Table VI. Kinetic Parameters for Ligand Exchange with ML_2X_2 [a] in $CDCl_3$ at 25° (L = TPP = Triphenylphosphine)

Complex	k_2, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
NiL_2Cl_2	3.2×10^5	8.1 ± 0.8	-7 ± 4
NiL_2Br_2	6.9×10^3	4.7 ± 0.4	-25 ± 2
NiL_2I_2	6.4×10^2	6.9 ± 0.6	-23 ± 3

[a] From ref 25.

of a free phosphine molecule on the tetrahedral ML_2X_2. In the cyanide systems the dominant four-coordinate species is the planar isomer. It has been assumed that k_2 relates to attack of a free phosphine on this planar species.

The differences in activation parameters and rate constants are consistent with these two assumptions. Alternatively, if attack were always on the planar form, even for the halide complexes, the slower rates and larger activation energies could be explained. The activation energies would be largely due to the value of $\Delta H°$ relating the high-energy planar form to the low-energy tetrahedral form.

It is of interest to note that the structures of the five-coordinated cyano complexes are well established with the cyano groups trans.[26] This is just what would be expected for addition of a third phosphine to *trans*-$NiL_2(CN)_2$. The three L ligands lie in an approximately trigonal plane.[18] As part of this study the comparison of solution and solid-state infrared and visible-uv spectra showed that in solution these complexes have the same trans structure as that determined in the crystals.

The structures of the five-coordinated halo complexes are not known. From spectral data it has been argued that $Ni(PMe_3)_3X_2$ is both cis[27] and trans.[28] If a phosphine attacked a tetrahedral complex in the usual SN2 mechanism, the intermediate NiL_3X_2 would have both halide ligands in the trigonal plane, and hence cis to each other.

The structure of PdL_3Br_2,[29] where L = 2-phenylisophosphindoline, is in fact square pyramidal, with Br axial. This lends support to the argument that the structures and behavior of the five-coordinated nickel(II)-cyano and -halo complexes are indeed different.

Acknowledgments. C. G. G. is indebted to the Danforth Foundation for a graduate fellowship during the period of this research. We wish to thank Miss H. E. Beck, Dan Netzel, and Mitchell Cooper of the Analytical Services Laboratory at Northwestern University for analyses of complexes and collection of nmr data. The work was supported in part by the National Science Foundation under Grant 31060X.

Registry No. $Ni(PhP(OEt)_2)_3(CN)_2$, 15282-55-0; $Ni(P(OEt)_3)_3(CN)_2$, 49756-79-8; $Ni(Ph_2POEt)_3(CN)_2$, 50322-08-2; $Ni(PhPMe_2)_3(CN)_2$, 24419-46-3; $Ni(PhPMe_2)_3Br_2$, 49756-80-1; $Ni(PhPMe_2)_2Cl_2$, 25456-42-2; $Ni(PhPMe_2)_2Br_2$, 25456-40-0.

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Nuclear Magnetic Resonance Studies of Configuration and Ligand Conformation in Paramagnetic Octahedral Complexes of Nickel(II). IX. 1,3-Diamine Chelates

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Proton nuclear magnetic resonance spectra have been utilized in detailing the stereochemistry of six-membered rings formed by chelation of nickel(II) ion with selected 1,3-diamines. A correlation between the magnitude of observed contact shifts for the $CH_2(NH_2)$ protons and their Ni-N-C-H dihedral angle analogous to that reported in the 1,2-diamine-nickel(II) chelates has been found. In addition, the existence of a definite angular dependence of the contact shifts across four bonds to the central methylene group protons has been elucidated. Rapid conformational interconversion of these chelate rings allows the utilization of the ligand proton contact shifts as a sensitive probe of chelate ring conformations in solution. As in other saturated six-membered rings, the chair conformation is found to be most stable; however, the skew-boat conformer lies at relatively low energy, with respect to the chair, $\Delta G = 1.4$ kcal/mol in the tetraaquo-1,3-diaminopropane-nickel(II) chelate. Data reveal that accommodation of alkyl groups in an axial environment of the chair conformation can engender unfavorable steric interactions, and this destabilization can introduce significant amounts of twist conformer in the equilibrium distribution; tetraaquo-*rac*-2,4-diaminopentanenickel(II) ion, for instance, exists in an essentially equal distribution of skew-boat and chair conformers at 300°K. The bis chelate of this latter ligand is found to be engaged in an octahedral square-planar equilibrium in solution, with octahedral species containing chelate rings of both chair and skew-boat conformations being identified. Tris(1,3-diaminopropane)nickel(II) ion is found to racemize rapidly on the nmr time scale, and this rate is estimated to be 1.1×10^4 sec^{-1} at 72°; the free energy of activation for this process is 14 kcal/mol at that temperature.

Introduction

The proton magnetic resonance spectra of pseudooctahedral paramagnetic nickel(II) complexes have recently been shown to contain a wealth of stereochemical information.[1,2] With the appreciation of the dihedral angular dependence of contact shift across the Ni-N-C-H moiety,[1,3] an extremely sensitive configurational and conformational probe has been elucidated for these chelates, and a number of useful applica-

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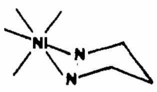
tions have already been reported.[1,4] Here we report an investigation into the solution conformational equilibria in chelated six-membered rings using this resonance technique.

The conformational properties of chelated 1,3-diamine ligands are expected to bear considerable resemblance to the stereochemical features exhibited by carbocyclic and heterocyclic six-membered ring systems. The usual steric and torsional factors[5] will contribute to the relative stabilities of the three distinct, available conformations: the chair, the rigid (or classical)-boat, and the skew-boat (or twist). However, the presence of a metal ion with its associated ligands as a participant in these chelate rings introduces changes in ring dimensions due to the relatively long metal–donor bond distances as well as compact N–Ni–N angle and will be expected to endow these ring systems with unique conformational properties.



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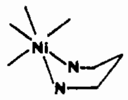

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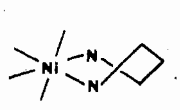

3

A chair conformation, **1**, with the usual pseudoaxial and -equatorial substituents, can only be constructed with significant interaction of two α substituents axially oriented on the ring with an axial, ligated molecule on the metal ion. This steric interplay can be partially relieved by a flattening of the chair structure as has been pointed out in recent conformational analyses and found in crystallographic investigations.[6,7] An alternative conformation, the rigid boat **2**, presents a system in which interaction between a β ring substituent and the axial ligand is quite severe. This proximity of groups and the usual eclipsing of ring substituents associated with this conformation combine to make such a structure rather unlikely in octahedral chelates. This unfavorable strain in the boat form can be partially offset by some bonding interaction of the β substituent with an axially coordinated ligand or by axial coordination of a group attached at the β position as in the nickel(II) chelate of 1,1,1-tris(aminomethyl)ethane.[8] The third possible conformer, the twist, **3**, is known from other conformational studies to be intermediate in stability between these two structures, engendering some unfavorable interaction by partial bond eclipsing in its stereochemistry.

Structural studies of 1,3-diamine chelates have generally evidenced a chair structure in the crystalline form[6] although two recent reports[9,10] demonstrate skew-boat conformations; however, little is known about the solution conformation of these systems. The solid-state results are in agreement with a conformational analysis on chelated 1,3-diaminopropane[6] which indicates that a skew-boat (or twist) conformation is only 1.7 kcal/mol (ΔH) less stable than the chair species in 1:1 octahedral metal complexes. This result is in marked contrast to conformational enthalpy differences in other six-membered ring systems where values have been found to range from 3.4 kcal/mol in the 1,3-dithianes to *ca.* 8 kcal/mol in the 1,3-dioxanes.[11] In these heterocyclics, the twist form, when found, often (but not always) owes its existence to sizable, enhancing entropy factors.[12] The predicted low enthalpy difference between chair and twist forms in octahedral metal chelates raises the likelihood that twist forms may be present in solution (1) if the twist conformation possesses an appreciable entropy advantage or (2) if steric features built into the ligand seriously and selectively destabilize the chair conformer.

