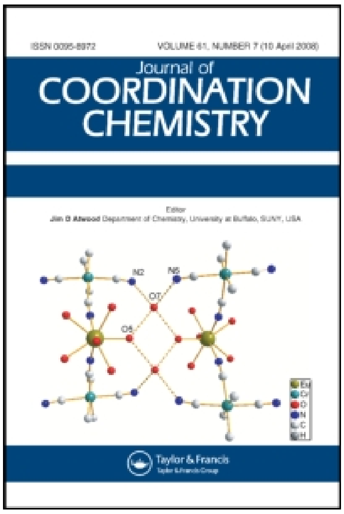

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# NUCLEAR MAGNETIC RESONANCE STUDIES OF CONFIGURATION AND LIGAND CONFORMATION IN PARAMAGNETIC OCTAHEDRAL COMPLEXES OF NICKEL(II) VIII. Tridentate Ligands Containing Oxygen Donors

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

## VIII. Tridentate Ligands Containing Oxygen Donors

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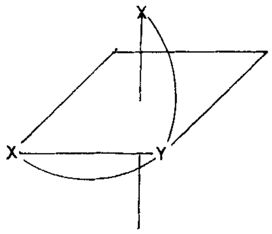
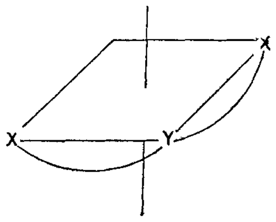
The proton magnetic resonance spectrum of the nickel complexes of iminodiethanol (ide), 2,2′-ethylether diamine (eeda), diethylenetriamine (dien), dipicolinic acid (dpa), and *cis*, *cis*, 1,3,5, cyclohexanetriamine (tach) are reported. Spectra are also reported for the mixed 1:1:1 Ni(II) complexes of the above ligands and dpa and mixed complexes of Ni(dien)(tach) and Ni(eeda)(tach). Ni(dien)$(H_2O)_3^{2+}$ is found to exist in solution as a mixture of facial and meridonal forms with isomerization between the two forms being fast on the NMR time scale and with the facial isomer being ~ 1.17 Kcal/mole more stable at 300°K. Ni(eeda)$(H_2O)_3^{2+}$ is found to exist primarily as facially coordinated species, the facial isomer being more stable by at least 0.25 Kcal/mole at 300°K. $\Delta H$ for the facial $\rightleftarrows$ meridional reaction is positive for Ni(eeda)$^{2+}$ and almost zero for Ni(dien)$^{2+}$. $\delta \rightleftarrows \lambda$ conversion is rapid for all cases of facial coordination and slow for all cases of meridional coordination. $\delta \rightleftarrows \lambda$ conversion of meridional isomers is slow because this requires inversion of the central coordinating atom of the ligand.

## INTRODUCTION

The potentially tridentate ligands eeda and ide are interesting because they can coordinate in several ways. It is unlikely but possible that the oxygen atoms are not used in coordination, yielding an 8-membered chelate ring for eeda coordination and a non-chelated complex for ide coordination. If all three donors are utilized, they can coordinate either facially (I) or meridionally (II). These complexes have not been extensively studied in the past. A formation constant of $5.6 \times 10^5$ for Ni(eeda)$(H_2O)_3^{2+}$ has been reported.[1]



STRUCTURE I



STRUCTURE II

Ciampolini and Nardi have reported that the N,N,N′,N′-tetramethyl-2,2′-diamine ethyl ether Ni(II) complex exists as a trigonal bipyramid in non-polar solvents but as a distorted octahedron in polar solvents.[2]

The nickel complex of the nitrogen analogs of ide and eeda, dien and its N-alkyl derivatives, have been more extensively studied,[3,4,5,6,7] especially for cobalt(III) complexes.

An X-ray crystallographic study of Ni$(dien)_2Cl_2 \cdot H_2O$ demonstrated that, in the solid state, the two dien ligands coordinate meridionally.[3] This complex was considerably unsymmetrical, presumably due to crystal packing forces that would not be present in solution. A recent solution study of Co$(dien)_2^{3+}$ has indicated that the most stable form of this complex is dimeridional.[7]

Crayton and Mattern, based upon their spectrophotometric study, stated that in Co(dien)$(NO_3)_3$ the meridional isomer was preferred.[4] Later work by Legg and Cooke inferred that both meridional and facial isomers are probably present in Co(dien)$Cl_3$[5] from their NMR study of isomer distribution in Co(ida)(dien)$^+$.

Ciampolini and Speroni[6] have determined that the nickel(II) complex of N,N,N′,N′,N″-pentamethyldiethylenetriamine (medien) exists as a

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5-coordinate trigonal bipyramid structure in non-coordinating solvents (presumably the me dien is coordinated meridionally) but is extensively solvated in coordinating solvents to a hexacoordinate species. This hexacoordinate species would no longer require meridional coordination.

This work was undertaken in order to answer the following questions: (1) do all oxygen atoms coordinate in Ni(eeda)$^{2+}$ and Ni(ide)$^{2+}$ and (2) what type of geometry do the complexes Ni(eeda)$^{2+}$, Ni(ide)$^{2+}$, and Ni(dien)$^{2+}$ have in aqueous solution?

