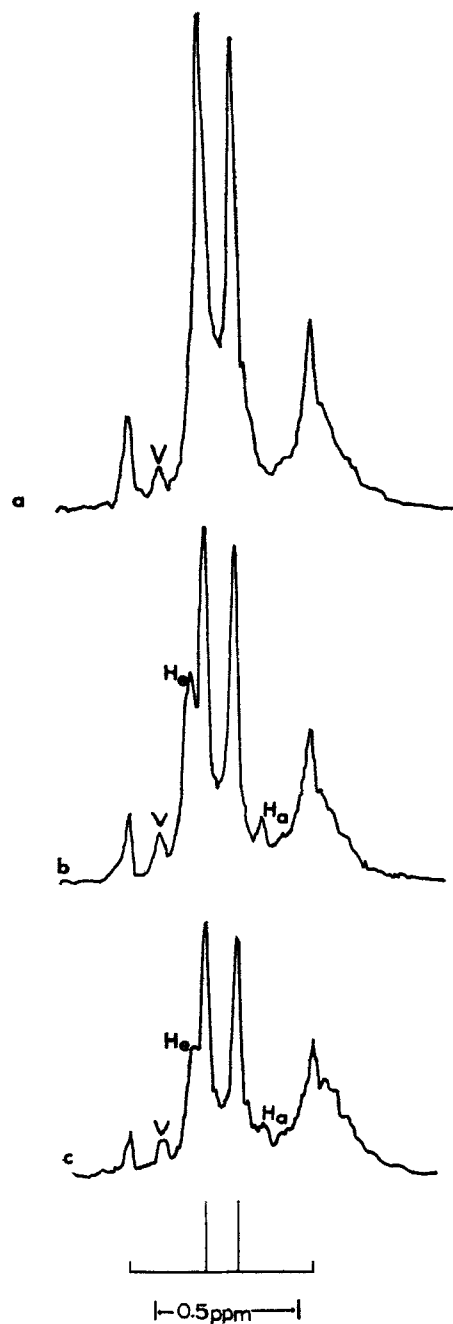


FIGURE 5 Proton exchange in $\text{Ni}(\text{rac-BDTA})_2^{2-}$ as monitored by the KCN-liberated free ligand. Peaks due to impurities are marked by v. The methyl resonances are not shown. Different instrumental sensitivities were used for each spectrum.

- (a) $t = 0$.
 (b) $t = 20$ min.
 (c) $t = 240$ min.

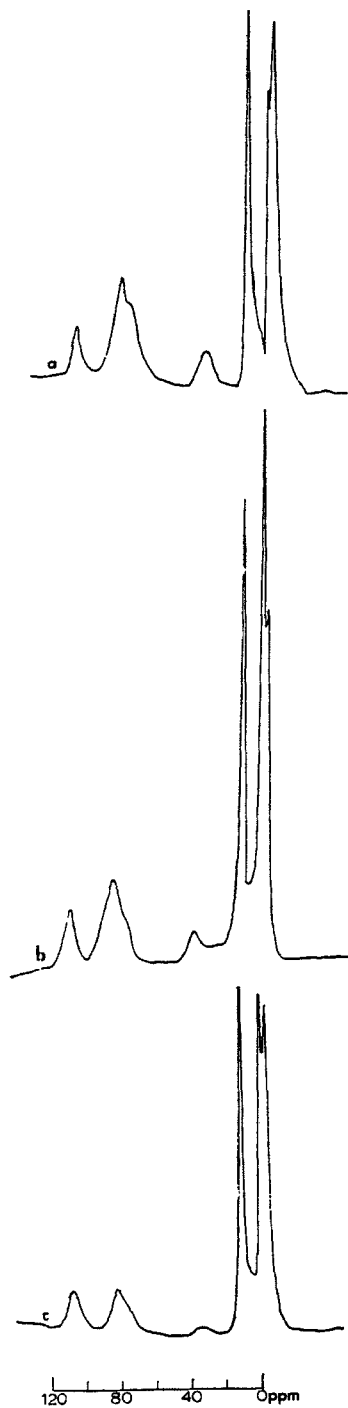


FIGURE 6 Proton exchange in $\text{Ni}(\text{meso-BDTA})_2^{2-}$ at $T = 72^\circ\text{C}$ and $\text{KOD} = 0.1\text{ M}$.