Appleton and Hall[13] have recently reported a series of investigations into the conformation of some palladium and platinum chelates of 1,3-diamines using proton nmr spectroscopy. From their analysis of proton–proton and platinum–proton coupling constants, they were able to establish the general predominance of the chair conformation in solution. A more detailed analysis of these solution equilibria was precluded by the relative insensitivity of the small coupling constants and, in certain cases, by inherent signal-to-noise problems in spectra obtained.

The known conformational sensitivity of proton contact shifts in nickel(II) complexes can provide a better probe of the conformational behavior of these ring systems and allows a method of quantitatively studying conformer equilibria in these chelates. To this end, we have undertaken the analysis of the proton nmr spectra of the nickel chelates of certain substituted 1,3-diamines chosen to represent a variety of steric situations in the chair and twist conformations.

Experimental Section

Ligands. 1,3-Diaminopropane and *N*-methyl-1,3-diaminopropane were purchased from the Aldrich Chemical Co. 2,4-Diaminopentane was prepared by a literature method;[14] its racemic and meso isomers were separated by a published procedure[14] (>98% purity *via* nmr spectra of amine hydrochlorides). 1,3-Diaminobutane was synthesized by the Gabriel synthesis of dimethylformamide.[15] 2-Ethyl-1,3-diaminopropane and 2,2-dimethyl-1,3-diaminopropane were generously provided by Dr. Ernest L. Eliel and Dr. L. D. Kopp. All ligands were distilled and then converted to hydrochloride salts for storage. These ammonium salts were exchanged in D_2O twice before preparing the desired complexes and their purity was monitored by proton nmr spectra in D_2O.

Complexes. In general, satisfactory 1:1 complexation of the 1,3-diamines required excess ligand dihydrochloride present to buffer the solution. Thus, the following general method was employed to generate the desired species. A 1.5-mmol amount of deuterium-exchanged ligand was dissolved in ~1 ml of D_2O (99.8%, Columbia Organic Chemicals Co., Inc.) containing 1.0 mmol of anhydrous $NiCl_2$ (Alfa Inorganics). To this clear green solution was added dropwise 0.22 ml (1.70 mmol) of 7.7 *N* NaOD. Generally, this procedure yielded blue solutions of pD 6.9–7.4 with little $Ni(OD)_2$ precipitate, although after standing several hours all solutions gave some insoluble, flocculent material. In the preparation of the 1:1 chelate of racemic 2,4-diaminopropane the procedure was adapted to provide a solution free of 2:1 chelate contaminant. A 1.04-mmol sample of ligand hydrochloride, 0.78 mmol of nickel chloride, and 0.1 ml (0.77 mmol) of 7.7 *N* NaOD were employed. The least stable complex of this group was that of *N*-methyl-1,3-propanediamine, and in this case the amount of acidic ligand salt in excess was increased to 4.00 mmol to suppress hydrolysis (pD of solution 6.5).

The 2:1 complexes of 1,3-diaminopropane and racemic 2,4-pentanediamine were prepared by a method analogous to the one above using, however, 2.52 mmol of the ligand hydrochloride and 0.92 mmol of nickel chloride in D_2O. A 0.48-ml quantity of 7.7 *N*

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NaOD was added to liberate the amine for complexation. The tris complex of 1,3-diaminopropane was also prepared using 3.46 mmol of ligand hydrochloride, 0.91 mmol of nickel chloride, and 0.71 ml (5.46 mmol) of 7.7 *N* NaOD. The pD was measured to be 10.4.

Measurements. ^1H nmr spectra were recorded *vs.* TMS* (sodium 3-(trimethylsilyl)-1-propanesulfonate) on a JEOL C60-HL spectrometer in the wide-sweep mode using calibrated 16-kHz modulation supplied by an external audio oscillator. In the case of $Ni(1\text{-}Metn)^{2+}$ 22-kHz modulation was necessary. Spectral calibration was effected using the 4-kHz internal oscillator on the instrument. Probe temperature was varied using the JES VT-3 temperature controller accessory for this unit and was calibrated with ethylene glycol and methanol samples by standard procedures. Ligand field spectra were obtained on a Cary 14 spectrophotometer using the same solutions (D_2O) as were employed in the nmr measurements. Integrations were manually performed using a planimeter. pD's were measured by the method previously described.[1]

Results

Nmr Spectra. The proton spectra of 1,3-diamine[16] complexes of nickel(II) obtained during this investigation are presented in a stick-spectral representation in Figure 1. Resonances are reported relative to their positions in diamagnetic platinum(II) complexes.[13] In the stick spectra, resonances due to excess ligand hydrochloride and residual HDO have been omitted; similarly amine protons have been deuterium exchanged and are not shown. A tabulation of these data (Table I) also includes the slope of the least-squares fit of the line in the δT *vs.* T plot for the resonances.

Identification of the individual resonances in these spectra (Table I) is based on an overall internal consistency of assignment in this series and agreement with basic stereochemical tenets. In all complexes, the requisite numbers of α and β protons[17] were accounted for and the proposed assignments are in agreement with integrated intensities. Spectra are all in accord with ligand chelation rather than monodentate binding and are consistent with rapid conformational interchange and a long lifetime of the Ni-N bonds on the nmr time scale.

In all cases, β protons in the six-membered rings were found to resonate upfield from their diamagnetic chelate resonance frequency. In $Ni(2,2\text{-}Me_2tn)^{2+}$,[18] this resonance, of course, was absent; and in $Ni(2\text{-}Ettn)^{2+}$ only a resonance of one proton intensity was observed upfield (Figure 1E and D, respectively). In certain cases two distinct, equally intense resonances for these protons were found (Figure 1B, C, F).

All remaining protons (non β) gave resonances shifted downfield. The peaks due to methyl substituents were readily recognized because of their unique intensity. Methyl protons of $Ni(2,2\text{-}Me_2tn)^{2+}$ and the protons of the ethyl substituent in $Ni(2\text{-}Ettn)^{2+}$ were not observed, no doubt obscured by residual ligand and HDO resonances. In an observation similar to that for the α-proton contact shifts in nickel(II) complexes of 1,2-diamines[1], the α-proton resonances were found to be widely distributed over the range −30 to −300 ppm.

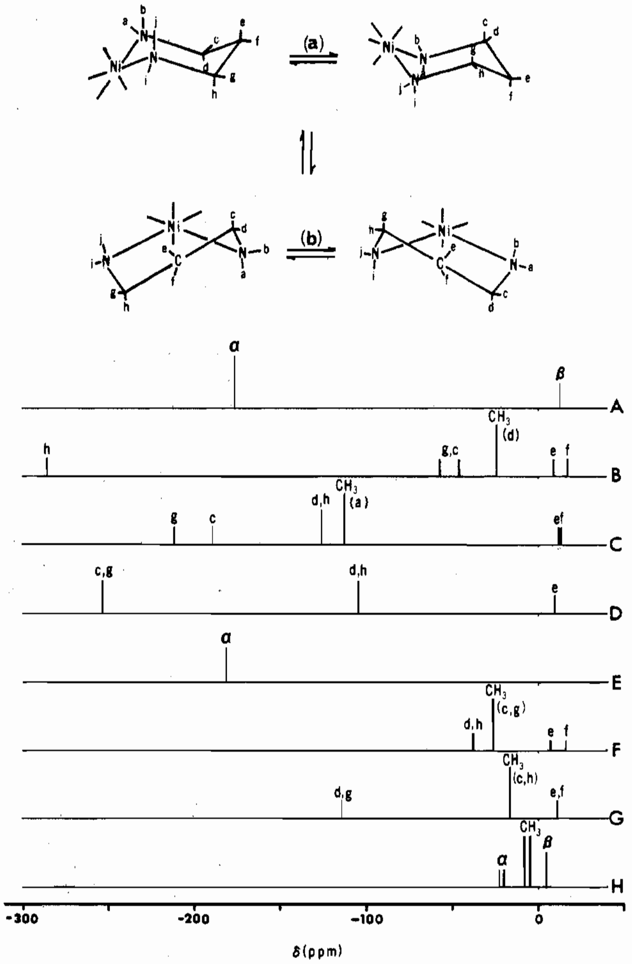

Figure 1. Schematic representation of nmr spectra of nickel(II) complexes of various 1,3-diamine ligands[16] in D_2O. Resonance assignments are based on structures shown and ref 17. All data presented as contact shifts *vs.* diamagnetic platinum(II) chelates:[13] (A) $Ni(tn)^{2+}$, (B) $Ni(1\text{-}Metn)^{2+}$, (C) $Ni(N\text{-}Metn)^{2+}$, (D) $Ni(2\text{-}Ettn)^{2+}$, (E) $Ni(2,2\text{-}Me_2tn)^{2+}$, (F) $Ni(meso\text{-}1,3\text{-}Me_2tn)^{2+}$, (G) $Ni(rac\text{-}1,3\text{-}Me_2tn)^{2+}$, (H) $Ni(rac\text{-}1,3\text{-}Me_2tn)_2{}^{2+}$. Chair-chair (a) and twist-twist (b) equilibria in the 1,3-diamine nickel(II) chelates are shown. Letters are assigned to various substituents in order to facilitate following a given group throughout the entire equilibrium process.