The contact shift of ligand protons was obtained and the results interpreted on the basis of earlier studies of similar model systems.[8,9]

## EXPERIMENTAL

All PMR spectra were recorded on a JEOL C60-HL spectrometer using an external 16 KHz oscillator for field modulation and a sweep width of 300 ppm. All spectra are reported *v.* TMS* (sodium 3-(trimethylsilyl)-1-propane-sulfonate). The sweep width was calibrated by the sideband technique using 4 KHz field modulation.

Dien, 2.2′-dichloroethylether and dipicolinic acid were obtained from Aldrich Chemical Company. Imino diethanol was obtained from Eastman Organic Chemical Company. Nickel perchlorate hexa hydrate was obtained from G. F. Smith Chemical Company. Anhydrous nickel chloride was obtained from Alfa Inorganics. Eeda was prepared from 2,2′-dichloroethylether by a Gabriel synthesis using potassium phthalimide as modified by Ing and Manske[10] and was purified by recrystallization of the dihydrochloride from ethyl alcohol.

The complexes were prepared by mixing the appropriate free ligand with an equimolar amount of either nickel perchlorate or nickel chloride and dissolving in deuterium oxide. The solutions were taken to dryness at reduced pressure and redissolved several times in $D_2O$ to reduce the HOD peak. The mixed dpa complexes were prepared by adding the ligand of interest (eeda, ide, or dien) to a previously prepared Ni(dpa)$(D_2O)_3$ solution. Mixing of equal amounts of Ni$^{2+}$, ligand and dpa$^{-2}$ led to formation of a solution containing Ni(dpa)$_2^{2-}$ and Ni(ligand)$_2^{2+}$ for the ligands eeda and ide. The final solution concentration of the complexes was *c.* 0.5 *M*. All resonance positions were independent of concentration.

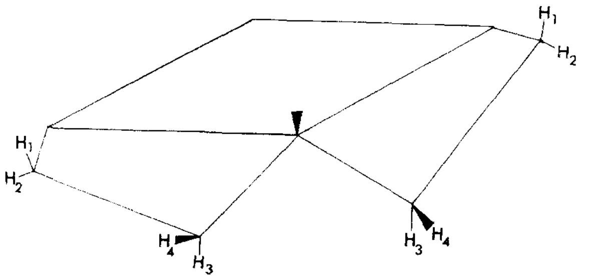
## RESULTS

Schematic spectra of all the complexes studied are shown in Figure 1, and the assignments are summarized in Table I. All contact shifts are reported relative to internal TMS*. The temperature dependence of the chemical shifts are shown in Figures 2 and 3.

## DISCUSSION

It is important to consider the possible geometries and isomerization pathways available to these complexes in order to properly analyze the spectra reported in this paper.

*Dien Chelates*: Consider, for example, the complex Ni(dien)$(H_2O)_3^{2+}$. In the meridional isomer, III, there are four different types of alkyl protons labelled $H_1$ through $H_4$.