- (a) $t = 0$.
 (b) $t = 40$ min.
 (c) $t = 120$ min.

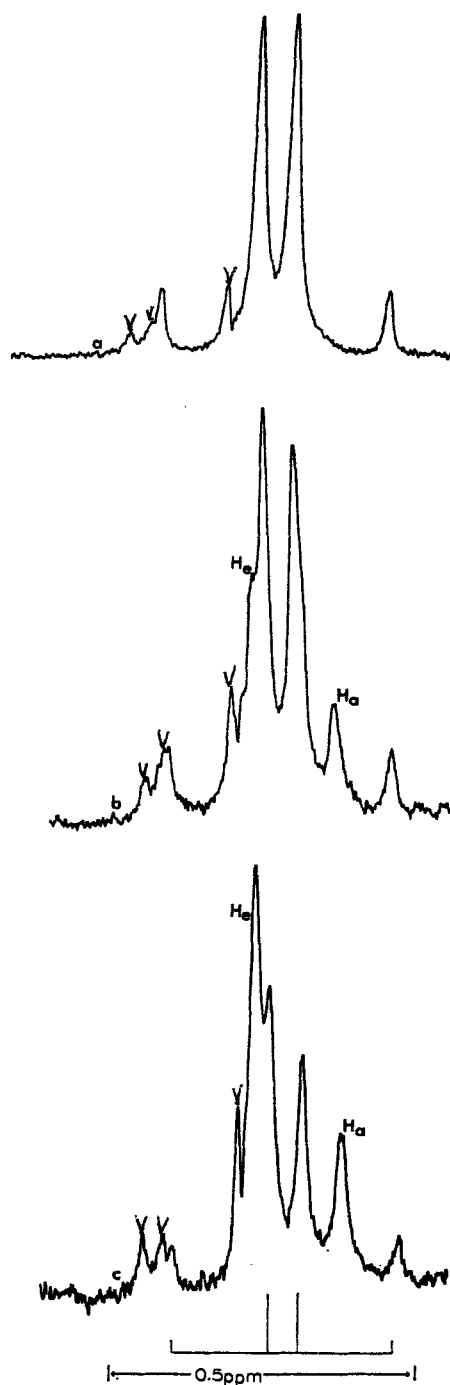


FIGURE 7 Proton exchange in $\text{Ni}(\text{meso-BDTA})_2^{2-}$ as monitored by the KCN-liberated free ligand. Peaks due to impurities are marked by v. Only the acetate portion of the spectrum is shown. The instrumental sensitivity is not the same for each spectrum.

- (a) $t = 0$. (b) $t = 40$ min. (c) $t = 120$ min.

$Ni(rac-BDTA)^{2-}$ Table II indicates that the peak at -43 ppm, due to the out-of-plane axial protons, disappears about three times faster ($k = 9.2 \times 10^{-4} \text{ sec}^{-1}$) than the peak due to the out-of-plane equatorial protons (-87 ppm, $k = 3.1 \times 10^{-4} \text{ sec}^{-1}$). Such an observation is consistent with similar experiments on $Ni(CyDTA)^{2-}$ and $Ni(PDTA)^{2-}$ where the ratio of the axial and equatorial pseudo-first order rate constants was also about three.¹

This stereospecificity is reflected in the spectrum of the liberated ligand (Figure 5) where one monodeutero isomer predominates throughout the deuteration. Liberated ligand spectra of $CyDTA^{4-}$ and $PDTA^{4-}$ also showed the monodeutero isomer predominance which is caused by collapse of the AB pattern by disappearance of only one proton of the AB pair.¹ The other shows a "new" peak at its calculated shift position.