One feature not conveyed in the stick spectra occurred in the spectrum of $Ni(N\text{-}Metn)^{2+}$. At pD's lower than 6.5, an additional resonance was detected at −55 ppm, the intensity of which was found to increase at the expense of the other resonances when the pD was decreased. Since this peak does not seem to arise in the spectrum of the chelated species, another origin must be sought. The secondary amine of this ligand is expected to possess an enhanced basicity[19] relative to the primary amines, and at pD's lower than 6.5 protonation of the secondary amine donor may be starting to occur. The peak at −55 ppm could then represent the α protons adjacent to the primary amine donor in a nonchelated complex. Such large downfield shifts have been reported previously for α protons of monodentate amines complexed to nickel(II).[20]

Electronic Spectra. Ligand field spectra were recorded for aqueous solutions of the 1,3-diamine complexes utilized in these nmr studies and are presented in Table II along with some data for nickel(II) ethylenediamine chelation from the

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(16) Abbreviations adopted for this text are based on the skeletal framework as labeled, N-C(1)-C(2)-C(3)-N: tn, 1,3-diaminopropane; 1-Metn, 1,3-butanediamine; 1,3-Me_2tn, 2,4-diaminopentane; *N*-Metn, *N*-methyl-1,3-diaminopropane; 2,2-Me_2tn, 2,2-dimethyl-1,3-propanediamine; 2-Ettn, 2-ethyl-1,3-propanediamine. Other abbreviations utilized are as follows: en, ethylenediamine; *N*-Meen, *N*-methylethylenediamine; *cis,cis*-tach, *cis,cis*-1,3,5-triaminocyclohexane.

(17) α and β have been chosen to define the position of a given proton with respect to the nickel ion in the framework shown in ref 16; α protons refer to those at carbons 1 and 3; β to those on 2.

(18) Use of abbreviated forms $Ni(nn)_x{}^{2+}$ ($x = 1, 2, 3$) will be employed throughout this paper to indicate the number of ligands chelated. The metal ion is octahedrally coordinated unless otherwise indicated. Other potentially bound ligands are water and chloride ion.

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Table I. Contact Shift[a] Data and Slope[b] of the δT *vs.* T Plot for Nickel(II) Complexes

	Shift (slope)			
1,3-Diamine ligand	α-CH[c]	β-CH[d]	CH_3[c]	Temp range, °K
tn	−175 (∿0)	+14.0		289–360
meso-1,3-Me_2tn	−36.8 (∿0)	+17.3 (∿0)	−25.1 (∿0)	273–356
		8.3 (∿0)		
rac-1,3-Me_2tn	−114 (+12 ± 3)	+11.5	−16.0 (+4 ± 1)	270–342
1-Metn	−285 (+66 ± 2)	+16.7		275–373
	−57.1 (−52 ± 1)	+8.9	−23.3 (+6 ± 1)	
	−45.6 (−30 ± 1)			
2,2-Me_2tn	−180 (−8 ± 4)			282–360
N-Metn	−211 (+66 ± 8)	+12.6	−109 (+3 ± 3)	282–344
	−188 (+53 ± 7)			
	−125 (−33 ± 2)	+14.3		
2-Ettn	−107 (+6 ± 1)	+9.7		282–360
	−256 (∿0)			
$(tn)_2$	−164	+12.3		
$(tn)_3$	−157[e]	+11.5		
(*rac*-1,3-Me_2tn)$_2$	−19.6 (+25 ± 2)	+5.0	−8.3 (+40 ± 4)	266–302
	−23.0 (+7 ± 1)		−5.3 (+28 ± 1)	

[a] In ppm from diamagnetic Pt(II) chelate at 300 ± 2°K; estimated errors in contact shift data: shifts >−100 ppm, ±1.5 ppm; <100 ppm, ±0.5 ppm. [b] In ppm °K/°K. [c] Negative shifts correspond to resonance shifts downfield from the position in the diamagnetic complex and represent positive spin density at that nucleus. [d] Because of small shifts, variations in the δT *vs.* T plot were not significant enough to measure. [e] See Figure 4.

Table II. Ligand Field Spectra for Nickel(II) Complexes[a]

Complex	$^3A_{2g} \rightarrow {}^3T_{2g}$ (10*Dq*)	$^3A_{2g} \rightarrow {}^3T_{1g}$(F)	$^3A_{2g} \rightarrow {}^3T_{1g}$(P)
$Ni(H_2O)_6^{2+}$[b]	8,500	13,500	25,300
$Ni(en)^{2+}$[b]	9,800	15,800	26,800
$Ni(en)_2^{2+}$[b]	10,500	17,900	28,100
$Ni(en)_3^{2+}$[b]	11,200	18,350	29,000
$Ni(tn)^{2+}$	10,000	15,900	26,500
$Ni(tn)_2^{2+}$	10,500	17,400	28,000
$Ni(tn)_3^{2+}$	11,000	17,800	28,300
Ni(*N*-Metn)$^{2+}$	9,700	15,800	26,500
Ni(1-Metn)$^{2+}$	10,150	16,000	26,600
Ni(2-Ettn)$^{2+}$	10,200	16,100	26,600
Ni(*rac*-1,3-Me_2tn)$^{2+}$[c]	10,290	16,000	26,400
Ni(*meso*-1,3-Me_2tn)$^{2+}$	10,200	16,100	26,800

[a] Absorption maxima in cm^{-1} in D_2O. [b] Data obtained from ref 21. [c] Additional band observed at 22,200 cm^{-1}.

literature[21] for comparison. Spectra characteristic of octahedral nickel(II) were obtained in all cases except in the chelation of racemic 1,3-Me_2tn, where an additional band at 22,200 cm^{-1} was found.

Discussion

Complex Stability and Stoichiometry. Unlike the complexation of nickel(II) by 1,2-diamines which exhibit stable 1:1 chelate formation, the 1,3-diamines produce hydrolytically unstable 1:1 complexes. This instability appears to arise from a combination of two sources. First, complexes of the 1,3-diamines are inherently less stable[22] than their ethylenediamine analogs, *viz.*, for $Ni(en)_x^{2+}$ $pK_1 = 7.51$, $pK_2 = 6.35$, and $pK_3 = 4.42$, while for $Ni(tn)_x^{2+}$ $pK_1 = 6.39$, $pK_2 = 4.39$, and $pK_3 = 1.23$. In conjunction with this decreased tendency for 1:1 complexation, the enhanced basicity of the 1,3-diamines (for en $pK_{1a} = 7.5$, $pK_{2a} = 10.2$; for tn $pK_{1a} = 9.1$, $pK_{2a} = 10.6$) helps generate conditions suitable for $Ni(OH)_2$ precipitation. In this study, stabilization of the desired 1:1 complexes was achieved by maintaining an excess of protonated amine in solution to suppress nickel hydroxide formation. To ensure predominance of the desired 1:1 chelate, the ratio of nickel(II) ion to free ligand was kept somewhat above 1.0. From a consideration of the formation constants for mono, bis, and tris complexes of 1,3-diaminopropane and nickel(II), the conditions utilized here are found to favor 1:1 chelation (80% of nickel present) with a considerable amount of excess aquated nickel ion (15%). The choice of the 1:1 chelate for the present investigation was motivated by an observation made in our earlier studies of 1,2-diamino nickel(II) complexes[23] that nickel complexes with only two nitrogen donors in the inner coordination sphere give proton resonances which are, in general, much sharper than those in complexes possessing three or more such donors.