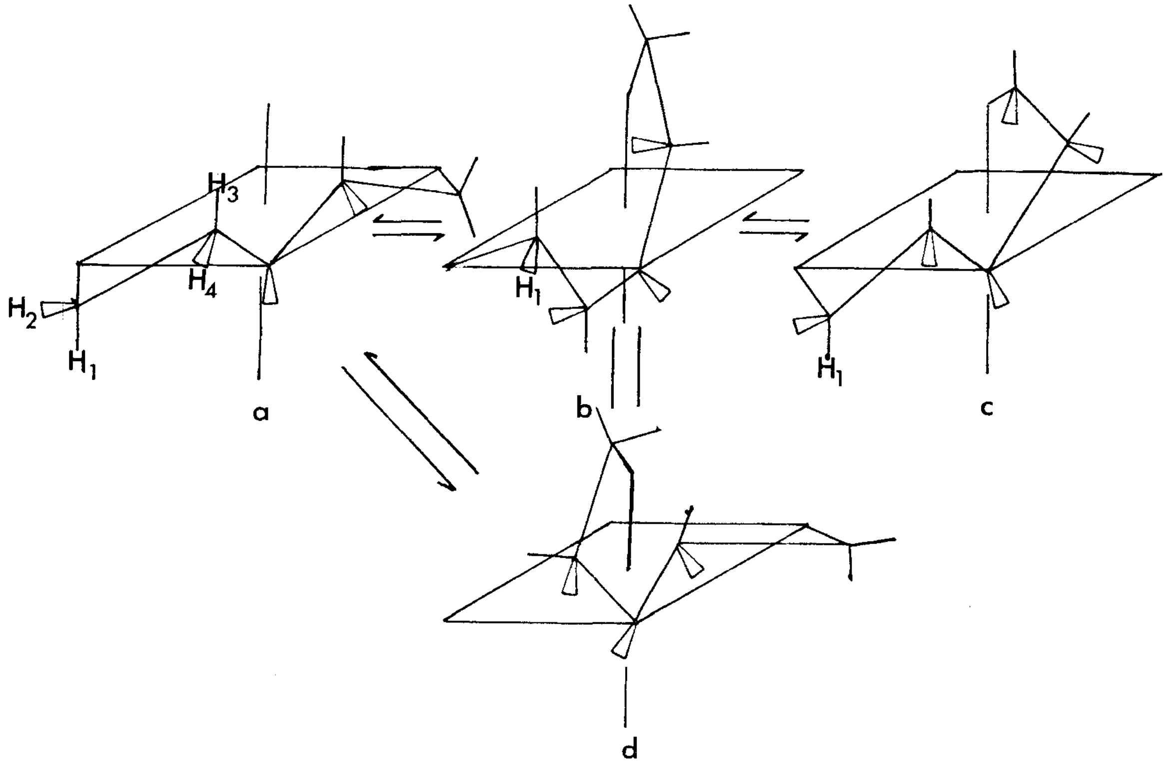
III

Thus, if this particular species exists in solution for long times, one would expect to see four resonance peaks: two peaks in the equatorial region (150–200 ppm downfield of TMS*) and two peaks in the axial region (0–50 ppm downfield of TMS*).[9] Because of the broadness of the peaks in these paramagnetic complexes, spin-spin splitting is not observed.

These contact shift differences could be averaged in several ways. If $\delta \rightleftarrows \lambda$ conversion is fast, the axial-equatorial differences between $H_3$ and $H_4$, and $H_2$ and $H_1$ would be averaged to single resonance positions, and a two-line spectrum in the region 75–125 ppm would be obtained. This is shown schematically in Figure 4.

Examination of Dreiding stereo models indicates, however, that $\delta \rightleftarrows \lambda$ conversion is not possible for meridionally coordinated species without simultaneous inversion of the central nitrogen: (1) via Ni-central nitrogen bond rupture (2) via N-D dissociation (i.e. at high *p*H), and (3) via Waldin inversion (attack of $D^+$ on central N). This seems extremely unlikely, on the NMR time scale, in view of the known long lifetime of Ni—N bonds.[11] Individual chelate rings can $\delta \rightleftarrows \lambda$ convert, but, because of the strain imposed, this occurs to a very slight extent.

It is also possible for the meridional isomer to convert to the facial isomer via an intramolecular twist mechanism without any Ni—N bond rupture. This conversion is shown in IV below:



STRUCTURE IV

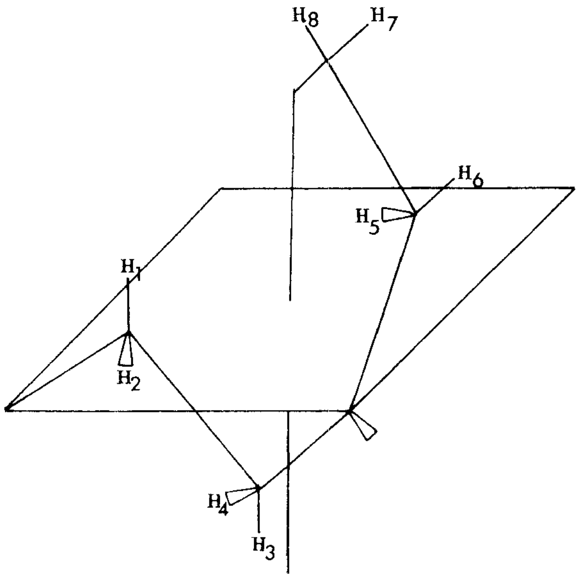
An important point to note in the above meridional $\rightleftarrows$ facial inter-conversion is that the two facial isomers shown (actually, different views of the same isomer) are the *only* ones possible and the reverse isomerization leads to the same meridional isomer—i.e. the central nitrogen is *not* inverted in the process. Thus, rapid facial $\rightleftarrows$ meridional isomerization without bond rupture at the central nitrogen atom retains the original configuration for the meridional isomer.

Consider now, the case of facial coordination, shown in V below.

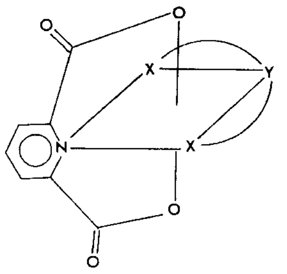
In this case, the complex contains eight different types of protons. The chemical-shift difference between $H_5$ and $H_3$, $H_6$ and $H_4$, $H_7$ and $H_1$, $H_8$ and $H_2$ arise from diamagnetic effects and would probably be too small to see on the contact-shift spectrum. If $\delta \rightleftarrows \lambda$ conversion is fast, the axial-equatorial differences would be averaged, and a two-line spectrum obtained because $\delta \rightleftarrows \lambda$ conversion occurs between equally energetic conformations. Thus, fast $\delta \rightleftarrows \lambda$ conversion results in the spectrum of the facial isomer changing from four peaks (or four groups of two peaks each) to two peaks (or two groups of two). This is shown in Figure 5.

Examination of Dreiding stereo models indicates that $\delta \rightleftarrows \lambda$ conversion of the facial isomer can occur rapidly and does not require simultaneous inversion of the central nitrogen atom.

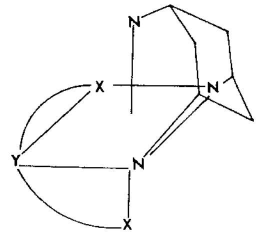
At this stage, it is desirable to give some experimental evidence to our principal conclusions above, namely, that rapid $\delta \rightleftarrows \lambda$ conversion is expected for the facial isomer but not for the meridional isomer. The routes we now take is to prepare a mixed chelate with a third ligand, choosing first one which can coordinate only meriodionally and then one which can coordinate only facially. For the first, dipicolinic acid is selected, and its mixed chelate with dien is given as VI. For the facial isomer, *cis,cis*,—1,3,5-cyclohexane triamine is utilized, and its mixed chelate with dien is given as VII.