The peak at -87 ppm is made up of two different kinds of protons, the in-plane and out-of-plane equatorial protons. These different kinds of protons are observed to disappear with different rate constants. Thus, the peak is observed to decay to about half its original area with a rate constant $k = 3.1 \times 10^{-4} \text{ sec}^{-1}$, then it disappears much more slowly ($k = 1.2 \times 10^{-5} \text{ sec}^{-1}$) until it vanishes altogether. The more rapid decay is associated with the deuteration of the out-of-plane equatorial protons. The second, slower, decay can be attributed to deuteration of the in-plane equatorial protons which are allowed to get into the reactive out-of-plane position by slow partial unwrapping followed by nitrogen inversion.

The following experiments demonstrate that acetate scrambling does occur and that there are protons, namely the in-plane axial protons, which are not observed in the spectrum: First, deuterium exchange was carried out until the out-of-plane axial peak (-43 ppm) just disappeared; then the complex was decomposed with excess KCN. This liberated the ligand from the complex and, therefore, allowed the nitrogens to undergo umbrella inversion. After the $Ni(CN)_6^{2-}$ had been destroyed by several additions of acid (hood!) and the original complex reformed by addition of base, the spectrum revealed a peak at -43 ppm of about half the intensity of the original peak. The peak at -87 ppm was unchanged by this experiment.

An exactly similar experiment with $Ni(CyDTA)^{2-}$ ¹ established that, upon nitrogen inversion, in-plane axial protons and out-of-plane protons are interchanged as shown in Figure 1b.

Assuming the same relative acetate ring conformations in $Ni(rac-BDTA)^{2-}$ and $Ni(CyDTA)^{2-}$, the new peak is due to originally in-plane axial acetate protons which were scrambled with the out-of-plane axial acetates by nitrogen inversion.

In the second experiment, another sample of $Ni(rac-BDTA)^{2-}$ was deuterated until the out-of-plane axial acetate peak (-43 ppm) was nearly gone. The sample was then adjusted to $pH = 7$ where further deuterium exchange is negligibly slow, and it was heated. The peak at -43 ppm was observed to increase, with a rate constant slightly smaller than the rate constant for the decrease of the in-plane equatorial peak (-87 ppm) under deuterium exchange conditions ($k = 6 \times 10^{-6} \text{ sec}^{-1}$ vs. $1.2 \times 10^{-5} \text{ sec}^{-1}$). The slight difference in rate constants probably reflects the tendency for acetate oxygens to be bound to the metal a smaller fraction of time at high pH .⁶

$Ni(meso-BDTA)^{2-}$ The rate constant for the disappearance of the peak attributed to the out-of-plane axial acetate protons at -40 ppm is about twice as great ($k = 2.2 \times 10^{-4} \text{ sec}^{-1}$) as the rate constant for the disappearance of the peak at -85 ppm ($k = 1.1 \times 10^{-4} \text{ sec}^{-1}$). The peak at -80 ppm decreases with a rate constant of $1.7 \times 10^{-4} \text{ sec}^{-1}$. As in the case of other ligands

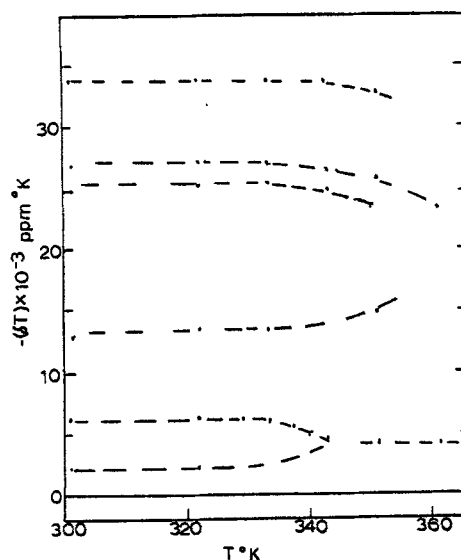


FIGURE 8 Plot of $-\delta(T)$ vs. T for $Ni(meso-BDTA)^{2-}$. The dots are experimental points. The dotted lines indicate trends in the data. Peaks may be identified in this plot by referring to Figure 3.

exhibiting AB patterns in their uncomplexed spectra, the stereoselectivity is observed by the predominance of one monodeutero isomer in the liberated ligand.