Electronic Spectra. The nature of chelation in this series of 1,3-diaminenickel complexes can quite readily be established by monitoring the ligand field spectra of the complexes. Nickel(II) ion in a pseudooctahedral ligand environment gives a well-characterized electronic spectrum[24] in which the ligand field splitting parameter, 10*Dq* (equal to the energy of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition), is found to mirror successive entry of amine donors into the inner coordination sphere, *viz.*, data for ethylenediamine chelates[21] in Table II. The other two spin allowed d–d transitions are also seen to be reflective of the coordination alterations.

Ligand field spectra for the 1,3-diamine chelates presented in Table II are all characteristic of pseudooctahedral metal ion coordination. The internal consistency of spectral data reflects similar donor interactions in this entire series of 1:1 complexes, and their close correspondence with the spectrum of $Ni(en)^{2+}$ affirms the predominance of the desired 1:1 chelate. Quantitative comparison of ligand field strength (10*Dq*) across this series is, however, not desirable because the position of the first spin-allowed band will be influenced by the presence of hexaaquonickel(II) and also various mixed chloroaquo chelates in solution. Both 2:1 and 3:1 chelates of nickel(II) by 1,3-diaminopropane show the expected high energy shift of all d–d transitions.

Although chelation of racemic 1,3-Me_2tn to nickel(II) produces a typically octahedral spectrum, an additional band at 22,200 cm^{-1} whose intensity becomes dominant under conditions of 2:1 complex formation is also present. This band is indicative of the ligation of nickel(II) in a square-

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(22) I. Poulson and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955).

(23) F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).

(24) B. N. Figgis, "Introduction to Ligand Fields," Interscience Pub., N. Y., 1966.

planar configuration. Ligand field spectra of bis nickel(II) complexes of other bulky diamine ligands which are known to engender square-planar coordination by steric expulsion of axially ligated groups are found to possess a spectrum consisting of a single band of considerable extinction at ∿22,000 cm^{-1}.[25]

Conformation. The ability of nmr to act as a probe of conformation in these chelates relies on an inherent difference in environment of various protons in given conformers. The chair structure, **1**, has α and β protons of distinct axial and equatorial character. In the twist conformer, **3**, three distinct types of ring positions are found. The α-carbon atoms possess substituents which have pseudoaxial and equatorial character as in the chair species. However, the β protons are identically disposed ("isoclinal") in the twist structure, being related by a C_2 symmetry axis.

The present investigation into the conformational equilibria utilizes the contact shift experienced by protons located on the ligand network. These rather large shifts[26] described by eq 1 have been shown to be essentially contact (electron-nuclear hyperfine coupling) in nature for pseudooctahedral nickel(II) chelates.[27] By virtue of the inverse dependence of this expression on temperature (Curie behavior), the measured contact shift is expected to vary with temperature; however, it has been shown[1] that the product δT is, in fact, temperature independent for a given nucleus locked rigidly into one orientation in a given conformation, and this has been termed the "frozen" shift-temperature product δT. Under the influence of rapid chelate ring inversion on the nmr time scale, the measured contact shift (and consequently its δT) for each nucleus will be a time-averaged shift over all species present in conformational equilibrium. This relationship may be conveniently expressed in terms of the δT product by eq 2 where $(\delta T)_{\text{obsd}}$ for a proton contains the weighted mole fraction average contribution of the individual "frozen" shift-temperature product (δT) of the proton in each of i conformers.

$$\delta_i = \frac{(H_\text{p} - H_\text{d})_i}{H_0} = -A_i\left(\frac{\gamma_\text{e}}{\gamma_\text{H}}\right)\frac{g\beta S(S + 1)}{6SkT} \qquad (1)$$

$$(\delta T)_{\text{obsd}} = \sum_i X_i(\delta T)_i \qquad (2)$$

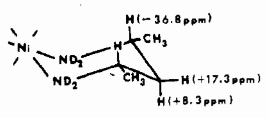
It has previously been demonstrated in our studies[1,4] of nickel(II) chelates of 1,2-diamines that the dihedral angle across the Ni-N-C-H fragment governs the magnitude of the "frozen" δT for an α proton. Maximum contact shift is visible for protons making dihedral angles near 180°, *i.e.*, equatorial α protons in the 1,2-diamine ring; minimum shift, for nuclei oriented with nearly a 90° dihedral angle (axial chelate ring α protons). It is readily recognized then that the time-averaged character of a given nucleus, whether mostly axial or equatorial, is mirrored in the magnitude of its contact shift and that a knowledge of these "frozen" δT's for the α protons for all conformers in solution will allow quantitative definition of equilibrium populations.

Additionally, this method allows the study of conformer populations at various temperatures permitting determination of the thermodynamic parameters for such equilibria *via* an Arrhenius plot, $-\ln K$ *vs.* $1/T$. Conformational redistribution between unequally populated diamine chelate conformers will alter the time-averaged axial and equatorial character of α protons and will be visible by their behavior in a δT *vs.* T plot (non-Curie behavior); predominantly axial α-CH resonances show an increase in δT as the less favorable conformer is populated at higher temperatures, the δT for the more equatorial species decreasing under the same circumstances.[1,28]

^{1}H Nmr Spectra. Individual spectra and their stereochemical implications will now be discussed in detail.

Ni(*meso*-1,3-Me$_2$tn)$^{2+}$ (4). In the assignment of this spectrum (Figure 1F) the α-CH(d,h) is found to exhibit a comparatively small contact shift, −37 ppm, suggesting from earlier studies of contact shifts[1] in nickel(II) chelates that it possesses a highly axial time-averaged environment. Significantly, the δT products for the α- and β-proton resonances were found to be invariant over the temperature range investigated.

From a knowledge of the configuration of the meso ligand, one can explain these data in terms of a strong preference for a chair conformation which accommodates both methyl groups in equatorial environments, **4**, placing the β protons into two distinct orientations and conferring axial character on the α protons. The lack of variation in the δT *vs.* T plots for these resonances eliminates the presence of significant amounts of other conformers in solution with **4** and these data provide "frozen" shift (and hence (δT)) parameters for protons locked into α axial, β axial, and β equatorial chair sites in 1,3-diaminenickel(II) chelates.



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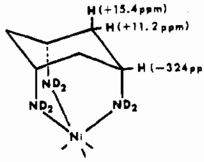

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Proton-proton and platinum-proton coupling constant data reported for the platinum chelates of this ligand support this structure in those complexes.[13] Intuitively, one would expect very little contribution in solution from the alternative chair structure formed by ring inversion because that structure places the methyl groups in syn axial sites.[29,30] In a twist conformation, the methyl groups must, by virtue of the ligand stereochemistry, occupy one pseudoaxial and one pseudoequatorial site. Apparently this conformer is also relatively high in energy.

In order to proceed in analyzing data for various 1,3-diamine systems, it is necessary to establish the "frozen" shift parameter for an α proton in a pseudoequatorial disposition. Experimental data are available for this parameter from the spectrum of the 1:1 complex of nickel(II) with *cis,cis*-1,3,5-triaminocyclohexane (**5**) which has been shown to be a tridentate chelate.[25] This complexation produces an "adamantoid" structure with three six-membered chelate rings rigidly confined to chair conformations. The α protons of these 1,3-diamine chelate rings are forced into "frozen"

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(25) F. L. Urbach, J. E. Sarneski, L. J. Turner, and D. H. Busch, *Inorg. Chem.*, 7, 2169 (1968).

(26) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965).

(27) J. P. Jesson, *J. Chem. Phys.*, 47, 582 (1967).

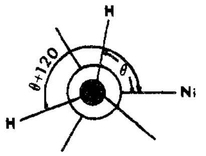
(28) F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, 9, 1139 (1970).

(29) An estimate of the energy difference between the diequatorially substituted chair and its syn axial form of 5.4 kcal/mol has been made for 1,3-dimethylcyclohexane.[30] Inspection of a model of the 1:1 nickel(II) chelate with *meso*-1,3-Me$_2$tn reveals that an even more severe interaction is expected because three bulky pseudoaxial substituents are required to be accommodated on one face of the chair conformer.