STRUCTURE V



STRUCTURE VI



STRUCTURE VII

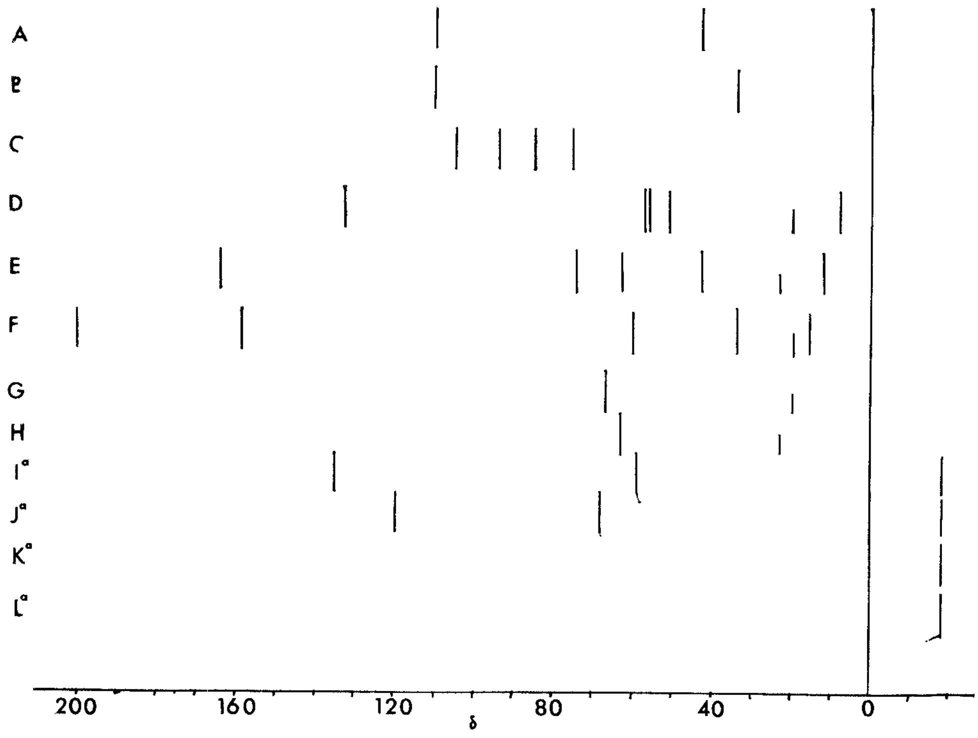


FIGURE 1 Contact shift spectra of complexes studied. Shifts are in ppm *v*. TMS*'

| | | | | | |
|---|---|---|---|---|---|
| A | Ni(eeda)$(H_2O)_3^{2+}$ | E | Ni(ide)(dpa) | I | Ni(dien)(tach)$^{2+}$ |
| B | Ni(ide)$(H_2O)_3^{2+}$ | F | Ni(dien)(dpa) | J | Ni(eeda)(tach)$^{2+}$ |
| C | Ni(dien)$(H_2O)_3^{2+}$ | G | Ni(dap)$(H_2O)$ | K | Ni(tach)$(H_2O)_3^{2+}$ |
| D | Ni(eeda)(dpa) | H | Ni(dap)$_2^{-2}$ | L | Ni(tach)$_2^{2+}$ |

(*a*) extreme downfield peak (−327 ppm) not shown

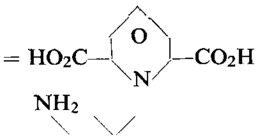
## TABLE I

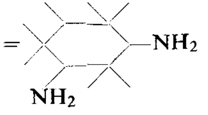
Assignment of spectral lines for tridentate nickel(II) complexes

| Species | Shift[a] | Assignment |
|---|---|---|
| $Ni(eeda)(H_2O)_3{}^{2+}$ | 43 | O—$CH_2$ |
| | 110 | N—$CH_2$ |
| $Ni(ide)(H_2O)_3{}^{2+}$ | 34 | O—$CH_2$ |
| | 110 | N—$CH_2$ |
| $Ni(dien)(H_2O)_3{}^{2+}$ | 75.5 | N—$CH_2$ (axial)[b] |
| | 85 | N—$CH_2$ (equatorial)[b] |
| | 94 | $CH_2$—$CH_2$ (axial)[b] |
| | 105 | $CH_2$-$NCH_2$ (equatorial)[b] |
| Ni(eeda)(dpa) | 8 | O—$CH_2$ (axial) |
| | 20 | DPA—2*p* proton |
| | 51 | O—$CH_2$ (equatorial) |
| | 56 | N—$CH_2$ (axial) |
| | 57 | DPA — *m* protons |
| | 132 | N—$CH_2$ (equatorial) |
| Ni(ide)(dpa) | 12 | O—$CH_2$ (axial) |
| | 23 | DPA — *p* proton |
| | 43 | O—$CH_2$ (equatorial) |
| | 63 | DPA — *m* protons |
| | 74 | N—$CH_2$ (axial) |
| | 164 | N—$CH_2$ (equatorial) |
| Ni(dien)(dpa) | 15.5 | N—$CH_2$ (axial) |
| | 20 | DPA — *p* proton |
| | 34 | $CH_2$—N—$CH_2$ (axial) |
| | 60 | DPA — *m* protons |
| | 159 | N—$CH_2$ (equatorial) |
| | 200 | $CH_2$-N-$CH_2$ (equatorial) |
| $Ni(dpa)(H_2O)_3$ | 20 | *p*— proton |
| | 67 | *m*— protons |
| $Ni(dpa)_2{}^{2-}$ | 23 | *p*— proton |
| | 63 | *m*— protons |
| $Ni(eeda)(tach)^{2+}$ | 59 | $OCH_2$ |
| | 135 | $NCH_2$ |
| | 18[c] | β protons of tach |
| Ni(dien)(tach) | 68 | averaged axial-equatorial |
| | 120 | dien methylene protons |
| | 18[c] | β protons of tach |
| $Ni(tach)_2(H_2O)_3{}^{2+}$ | 18[c] | β protons of tach |
| $Ni(tach)^{2+}$ | 18[c] | β protons of tach |
| | 327 | α CH protons of tach |