The variation of contact shift with temperature was investigated for $\text{Ni}(\text{meso-BDTA})^{2-}$. The results of that study for the observed peaks are presented as a plot of (δT) vs. T in Figure 8. The plot is expected to be a straight line having no slope if the contact shifts vary according to the Curie law, i.e. inversely with absolute temperature. Deviations from the Curie law are observed for all peaks until about 80° . At higher temperatures the Curie law is obeyed.

Examination of Figures 8 and 9 shows that the axial and equatorial methyl resonances move toward each other and coalesce at about 72°C . This behavior is attributed to a rapid rate of Δ, Λ -conversion relative to the expected contact shift difference at that temperature.

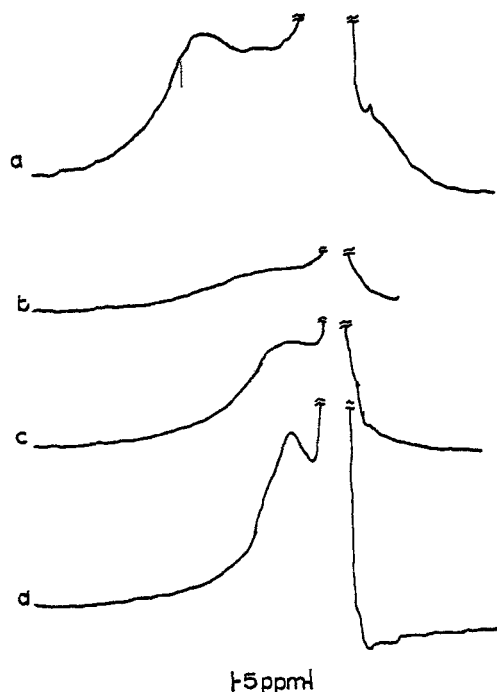


FIGURE 9 Variation of the methyl portion of the $\text{Ni}(\text{meso-BDTA})^{2-}$ spectrum with temperature. The intense interfering resonance is the HOD peak.

- (a) $T = 60^\circ\text{C}$.
 (b) $T = 70^\circ\text{C}$.
 (c) $T = 78^\circ\text{C}$.
 (d) $T = 88^\circ\text{C}$.

The rate of Δ, Λ -conversion at 72° may be calculated from reference 7

$$\frac{1}{\tau_c} = \frac{\pi\Delta}{\sqrt{2}} = 1.5 \times 10^3 \text{ sec}^{-1} \quad (1)$$

where Δ is the contact shift difference between the two peaks at 72° and is estimated to be 666 Hz by using calculated curves (Figure 8).

The free energy of activation for Δ, Λ -conversion can be estimated at the coalescence temperature by assuming that the Eyring equation holds with a transmission coefficient of unity.

$$\frac{1}{\tau_c} = \frac{kT}{h} \exp\left(-\frac{\ddagger, \Delta G}{RT}\right) \quad (2)$$

Using the calculated rate constant from Eqn. 1, ΔG^\ddagger is 15.2 kcal/mole. This activation energy allows the correct prediction that the other peaks should not have coalesced at 363° .

DISCUSSION

The effects of Δ, Λ -conversion and N-inversion on pmr spectral changes accompanying acetate deuterium exchange are discussed in great detail in Reference 1. With such a discussion in mind it is possible to classify the two complexes according to their behavior.

$\text{Ni}(\text{rac-BDTA})^{2-}$ is much like $\text{Ni}(\text{CyDTA})^{2-}$ in its behavior toward deuterium exchange. $\text{Ni}(\text{CyDTA})^{2-}$ was inert to all acetate scrambling processes so that only half the acetate protons exchanged in reasonable times. Likewise, only half of the $\text{Ni}(\text{rac-BDTA})^{2-}$ acetate protons exchange with rate constants typical of acetate protons that can be in the out-of-plane positions easily. However, the last half of the acetate protons disappear faster, in the case of $\text{Ni}(\text{rac-BDTA})^{2-}$, than could be expected for simple in-plane acetate proton exchange.