(30) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, 83, 2145 (1961).

equatorial positions and exhibit a shift[31] of −324 ppm.

A knowledge of the frozen contact shifts for the α-CH_2 in the chair conformation permits an estimation of the angular orientation of these protons in the Ni-N-C-H framework and a qualitative description of structure of the chelate ring in solution. If one views the complex down the C-N bond and assumes tetrahedral angles are maintained at the α-carbon center (a reasonable assumption in view of crystal structure information summarized in ref 6), one observes **6**.



6

The hyperfine coupling across such three-bond systems is described[1,3] by

$$A_i = B_0 + B_2 \cos^2 \theta_i \qquad (3)$$

Making the assumption that $B_0 \ll B_2$[32] one can formulate eq 4 for the α protons. Using shift values −37 ± 5 and

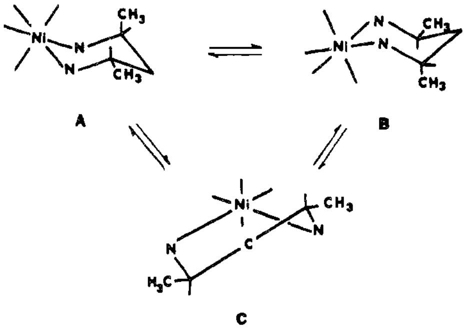
$$\frac{\delta_{H_{ax}}}{\delta_{H_{eq}}} = \frac{\cos^2 \theta}{\cos^2 (\theta + 120)} \qquad (4)$$

−324 ± 10 ppm for the axial and equatorial α protons, respectively, one finds a value of 70 ± 2 or 104 ± 1° for θ. Only the former is consistent with the axial environment in the chair stereochemistry. From an inspection of Dreiding models, a significant flattening of the rigid-chair structure must be invoked in order to account for this dihedral angle for the axial α proton, in line with evidence from solid-state structural information.[6]

As structure **4** requires, the contact shift transmitted across four saturated bonds to the β protons also shows a definite angular dependence. This finding is not totally surprising since $^4J_{H-H}$ values, although generally quite small, are known to exhibit orientational dependence.[33] Significantly, Ni(*cis,cis*-tach)$^{2+}$, **5**, also exhibits separate upfield resonances[34] for the β protons. An assignment of these protons is given in **4** and **5**; however, its basis will be taken up in a later section.

Ni(*rac*-1,3-Me$_2$tn)$^{2+}$ (7). Several equilibrium situations can be envisioned which are compatible with the three-line spectrum (Figure 1G) of this system: (1) an exclusively chair–chair equilibrium between two equienergetic conformers, **7A** ⇌ **7B**, (2) a skew-boat system with the methyl diequatorial conformer overwhelmingly favored, **7C**, or (3) a rapid equilibrium between the skew-boat and chair conformation (**7A** ⇌ **7B** ⇌ **7C**). The magnitude of the shift for the α proton allows differentiation among the possibilities.

In contrast to the meso isomer, this ligand produces a chelated chair structure in which one of the methyl substituents is required to be axial in character and the other, equatorial. Rapid conformational exchange (**7A** ⇌ **7B**) would simply produce equienergetic species with consequent interchange of the environment of all protons on the ring and would be expected to produce an averaged α-CH shift which is the mean of the "frozen" axial and equatorial shifts.[35] The considerably lower value of the α-CH shift, −114 ppm, as compared with the chair, −180 ppm, argues against a simple chair–chair equilibrium in solution.



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An alternative structure skew-boat conformation (**7C**) allows both methyl groups to occupy favorable equatorial environments. Such a twist conformation has been identified in the solid state for this ligand when chelated in Λ-λλλ-Co(*R,R*-1,3-Me$_2$tn)$_3$$^{3+}$.[9] There is, of course, a second skew-boat structure in which these methyl functions are both confined to axial environments; however, it is expected to be very high in energy, like the diaxially substituted chair species in Ni(*meso*-1,3-Me$_2$tn)$^{2+}$. In structure **7C** the α proton occupies an axial position on the ring and would give rise to a single resonance; the β protons are isoclinal in such a structure and would exhibit a single resonance. An inspection of models reveals that the α proton locked into this conformation displays a dihedral angle across the Ni-N-C-H framework of a similar magnitude to an axial α-CH in the chair structure, which from data for Ni(*meso*-1,3-Me$_2$tn)$^{2+}$ is known to resonate at −37 ppm. The observed shift of −114 ppm for the α proton is considered to be too far downfield to reflect the sole presence of this skew-boat conformer in solution.[36,37]

The most adequate explanation of the experimental data involves a rapid conformation equilibrium **7A** ⇌ **7B** ⇌ **7C** between chair and skew-boat conformers. The δ*T* product for the α protons can be written as a function of the equilibrium of 7 by eq 5. Employing the known "frozen" axial and

$$(\delta T)_{\text{obsd}} = X_{\text{A}}(\delta T)_{\text{Ch,ax}} + X_{\text{B}}(\delta T)_{\text{Ch,eq}} + X_{\text{C}}(\delta T)_{\text{SB,ax}} \qquad (5)$$

equatorial δ*T* parameters for a chair conformer and estimating the "frozen" δ*T* for an axial proton in the skew boat as −15,000 ± 3,000 ppm °K, one finds that the equilibrium ratio at 300°K is 54:46 in favor of the chair conformer. From an Arrhenius plot one obtains $\Delta H = 0.20 \pm 0.03$ kcal/mol and $\Delta S = 1.8 \pm 0.5$ eu for the chair–skew boat equilibrium (**7A** ⇌ **7C**). This value of Δ*S* may reflect the enhanced flexibility of the skew boat relative to the chair in the octahedral system, but of course, can also reflect variations in the solvational properties of the two conformers. The rather small enthalpy difference observed between these conformers

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(31) R. F. Evilia, D. C. Young, and C. N. Reilley, *J. Coord. Chem.*, 3, 17 (1973).

(32) C. Heller and H. M. McConnell, *J. Chem. Phys.*, 32, 1535 (1960).

(33) M. Barfield and B. Chakrabarti, *Chem. Rev.*, 69, 757 (1969).

(34) J. E. Sarneski, Ph.D. Dissertation, Case Western Reserve University, Jan 1971.

(35) This analysis presupposes that the methyl group in an axial site has not drastically altered the chair geometry.

(36) This consideration is based on the idealized skew-boat structure. However, the skew boat being flexible can perhaps librate[37] about this conformation, introducing orientations of the α-CH which give larger contact shifts. In such a case the contact shift for the twist conformer would be time averaged over these librations and may lead to an observed shift larger than that predicted by the angular features of the idealized conformation.

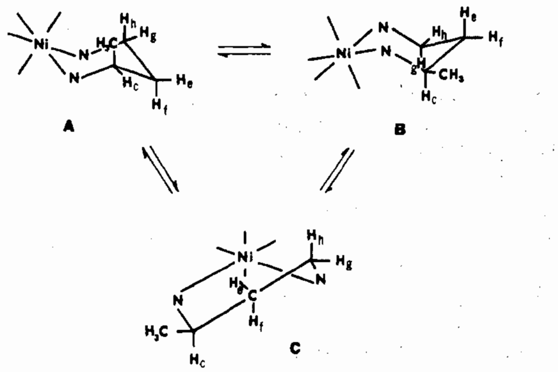
(37) See ref 5, p 127.

may be attributed to selective destabilization of the chair structure through steric interplay of an axial methyl group on the chelate ring with a ligated water molecule.

The presence of substantial skew-boat conformer in this octahedral complex is in agreement with the contention of Appleton and Hall for an analogous Pt(IV) complex.[13b] Their coupling constant data, however, do not provide quantitative measure of this equilibrium, though they suggested that the skew boat was favored.