[a] ppm downfield from TMS*.
[b] refers to conformation in meridional isomer.
[c] ppm upfield of TMS*.

eeda = $NH_2CH_2CH_2OCH_2CH_2NH_2$
ide = $HOCH$—$CH_2NHCH_2CH_2NH_2$
dien = $NH_2CH_2CH_2NH_2CH_2CH_2NH_2$

dpa =


tach =


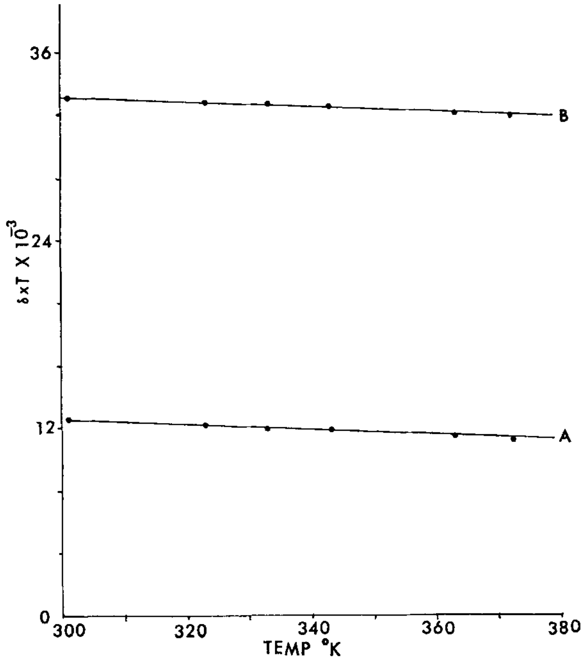


FIGURE 2 Variation of the product δ × *T* v. *T* for $Ni(eeda)(H_2O)_3{}^{2+}$. Line A is for $OCH_2$, line B for $NCH_2$.

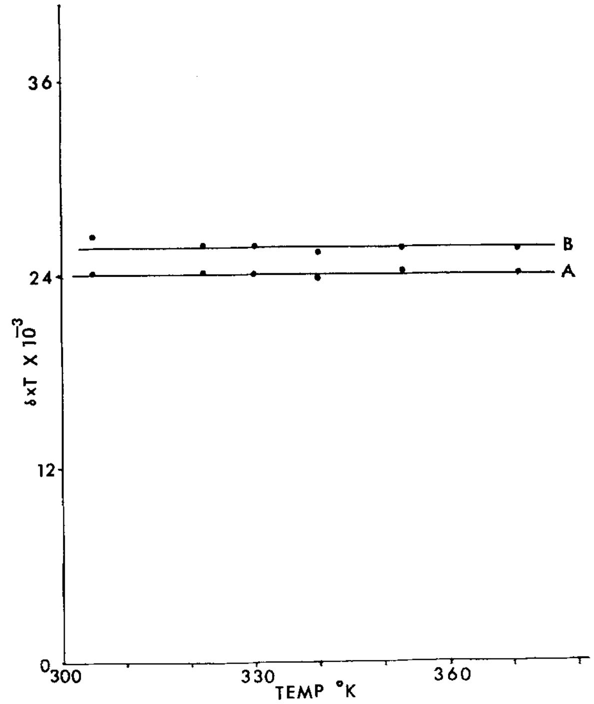


FIGURE 3 Variation of the product δ × *T* v. *T* for $Ni(dien)(H_2O)_3{}^{2+}$. Line A is the variation of N—$CH_2$ (axial); line B is for the variation of N—$CH_2$ (equatorial). The variation of the two other peaks is not shown because the greater broadness of the peaks prevented accurate assignment of the resonance positions.

In the mixed complexes Ni(dien)(dpa), the presence of dpa, which can only coordinate meridionally, forces the dien to also coordinate meridionally. Thus, this spectrum, once the dpa peaks are assigned, is that of meridionally coordinated dpa without complications from facially coordinated ligand.