In the previous section arguments were put forth to show that this increased rate constant (relative to that expected if acetate scrambling processes were slow compared to deuterium exchange) for the last half of the $\text{Ni}(\text{rac-BDTA})^{2-}$ proton exchange was due to a slow but measurable rate of acetate scrambling by nitrogen inversion. The nitrogen inversion rate is slow enough so that it, rather than the rate of deuterium exchange, determines the value rate constant for the disappearance of the in-plane equatorial protons.

The alternative explanation that the deuterium exchange of the final portion of the $\text{Ni}(\text{rac-BDTA})^{2-}$

acetate protons is due to acetate scrambling by Δ, Λ -conversion may be eliminated by the following reasoning: Granted that the Δ, Λ -conversion may be rapid, one of the forms will be unfavorable thermodynamically because of the preference by the methyl groups for the equatorial position in the chelate ring. One can estimate the magnitude of the stability by a consideration of a similar estimation for the $\text{Ni}(\text{rac-bn})^{2+}$ complex where $\text{bn} = 2,3$ -diaminobutane. The enthalpy difference between forms having equatorial methyl groups and those having axial methyl groups was estimated to be 2.5 kcal/mole.⁸ This corresponds to about 2% in the unfavorable form assuming $\Delta S = 0.5 \text{ eu}^2$. The free energy difference for a tetraacetic acid analog is estimated to be greater than the diamine by at least a factor of 2.⁹ This corresponds to 0.04% in the unfavorable form.

The maximum rate constant for acetate scrambling by Δ, Λ -conversion is given by:

$$k_{\Delta, \Lambda} = k_{oa} f_{\Delta, \Lambda} \quad (3)$$

where k_{oa} is the observed out-of-plane axial exchange rate ($9.2 \times 10^{-4} \text{ sec}^{-1}$). The calculated rate constant for acetate scrambling by Δ, Λ -conversion ($k_{\Delta, \Lambda} = 3.6 \times 10^{-8} \text{ sec}^{-1}$) is about 300 times smaller than the rate constant observed for the disappearance of the in-plane equatorial protons ($k = 1.2 \times 10^{-5} \text{ sec}^{-1}$). Therefore, Δ, Λ -conversion may be eliminated as the dominant acetate scrambling process for $\text{Ni}(\text{rac-BDTA})^{2-}$.

The Δ and Λ forms of $\text{Ni}(\text{meso-BDTA})^{2-}$ have the same energy by virtue of having one methyl group in each type of environment, axial and equatorial. Furthermore, the study by Day and Reilley of labile diamagnetic metal complexes of *meso*-BDTA showed that the methyl substituents slowed the nitrogen inversion rate relative to the nitrogen inversion rate exhibited by EDTA complexes of the same metal.³ Thus, one might expect that $\text{Ni}(\text{meso-BDTA})^{2-}$ should show rapid Δ, Λ -conversion between the equally populated forms, and slow nitrogen inversion relative to the rate of deuterium exchange. This case was considered in reference 1, but it was not observed for any of the ligands studied there.

The spectral changes upon first inspection appear to be consistent with the inverse case, slow or non-existent Δ, Λ -conversion and rapid nitrogen inversion. This type of behavior was observed for $\text{Ni}(\text{PDTA})^{2-}$.

However, the interpretation above is inconsistent with the variation of contact shifts with

temperature which indicates that the methyl resonances coalesce at 72° C. The only process that will interchange the methyl groups is Δ, Λ -conversion. Therefore, at 72° C, Δ, Λ -conversion is rapid relative to both the pmr time scale and the rate of deuterium exchange.

Closer inspection of the structure of the $\text{Ni}(\text{meso-BDTA})^{2-}$ complex in Figure 3 reveals that protons on the two out-of-plane acetate rings could undergo deuterium exchange at different rates. The axial methyl group, from molecular models, is close enough to the out-of-plane ring containing H(1) and H(2) to hinder its attaining the planar carbanion intermediate required for deuterium exchange.¹⁰ The other out-of-plane ring is free from this direct steric deceleration of the rate because both methyl groups tend to point away from it.