Ni(1-Metn)$^{2+}$ (8). The ^{1}H nmr spectrum (Figures 1B and 2) of this 1:1 chelate reveals six well-separated resonances. The distribution of the α-proton contact shifts, one downfield at −285 ppm and two at −45 to −60 ppm downfield, suggests the predominance of a structure in which the methyl substituent is located in an equatorial environment. The intermediate nature of the shifts observed for the α protons compared to the "frozen" chair shifts of −37 and −324 ppm indicate that the methyl group does not reside exclusively in an equatorial site and the δT *vs.* T data for these protons (Figure 2, Table I) indicate a redistribution of conformer populations with temperature.

Utilizing the conformational insights derived from the analysis of Ni(*rac*-1,3-Me$_2$tn)$^{2+}$ data one might expect that the equilibrium for Ni(1-Metn)$^{2+}$ may best be described in terms of three species, **8A–C**.



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The observed temperature product for proton h (*a priori* assignment of c and g is not possible) can be conveniently expressed[35]

$$(\delta T)^{h}_{obsd} = X_A(\delta T)_{Ch,ax} + X_B(\delta T)_{Ch,eq} + X_C(\delta T)_{SB,ax} \quad (6)$$

From measured thermodynamic data in Ni(*rac*-1,3-Me$_2$tn)$^{2+}$ **8A** and **8C** can be related by eq 7, where $-\Delta G = 200 -$

$$X_A/X_C = e^{-\Delta G/RT} \quad (7)$$

1.8(T) cal/mol. If one employs an estimated frozen δT for a skew-boat axial α proton, −15,000 ppm °K, along with experimentally determined chair frozen δT values for the α protons, then eq 6 and 7 and the obvious fact that $X_A + X_B + X_C = 1$ can be used to evaluate X_A, X_B, and X_C as 0.04, 0.88, and 0.08 at 300°K. By fitting the deduced equilibrium concentration data at various temperatures to plots of $-\ln K$ *vs.* $1/T$, the following thermodynamic data can be established: **8A** → **8B**, $\Delta H = -1.2 \pm 0.1$ kcal/mol, $\Delta S = 1.9 \pm 0.5$ eu; **8B** → **8C**, $\Delta H = 1.4 \pm 0.1$ kcal/mol, $\Delta S \approx 0$ eu.

Support for this analysis is available from the observed shifts of the β protons which show a separation very nearly as large as that observed in Ni(*meso*-1,3-Me$_2$tn)$^{2+}$, where these protons are conformationally frozen. The observed δT products for the β protons, f and e in **8**, can be formulated

$$(\delta T)^{e}_{obsd} = X_A(\delta T)^{\beta}_{Ch,eq} + X_B(\delta T)^{\beta}_{Ch,ax} + X_C(\delta T)^{\beta}_{SB,iso} \quad (8)$$

$$(\delta T)^{f}_{obsd} = X_A(\delta T)^{\beta}_{Ch,ax} + X_B(\delta T)^{\beta}_{Ch,eq} + X_C(\delta T)^{\beta}_{SB,iso} \quad (9)$$

Subtraction of eq 8 from eq 9 eliminates the last term (in the skew boat the isoclinal β protons being equivalent) and one obtains eq 10 which is a measure of the inherent population difference between the chair conformers at equilibrium.

$$X_A - X_B = \frac{(\delta T)^{f}_{obsd} - (\delta T)^{e}_{obsd}}{(\delta T)^{\beta}_{Ch,ax} - (\delta T)^{\beta}_{Ch,eq}} \quad (10)$$

Utilizing the β-proton resonance data from Ni(*meso*-1,3-Me$_2$tn)$^{2+}$ as frozen δT parameters (denominator), one finds that the 300°K data indicate $X_A - X_B$ is −0.83, in good agreement with data from the independent analysis of the α-proton resonance data.

The thermodynamic data for **8A** ⇌ **8B** represent a measure of the difference in energy requirements for the 1-methyl axial and equatorial chair conformers in the 1,3-diamine chelates of nickel(II). The enthalpy difference of 1.2 kcal/mol is significantly lower than the 5.4 kcal/mol estimated for 1,3-dimethylcyclohexane[30] and may reflect a pronounced flattening of the chair structure in these metal complexes providing some relief from the interaction between the axially coordinated donor and this methyl ring substituent. The Ni–N bond distances in the chelate may also provide assistance in achieving some separation of these bulky substituents.

The thermodynamics for a chair–skew boat interconversion unbiased by the presence of unfavorable steric forces are available from these data (**8B** ⇌ **8C**) by assuming that the methyl group in an equatorial environment in either conformer is sterically equivalent. ΔG of 1.4 kcal/mol agrees reasonably with the predicted value of 1.7 kcal/mol which Gollogly and Hawkins[6] calculated in a recent conformational analysis on the 1:1 octahedral metal chelate of 1,3-diaminopropane. It is certainly this relatively low-energy difference between the chair and skew-boat conformers which is manifest in the unusual conformational distribution recently observed[10] in a Cr(tn)$_3$$^{3+}$ complex, in which one ring was a twist conformation while the other two maintained chair structures.

ΔG's found here allow a free energy profile for the chair and skew-boat conformers in the 1,3-Me$_2$tn complexes to be constructed (Figure 3). Although there is no pathway for the chair–chair interconversion of chelates of the meso and racemic ligand, the energy difference between these species can be compared from the data available in **7A** ⇌ **7C** and **8A** ⇌ **8B**. The latter process measures the energy needed to transfer a methyl group from an equatorial to axial chair site. The energy necessary to bring about the conformational inversion of the stable meso chair conformer to the diaxial form must therefore be at least twice as great and, in all probability, is in excess of this 3.5 kcal/mol estimate. Using these data, one can well understand the conformational preference in Ni(*meso*-1,3-Me$_2$tn)$^{2+}$ because the favored form is at least 3.5 kcal/mol more stable than either other kinetically possible species. Assuming a similar destabilization of an axial methyl group in a skew-boat conformation, the absence of substantial skew-boat conformer in solution for Ni(*meso*-1,3-Me$_2$tn)$^{2+}$ can also be rationalized.

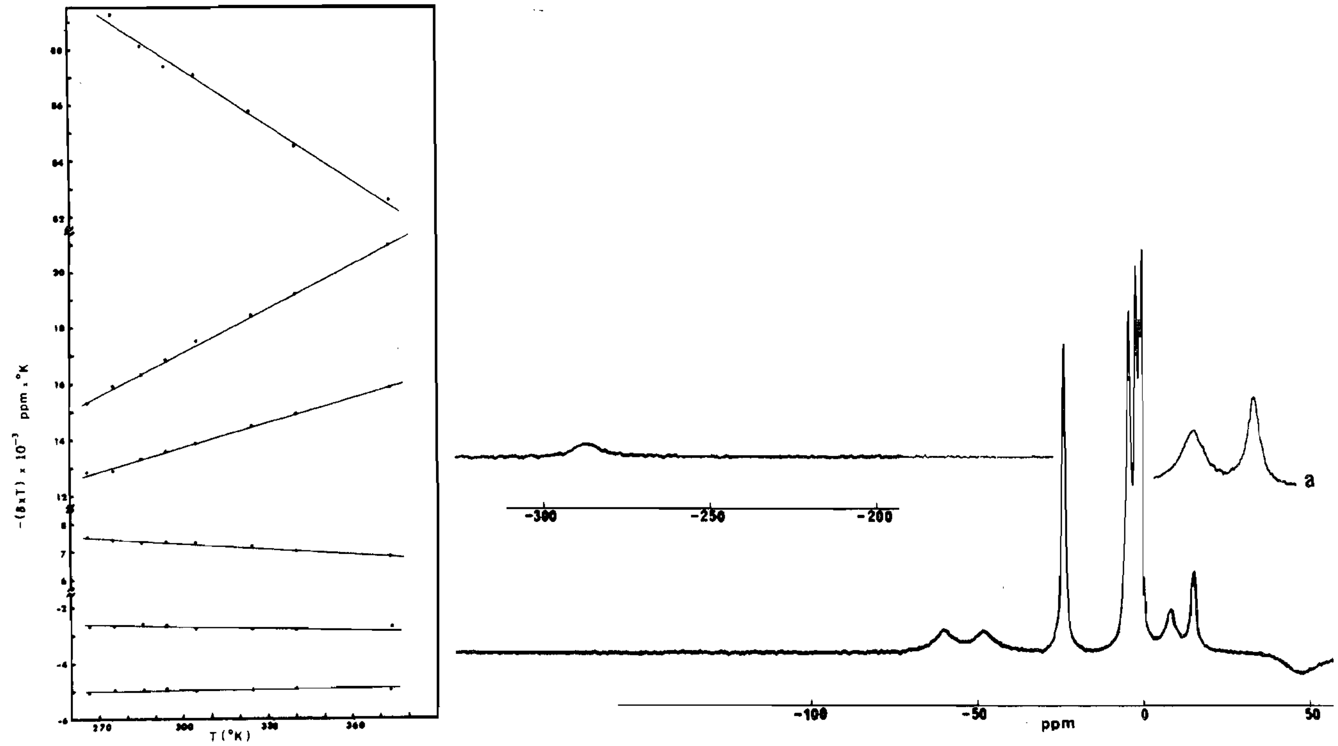

Figure 2. Proton nmr spectrum of Ni(1-Metn)$^{2+}$ at 300°K in D_2O; shifts relative to TMS* (0 ppm). Insert a shows expanded scale view of upfield resonances. A δT *vs.* T plot for all contact shifted resonances is provided.