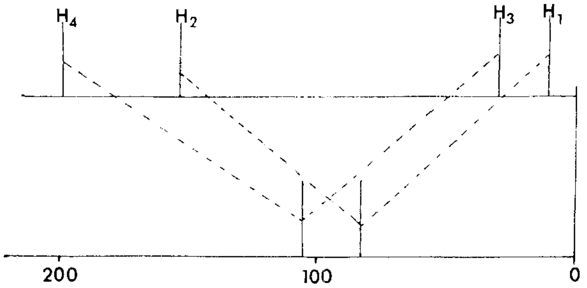


FIGURE 4 Coalescence of the peaks of meridional Ni(dien)$^{2+}$ by rapid $\delta \rightleftarrows \lambda$ conversion with inversion of the central nitrogen atom.

The spectrum of meridionally coordinated dien (Figure 1) consisting of four widely spaced peaks shows, on the basis of earlier arguments, that $\delta \rightleftarrows \lambda$ conversion is slow and that the rate of inversion of the central nitrogen is also slow ($< 10^4$ sec$^{-1}$) on the NMR time scale for this type of coordination.

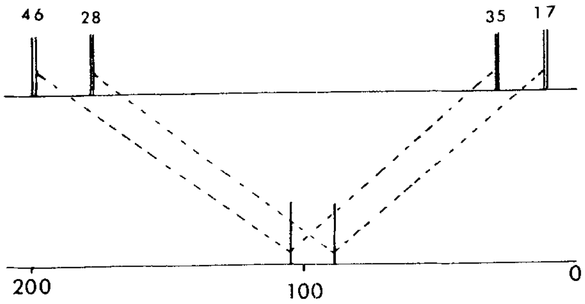


FIGURE 5 Coalescence of the peaks of facially coordinated Ni(dien)$^{2+}$ by rapid $\rightleftarrows$ $\delta$ $\lambda$ conversion without inversion of the central nitrogen atom.

Examination of the spectrum of the mixed complex Ni(dien)(tach)$^{2+}$ which forces the facial configuration, shows that $\delta \rightleftarrows \lambda$ conversion under conditions of facial coordination is fast and occurs between equally energetic species. It is assumed that inversion of the central nitrogen atom is slow, but these data in themselves do not offer any proof of it. Data to be discussed later, however, will demonstrate the slow nitrogen inversion assumed at this point. Mention should be made of the fact that the dien peaks of Ni(dien)(tach)$^{2+}$ are extremely broad ($\sim$ 2000 Hz at half height) and separated by a much greater chemical-shift difference than expected on the basis of other data and calculations to be discussed later. The upfield shift of the $\beta$ protons of Ni(tach)(H$_2$O)$_3^{2+}$ is not unusual for ligands of this type.[12] The important observation for the purposes of this paper is, however, that only two peaks are observed for the facially coordinated dien ligand, indicating that $\delta \rightleftarrows \lambda$ conversion is rapid in this geometry.

It is now possible to interpret the spectrum of Ni(dien)(H$_2$O)$_3^{2+}$. This spectrum consists of four approximately equally intense peaks (accurate area measurements were not possible) at contact-shift values indicative of partially averaged axial-equatorial differences.

There are several ways in which four resonance peaks could be rationalized for Ni(dien)(H$_2$O)$_3^{2+}$. These are:

(1) the two chelate rings formed by dien are not equivalent, and each resonance peak is due to a different averaged axial-equatorial pair, and there is only one isomer present in solution;

(2) each peak arises from an incompletely averaged axial-equatorial pair, and only one isomer is present in solution;

(3) two peaks are due to facially coordinated species, and two peaks are due to meridionally coordinated species. This implies that $\delta \rightleftarrows \lambda$ conversion is fast, and there is no conformational preference in both isomers and that meridional $\rightleftarrows$ facial isomerization is slow;

(4) $\delta \rightleftarrows \lambda$ conversion is slow for one type of coordination but fast for the other type and meridional $\rightleftarrows$ facial isomerization is fast. Both isomers are present in solution.

Three of these four possibilities can be eliminated by considering data for the mixed complexes with dien and dpa. The first possibility can be dismissed as being inherently unreasonable in solution despite the solid-state results.[3] More importantly, the spectrum is inconsistent with either the Ni(dien)(dpa) or the Ni(dien)(tach)$^{2+}$ data. If only the meridional isomer were present in solution, 8 lines would be expected if the two chelate rings were non-equivalent because of slow $\delta \rightleftarrows \lambda$ conversion. If only the facial isomer were present, a spectrum similar to the observed could be rationalized because rapid $\delta \rightleftarrows \lambda$ conversion of this isomer will average the eight lines to four. The Ni(dien)(tach)$^{2+}$ spectrum, however, consists of only two peaks, which indicates that on the average both rings are the same.

Possibility two can also be dismissed because incomplete averaging of the axial-equatorial differences requires either slow $\delta \rightleftarrows \lambda$ conversion or a preference for one conformation over the other.[8] For example, species IVb could be lower energy than species IVc. Slow conversion, however, would lead to much larger contact-shift differences than observed (see the spectrum for Ni(dien)(dpa)) except at temperatures where the rate of $\delta \rightleftarrows \lambda$ conversion is compatible to the chemical-shift difference. The observed four-peak spectrum, however, persists from 30°C to 100°C. Furthermore, the symmetry of dien is inconsistent with any conformational preference in either meridional or facial form.