A model which invokes the above non-equivalence of out-of-plane acetate groups toward deuterium exchange, retains the usual 3:1 axial:equatorial exchange rate ratio for a specific out-of-plane acetate, and assumes rapid Δ, Λ -conversion but slow nitrogen inversion relative to the rate of deuterium exchange, is able to account for the observed relative rate constants for deuterium exchange. This can be seen by considering the consequences of the similar case treated earlier¹ while invoking *four* different rate constants instead of two.

The acetate protons are labeled in Table III, which also labels expected rate constants for disappearance of each acetate proton upon rapid Δ, Λ -conversion. The rate constant labels indicate

TABLE III

Acetate proton interchanges accompanying Δ, Λ -conversion and rate constant labels for $\text{Ni}(\text{meso-BDTA})^{2-}$

Proton	Position*	Proton	Position*	Rate constant label
H(1)	oe	H(8)	ia	k_1
H(2)	oa	H(7)	ie	k_2
H(3)	ie	H(6)	oa	k_6
H(4)	ia	H(5)	oe	k_5
H(5)	oe	H(4)	ia	k_4
H(6)	oa	H(3)	ie	k_3
H(7)	ie	H(2)	oa	k_2
H(8)	ia	H(1)	oe	k_1

*The position of the proton in the complex is either out-of-plane (o) or in-plane (i) in addition to being axial (a) or equatorial (e).

half the intrinsic out-of-plane rate constants because each out-of-plane proton is interchanged with an in-plane proton upon Δ, Λ -conversion.

TABLE IV
Equivalent protons in *meso*-BDTA⁴⁻

Set	Equivalent protons
1	H(1) = H(8) = H(3) = H(6)
2	H(2) = H(7) = H(4) = H(5)

The KCN-liberated ligand further reduces the number of non-equivalent protons by rapid umbrella inversion of both nitrogens. The protons on the liberated ligand are seen to break into two sets of equivalent protons as delineated in Table IV. These two non-equivalent sets of protons give the AB pattern observed in the spectrum of the free ligand.

The observed spectral changes are reflected by apparent stereoselectivity in the liberated ligand by a ratio of 2 : 1 (Figure 7). This means that when the ligand is complexed, the average rates of disappearance of the two sets of protons are different by a factor of 2. Furthermore, it may be seen that set 1 contains H(1) which should exhibit the smallest observed rate constant for steric reasons outlined above. Set 1 also contains H(6) which is the unhindered out-of-plane axial proton and should have the largest observed rate constant. Set 2, then, contains the two protons having intermediate rate constants. Because smooth decreases are observed for all acetate protons in the paramagnetic complex, the rates must not be radically different. Therefore, it is reasonable that set 1 should disappear faster than set 2 leaving monodeutero peaks due to set 2 protons more intense than set 1 protons.

The spectrum of the paramagnetic complex will undergo the following spectral changes which are summarized in Table V. The out-of-plane axial

TABLE V
Expected rate constants for decrease of peaks in the spectrum of Ni(*meso*-BDTA)²⁻

Contact shift	Protons*	Expected rate constants
-40 ppm	H(2), H(6)	$k_2 + k_6$
-40 ppm	H(3)	k_6
-85 ppm	H(1), H(5), H(7)	$k_1 + k_5 + k_2$

* From Figure 3.

peak (-40 ppm) will decrease with the sum of the two out-of-plane axial rate constants, $k_2 + k_6$. The expected rate constants for the decrease of the equatorial proton peaks will vary according to the specific assignment of the protons to the peaks. Assuming that H(3) is the single proton at -80 ppm, its observed rate constant is k_6 . The peak at -85 ppm should decrease with the sum of the rate constants of the protons making up the peak, namely $k_1 + k_2 + k_5$.