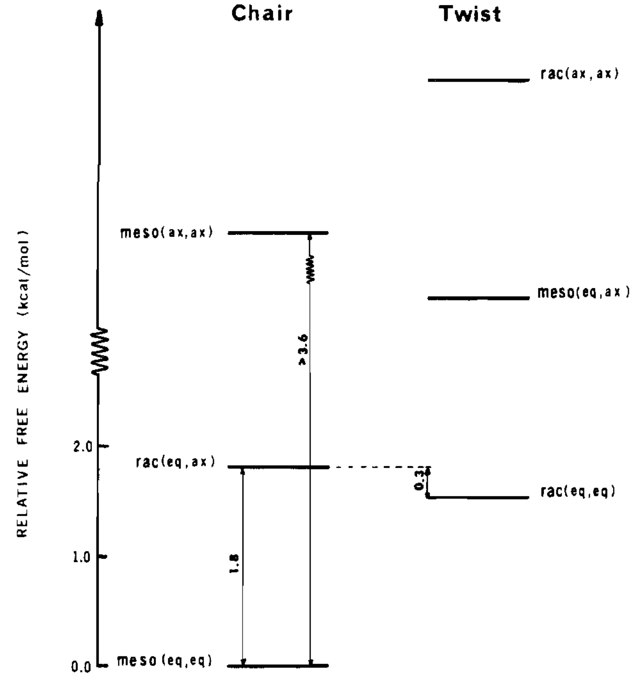

Figure 3. Relative free energies at 300°K for chair and twist conformers of 1:1 nickel chelates of 1,3-Me_2tn isomers. Ring character of methyl substituents given: ax, pseudoaxial; eq, pseudoequatorial.

Ni(tn)$^{2+}$. The two-line nmr spectrum (Figure 1A) exhibited by this complex implies that all the individual α (and β) protons experience identical time-averaged environments. Further, these resonances are found to obey Curie behavior (Table I) suggesting that a single chemical entity is under observation in solution. This might be rationalized in terms of the more stable chair conformation with its inherently axial and equatorial substituents (Figure 1(a)). Rapid ring inversion between equally populated chair conformers would equalize the time each proton spends in these environments and could account for the observed equivalence of the α (and β) protons. However, the thermodynamic data for **8B** ⇌ **8C** which can be used as a gauge of the free energy difference between chair and skew-boat conformations in Ni(tn)$^{2+}$ indicates that ∿9% of the chelate rings will be in the skew-boat conformation at 300°K. This distribution will be expected to be temperature dependent; however, conditions can exist[38] under which such changes in equilibrium populations are not manifest as changes in δT.

It is noteworthy that there is good agreement of the averaged α-CH_2 shift measured in Ni(tn)$^{2+}$, -175 ppm, and that obtained averaging the two frozen shift values determined for the chair conformation -37 and -324 ppm.

Ni(*N*-Metn)$^{2+}$. The presence of six resonances in its spectrum (Figure 1C) leads to the conclusion that this 1:1 chelate exhibits a conformational equilibrium with definite bias. This is not overly surprising considering the substitution of a methyl function on the nitrogen atom; however, from the observed magnitudes of the separations of the α (c,d; g,h) and β (e,f) proton resonances, it is obvious that the methyl group in Ni(*N*-Metn)$^{2+}$ has a greatly diminished influence in com-

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(38) In a conformational equilibrium involving more than one discrete structure, *e.g.*, chairs and skew boats here, certain conditions may be operative which will not allow one to discern the presence of more than one species. For a chair–skew boat equilibrium for Ni(tn)$^{2+}$ as depicted in Figure 1, conformational information can potentially be ascertained from the temperature dependence of $(\delta T)_{\mathrm{obsd}}$ *vs.* T for an α-CH proton where $(\delta T)_{\mathrm{obsd}}$ is defined by eq 2 as $(\delta T)_{\mathrm{obsd}} = X_{\mathrm{A}}(\delta T)_{\mathrm{Ch,ax}} + X_{\mathrm{B}}(\delta T)_{\mathrm{Ch,eq}} + X_{\mathrm{C}}(\delta T)_{\mathrm{SB,ax}} + X_{\mathrm{D}}(\delta T)_{\mathrm{SB,eq}}$. Since $X_{\mathrm{A}} = X_{\mathrm{B}}$ and $X_{\mathrm{C}} = X_{\mathrm{D}}$, $(\delta T)_{\mathrm{obsd}} = X_{\mathrm{A}} \cdot [(\delta T)_{\mathrm{Ch,ax}} + (\delta T)_{\mathrm{Ch,eq}}] + X_{\mathrm{C}}[(\delta T)_{\mathrm{SB,ax}} + (\delta T)_{\mathrm{SB,eq}}]$. Knowing that the chair population (X_{Ch}) is $2X_{\mathrm{A}}$ and the time-averaged axial–equatorial temperature product $(\delta T)_{\mathrm{Ch,av}}$ is half the bracketed sum of frozen (δT)'s for the chair conformation (similar relationships can be obviously formulated for the skew boat conformation), one can reformulate this expression to give $(\delta T)_{\mathrm{obsd}} = X_{\mathrm{Ch}}(\delta T)_{\mathrm{Ch,av}} + X_{\mathrm{SB}}(\delta T)_{\mathrm{SB,av}}$. Thus, the observed δT in an equilibrium between chairs and skew boats will not change with the temperature if the averaged δT's for the α-CH's in these conformers are not substantially different.

parison with that present in Ni(1-Metn)$^{2+}$. Models indicate that the equatorial placement of the *N*-methyl group engenders some eclipsing of this group with the adjacent in-plane metal ion ligand. This interaction should destabilize this conformer relative to the equatorially substituted chair conformers in Ni(1-Metn)$^{2+}$. Models also illustrate that the axially oriented *N*-methyl group is much less sterically crowded into the coordinated ligand than in the axially substituted chair conformation in Ni(1-Metn)$^{2+}$. These forces are certainly operative in making the axial–equatorial distribution of methyl groups in chair conformers of this chelate more equal as the nmr spectral data illustrate.

Ni(2-Ettn)$^{2+}$. The spectrum (Figure 1D) of this system exhibits two downfield resonances for the α protons reflecting their unequal axial and equatorial time-average character conferred by the conformational bias of the ethyl substituent.

Treating these data as originating from an exclusively chair-chair equilibrium and employing in eq 2 the frozen shifts established earlier for the chair α protons, one calculates a 0.77:0.23 conformer distribution at 300°K. Although this result is rational in terms of the expected effect of the bulky substituent, δT data for the α protons show virtually no alteration with temperature implying that the conformer distribution does not arise *via* enthalpy features. In terms of established ideas on the stereochemistry of six-membered ring systems[11] this explanation is untenable. Consideration of this equilibrium in terms of two chair species and two equienergetic skew-boat conformers is equally less than satisfying.[39]

In spite of these difficulties it is certain that the bulky ethyl group has induced a conformational bias in the chair distribution. This must be so because the α-proton differences cannot be explained on the basis of skew-boat conformers because rapid exchange between equal-energy twist conformers would be expected to produce a single, averaged α-CH_2 resonance. It is possible that the steric features associated with the ethyl group have introduced sufficient distortion of Ni-N-C-H diehdral angles making quantitative use of "frozen" shifts established earlier impractical.