Possibly three can be discarded quickly by noting that $\delta \rightleftarrows \lambda$ conversion of meridionally coordinated dien is slow; thus, its contribution to the spectrum would be four, widely spaced lines—not two. In short, the requirement of rapid $\delta \rightleftarrows \lambda$ conversion of the meridional isomer is contrary to observation.

Possibility four is consistent with all of the observations. Thus, for example, in the sequence IVa $\rightleftarrows$ IVb $\rightleftarrows$ IVc $\rightleftarrows$ IVa, proton $H_1$ spends some time in an axial-meridional environment and some time in an averaged facial environment. Because the central nitrogen atom is not inverted by meridional $\rightleftarrows$ facial isomerization, the contact-shtif difference between $H_1$ and $H_2$ does not average to a single value. This case can be analyzed mathematically in the following manner.

Let $f_m$ equal the fraction of time spent in meridional coordination.

$K_{mal}$ be the "frozen" contact shift of an axial meridional proton on carbon 1 ($H_1$) (structure IVa).

$K_{mel}$ is the contact shift of an equatorial meridional proton on carbon 1 ($H_2$) (structure IVa).

$K_{ma2}$ is the contact shift of an axial meridional proton on carbon 2 ($H_3$) (structure IVa).

$K_{me2}$ is the contact shift of an equatorial meridional proton on carbon 2 ($H_4$) (structure IVa).

$K_{fe1}$ is the "frozen" or intrinsic contact shift of an equatorial facial proton on carbon 1 ($H_1$) (structure IVb).

$K_{fa1}$ is the "frozen" or intrinsic contact shift of an axial facial proton on carbon 1 ($H_2$) (structure IVb).

$K_{fe2}$ is the "frozen" or intrinsic contact shift of an equatorial facial proton on carbon 2 ($H_4$) (structure IVb).

$K_{fa2}$ is the "frozen" or intrinsic contact shift of an axial facial proton on carbon 2 ($H_3$) (structure IVb).

$\delta_1$ is the observed resonance position for proton $H_1$.

$\delta_2$ is the observed resonance position for proton $H_2$.

$\delta_3$ is the observed resonance position for proton $H_3$.

$\delta_4$ is the observed resonance position for proton $H_4$.

The following relationships then hold:

$$\delta_1 = \text{fm}\, K_{mal} + (1 - \text{fm})\frac{K_{fe1} + K_{fa1}}{2} \qquad (1)$$

$$\delta_2 = \text{fm}\, K_{me1} + (1 - \text{fm})\frac{K_{fe1} + K_{fa1}}{2} \qquad (2)$$

$$\delta_3 = \text{fm}\, K_{ma2} + (1 - \text{fm})\frac{K_{fe2} + K_{fa2}}{2} \qquad (3)$$

$$\delta_4 = \text{fm}\, K_{me2} + (1 - \text{fm})\frac{K_{fe2} + K_{fa2}}{2} \qquad (4)$$

Equations 1–4 can easily be solved for $f_m$, yielding

$$f_m = \frac{\delta_1 - \delta_2}{K_{me1} - K_{ma1}} = \frac{\delta_3 - \delta_4}{K_{me2} - K_{ma2}} \qquad (5)$$

$K_{me1}$, $K_{ma1}$, $K_{me2}$, and $K_{ma2}$ are obtained from the spectrum of Ni(dien)(dpa) directly. Because $\delta \rightleftarrows \lambda$ conversion is slow, the spectral positions are the true "frozen" values, and no extrapolation procedure is necessary.[8] It is not possible to tell *a priori* which resonance is due to $H_1$ and which is due to $H_3$ (or $H_2$ and $H_4$) but by calculating $f_m$ for all the possible combinations only the following assignments were found to give the same value for $f_m$ regardless of which resonances were used in the calculations.

$K_{ma1} = -15.5$ ppm
$K_{me1} = -159$ ppm
$K_{ma2} = -34$ ppm
$K_{ma2} = -200$ ppm
$\delta_2 = -85$ ppm
$\delta_1 = -75.5$ ppm
$\delta_4 = -105$ ppm
$\delta_3 = -94$ ppm
$f_m = 0.066$

From $f_m$, the $\Delta G$ for the reaction meridional $\rightleftarrows$ facial is determined to be (after correcting for the statistical preference for the facial isomer) −1.17 Kcal/mole at 300°K. Thus, the facial isomer is more stable than the meridional isomer in $Ni(dien)(H_2O)_3{}^{2+}$. This calculation indicates that approximately 7% of the time dien is coordinated meridionally in aqueous $Ni(dien)(H_2O)_3{}^{2+}$. This is somewhat less than the 12% found by Legg and Cooke for $Co(dien)(ida)^{+}$ [5] and may indicate that steric interactions between facial ida and facial dien are significant.

*Eeda and ide Chelates*: As was true for dien, it is most instructive to first consider the spectrum of the mixed complexes Ni(eeda)(dpa) and Ni(ide)(dpa).