Substitutions of trial values of rate constants for the various protons gives an indication of the success of the model. Relative rate constants may be chosen so that the stereoselectivity ratio in the free ligand is correct. Then spectral changes in the paramagnetic complex may be predicted. Results for $k_1 = 1$, $k_2 = 3$, $k_5 = 3$, and $k_6 = 9$ are given in Table VI. Other assignments for the peaks at -80 ppm and -85 ppm did not fit well with the experimentally observed order of rate constants even though a number of "reasonable" trial value sets were tested.

TABLE VI

Comparison of observed spectral changes and spectral changes based on chosen relative rates

Rate constants	Ratio of free ligand Mono-deutero peaks	Relative rate of decrease of peaks		
		-40 ppm	-80 ppm	-85 ppm
$k_1 = 1, k_2 = 3$	1.7	1.7	1.3	1
$k_5 = 3, k_6 = 9$	2	2	1.5	1
Observed				

A similar procedure including the effects of rapid nitrogen inversion by the *complexed* ligand gave inconsistent relative rate constants. Allowing rapid nitrogen inversion in the complex invariably led to the prediction that the peak at -85 ppm should disappear first, but, in fact, it is observed to decrease most slowly of the three peaks. Thus, only one assignment of the spectrum and one allowed acetate scrambling process (Δ, Λ -conversion) are observed to fit with the data. The value of k_6 determined from the spectrum was used to calculate the values of the other rate constants under the assumption that the unhindered out-of-plane acetate would exhibit the normal axial : equatorial deuterium exchange rate ratio of 3 : 1. These

rate constants cannot be extremely accurate because of the large experimental error in k_6 and because of the assumption involved. The calculated rate constants are displayed in Table VII.

TABLE VII
Calculated pseudo-first order rate constants
for Ni(*meso*-BDTA)²⁻

Rate constant ^a	
$k_6 =$	$1.7 \pm 0.3 \times 10^{-4}$
$k_2 =$	$5 \pm 3 \times 10^{-5}$
$k_3 =$	$6 \pm 3 \times 10^{-5}$
$k_1 =$	$0 \pm 3 \times 10^{-5}$

^a T = 72°C and OD⁻ = 0.1M

Because analysis of the spectral changes showed that nitrogen inversion must be slow relative to the rate of deuterium exchange, it seems reasonable to assume that the rate of nitrogen inversion for the two BDTA complexes is about the same. Such an observation is consistent with the earlier work of Day and Reilley who showed that *meso*-BDTA complexes of labile diamagnetic metal ions exhibited slow rates of nitrogen inversion relative to the same EDTA complexes.³

Because Δ, Λ -conversion for Ni(*meso*-BDTA)²⁻ is quite rapid at moderate temperatures ($k = 1.5 \times 10^3$ at 72°C), it is of interest to establish the mechanism for this process. Fay and Piper¹¹ and Serpone and Fay¹² have attempted to elucidate the major pathway for optical inversion as well as *cis-trans* isomerization in some unsymmetrical β -diketone complexes. They suspect that a bond rupture mechanism may be the most prevalent mechanism for rearrangement of the complexes rather than one of the "twist" mechanisms such as the "trigonal" or "Bailar" twist illustrated in Figure 2.¹³

Ho and Reilley found that a trigonal twist mechanism adequately accounted for optical inversion of Ni(en)₃²⁺ as observed by pmr. The observed racemization rate was faster than the nickel-nitrogen bond lifetime, and hence a bond

dissociative mechanism was ruled out.⁷ A similar situation obtained for the Ni(*meso*-bn)₃²⁺ system.⁸ In addition, Cooke, Im, and Busch presented evidence that the trigonal twist mechanism was operative in the thermal racemization of Co(EDTA)²⁻.¹⁴

We are unable to rule out a bond rupture mechanism in the present case. Even though our calculated activation energy ($\Delta G^\ddagger = 15.2$ kcal/mole) is in the range of that where a trigonal twist mechanism has been established, it is conceivable that rupture of a nickel-oxygen bond could initiate the racemization process. Therefore, the twist mechanism illustrated in Figure 2 should be considered only as a possible mechanism.

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