These spectra can be readily interpreted in a manner analogous to the interpretation of the Ni(dien)(dpa) complex. The presence of four widely spaced lines is again indicative of slow $\delta \rightleftarrows \lambda$ conversion for these meridionally coordinated ligands. Slow $\delta \rightleftarrows \lambda$ conversion for eeda requires that the rate of inversion of the central oxygen atom be slow. Also, this suggests that the Ni—O bond lifetime is long for this central oxygen atom. This is consistent with the observations previously reported for various nickel(II) ethaonolamine complexes.[9]

The large contact shifts observed for the $-OCH_2$ protons of these complexes shows that the oxygen atoms are coordinated to the nickel ion in both Ni(eeda)(dpa) and Ni(ide)(dpa).

Because oxygen inversion is slow, meridional $\rightleftarrows$ facial isomerization should lead to the same type of spectra observed for $Ni(dien)(H_2O)_3{}^{2+}$, $Ni(eeda)(H_2O)_3{}^{2+}$, and $Ni(ide)(H_2O)_3{}^{2+}$ except that two of the four peaks should be in the region corresponding to oxygen coordination (20–50 ppm) and two of the peaks in the region corresponding to nitrogen coordination (80–120 ppm). Examination of the spectra for $Ni(eeda)(H_2O)_3{}^{2+}$ and $Ni(ide)(H_2O)_3{}^{2+}$ shows that only two peaks are observed. Thus, the axial-equatorial differences are completely averaged (within the peak width) for both of these complexes.

Because the peaks are relatively broad (~ 10 ppm at half height for the narrowest $Ni(eeda)(H_2O)_3{}^{2+}$ peak) splitting due to the meridional isomer content may not be readily observed. Assuming that peaks separated by the half width would be observed, equation 5 predicts that the facial isomer is at least 0.25 Kcal/mole more stable than the meridional isomer for $Ni(eeda)(H_2O)_3{}^{2+}$. Because the peaks are even broader for $Ni(ide)(H_2O)_3{}^{2+}$, no reasonable calculations can be performed for this complex. It is reasonable to assume, however, that the facial form is favored to about the same extent as in $Ni(eeda)(H_2O)_3{}^{2+}$ in view of the close similarity of their spectra.

The presence of at least some meridional isomer in $Ni(eeda)(H_2O)_3{}^{2+}$ is supported by the temperature dependence of the contact shifts shown in Figure 2. If no meridional isomer were present, the shifts would obey Curie law and be flat, horizontal straight lines.[8] As the temperature increases, the fraction present as meridional changes; thus, the average chemical shift changes.

It is not possible to analyze this dependence quantitatively because the chemical shifts of the pure facial form are not known. The shifts of $Ni(tach)(eeda)^{2+}$ were not used because of the disparity of the shifts of $Ni(dien)(tach)^{2+}$ from the calculated values for this complex. For this reason, it was felt that the $Ni(tach)(eeda)^{2+}$ shifts would not be reliable measures of the shifts of facial $Ni(eeda)(H_2O)_3{}^{2+}$. A least-squares procedure could be employed as previously,[8] but the deviation from Curie behavior is so slight that trustworthy results could hardly be expected.

An important point to note, however, is that the deviation from Curie behavior is to smaller shifts. Because the average chemical shift of the meridional isomer is less (−30 ppm *vs.* −43 ppm) than the averaged chemical shift of the mostly facial isomer, this type of deviation from Curie behavior indicates that the equilibrium is shifted toward formation of meridional form at higher temperature (i.e. $\Delta H$ for the isomerization facial $\rightleftarrows$ meridional is positive.)

A similar analysis of the temperature dependence of $Ni(dien)(H_2O)_3{}^{2+}$ (Figure 3) indicates that the $\Delta H$ for this facial $\rightleftarrows$ meridional isomerization is zero within experimental error. This conclusion follows from the fact that the $Ni(dien)(H_2O)_3{}^{2+}$ resonances obey Curie behavior (see Figure 3).

The greater stability of the facial isomer reported in this work than generally believed previously may be due to in part to stabilization of this geometry by coordinated water molecules.[7] Those studies which indicated a great preference for meridional conformation did not have coordinated water molecules.[3,6,7]

I is also important to point out that the previous studies were either for cobalt(III) complexes (4,5,7 and references therein) on non-aqueous nickel(II) complexes[8] or solid state.[3]

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## REFERENCES

1. J. R. Lotz, B. P. Block and W. C. Fernelius, *J. Phys. Chem.* **63,** 541 (1959).
2. M. Ciampolini and N. Nardi, *Inorg. Chem.* **6,** 445 (1967).
3. S. Biagini and M. Cannas, *J. Chem. Soc.* (*A*), 2398 (1970).
4. P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.* **13,** 248 (1960).
5. J. I. Legg and D. W. Cooke, *Inorg. Chem.* **5,** 594 (1966).
6. M. Ciampolini and G. P. Speroni, *ibid.*, **5,** 45 (1966).
7. F. R. Keene and G. H. Searle, *Inorg. Chem.* **11,** 148 (1972).
8. F. F.-L. Ho and C. N. Reilley, *Anal. Chem.* **41,** 1835 (1969).
9. R. F. Evilia and C. N. Reilley, submitted, *J. Coord. Chem.*
10. A. R. Ing and R. H. F. Manske, *J. Chem. Soc.* 2348 (1926).
11. A. K. S. Ahmed and R. G. Wilkens, *J. Chem. Soc.* 3700 (1959).
12. J. E. Sarneski, Ph.D. Dissertation, Case Western Reserve University, January 1971.