At this point it is possible to evaluate the influences that substituents at various ring positions have on the distribution of the two chair conformers. From the separation of the axial and equatorial α-CH resonances in the various 1:1 nickel chelates the preference of the substituent for an equatorial environment is *meso*-1,3-Me$_2$tn > 1-Metn > 2-Ettn > *N*-Metn, emphasizing the severity of the interaction of the axial α substituent in the chair structure with the ligand bound to the nickel ion.

Ni(*rac*-1,3-Me$_2$tn)$_2$$^{2+}$. A 2:1 mole ratio solution of this racemic ligand and nickel(II) ion gives a spectrum (Figure 1H) consisting of five lines; the two resonances farthest downfield are identified as the α protons; the two equally intense peaks at −5.3 and −8.3 ppm are assigned to the methyl protons.

Two conspicuous features makes this spectrum unique in the series under study here. Frist, all the shifts are very small and the δT *vs.* T plot (Table I) for each resonance shows a trend toward zero δT as the temperature is increased. These data are consistent with the existence of a square-planar (diamagnetic) ⇌ octahedral (paramagnetic) structural equilibrium; such processes have previously been reported[40] for nickel(II) complexes of 1,2-diamines in which the ligand possesses bulky groups which must occupy axial ring positions. The intense ligand field spectral band at 22,200 cm^{-1} (Table II) supports the presence of the diamagnetic complex in this solution.[25] Second, the α and methyl protons each show two distinct resonances, one for a meso complex (Ni(+)Me$_2$tn(−)Me$_2$tn) and the other for the optically active species, (Ni((+)Me$_2$tn)$_2$ and Ni((−)Me$_2$tn)$_2$). These diastereomers are present in equal abundances, a value expected for statistically governed conditions. The bis palladium complex of this ligand has also been shown to exist in meso and *dl* isomers.[13a]

A square-planar ⇌ octahedral equilibrium can be visualized as possessing three distinct contributions to the observed shifts (and δT) of all resonances. The octahedral species should, as in the 1:1 chelate of this ligand, be capable of existing in an equilibrium between species with chair and skew-boat ring conformations, with these different conformers (as in the 1:1 complex) possessing very different "frozen" δT values for given protons and hence grossly different weighted-average contributions to the observed δT's. The diamagnetic chelate has no contact shift (*i.e.*, $\delta T = 0$) and, therefore, regardless of ring conformation its total contribution to the observed δT in this equilibrium is zero.

This equilibrium of the three different bis chelates can be formulated mathematically using the "frozen" δT data for α and methyl protons in eq 11 and 12, where $X_{\text{Ch}} + X_{\text{SB}} +$

$$(\delta T)^{\alpha}_{\text{obsd}} = X_{\text{Ch}}(\delta T)^{\alpha}_{\text{Ch,av}} + X_{\text{SB}}(\delta T)^{\alpha}_{\text{SB,ax}} + X_{\text{diam}}(\delta T)^{\alpha}_{\text{diam}} \tag{11}$$

$$(\delta T)^{\text{CH}_3}_{\text{obsd}} = X_{\text{Ch}}(\delta T)^{\text{CH}_3}_{\text{Ch,av}} + X_{\text{SB}}(\delta T)^{\text{CH}_3}_{\text{SB,eq}} + X_{\text{diam}}(\delta T)^{\text{CH}_3}_{\text{diam}} \tag{12}$$

$X_{\text{diam}} = 1$. The frozen δT product for the methyl group in the skew boat is approximated by the shift of the equatorial methyl groups in the chair species Ni(*meso*-1,3-Me$_2$tn)$^{2+}$, −7500 ppm °K. The "frozen" average chair methyl δT is obtained *via* the data for Ni(*rac*-1,3-Me$_2$tn)$^{2+}$ taking into account the skew-boat contribution. A value of −2400 ppm °K was obtained. The δT values for the contact-shifted α CH in the chair and twist conformers are those utilized throughout in the analysis of the 1:1 chelates.

Although the α and CH_3 resonances cannot be positively assigned[41] to meso and racemic complexes, analyses of the data at 300°K by solving eq 11 and 12 simultaneously over all the various permutations of these resonances were found to give similar results and an estimate of the equilibrium concentrations of each species can be made: $X_{\text{SB}} = 0.25 \pm 0.08$, $X_{\text{Ch}} = 0.05 \pm 0.04$, $X_{\text{diam}} = 0.70 \pm 0.07$. Although the above solution characterization is necessarily subject to some inaccuracies, it is believed correctly to portray the equilibrium isomer distribution, with the large diamagnetic popula-

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(39) A crude analysis of the data at 300°K indicates the mole fraction of chair species to be 0.57 and 0.03 while the skew boat then has a composition of 0.40. This was arrived at by using eq 2 and frozen chair α-shift values to describe the equilibrium. First, the skew boat places the ethyl group in one of the isoclinal β positions and this species would undergo rapid torsional motion between equienergetic conformers to average the α shifts. Thus the skew boat will make an identical contribution to the observed δT of both resonances. Second, since there is no evidence for any conformational averaging of chair species at higher temperatures ΔG between these conformers was assumed to be >2.0 kcal/mol. However, the lack of any δT dependence on T seems to imply that this distribution is maintained at all temperatures studied, *i.e.*, that the chair species (ethyl equatorial) and skew-boat conformers were of similar energy.

(40) W. K. Musker, *Advan. Chem. Ser.*, No. 62, 481 (1967).

(41) Identification could be made using resolved amine to prepare the complex, eliminating the presence of (Ni(+)Me$_2$tn(−)Me$_2$tn).

tion reflecting the influence of the chair conformer with its inherent axial methyl group.

The existence of two paramagnetic species contributing to the contact shift in this structural equilibrium is supported by a close inspection of the δT *vs.* T data for the α and methyl protons (Table I) which reveal an unusual feature. Although the α protons exhibit the largest contact shifts, the methyl shift-temperature product decreases more rapidly with temperature. This behavior is in opposition to δT *vs.* T behavior expected for a structural equilibrium between one diamagnetic species and one paramagnetic species; there, the observed δT values for all nuclei are merely directly proportional to the contact shift of that nucleus in the paramagnetic complex and changes in the mole fraction population of paramagnetic complex with temperature will be reflected in a deviation from Curie behavior for all resonances, with those of largest shift showing the most deviation—*i.e.*, possessing the greatest slope in a plot of δT *vs.* T. The deviant behavior observed in Ni(*rac*-1,3-$Me_2tn)_2^{2+}$ arises because the δT for the α CH in the chair is very large (−54,000 ppm °K) compared to that for the skew boat (−15,000 ppm °K) enabling even small amounts of the chair conformer to make substantial contributions to the α proton δT. For the methyl protons, the δT parameters in the two conformers are much less disparate and the chair contribution is less weighty.

$Ni(tn)_2^{2+}$. The ^1H nmr spectrum of this chelate is, in general, virtually the same as that found for the monochelated complex, with the averaged α-proton shift ∿10 ppm more upfield than that in $Ni(tn)^{2+}$. A distinct broadening of the α-CH resonance is also noted, the mono complex possessing a half-bandwidth of ∿8.5 ppm while the bis complex shows a breadth of ∿20 ppm. Similar observations were previously made in our nmr studies of successive complexation of nickel(II) by ethylenediamine.[23]

$Ni(tn)_3^{2+}$. The spectrum of this 3:1 complex consists of two broad resonances: one downfield at −157 ppm (α) and the second upfield at +11.5 ppm (β). Accurate integration data are not possible for these bands because of overlapping of the upfield peak with the resonances due to residual HDO and excess ligand. An investigation of the temperature dependence of the downfield resonance is presented in Figure 4. As the temperature is raised above 300°K, this resonance is found to shift toward TMS* at a rate faster than is predicted by the Curie law; concomitantly, the half-bandwidth of this resonance increases dramatically, in opposition to the expected sharpening of contact shift resonances at higher temperatures.[42] At 345° and above, this downfield resonance clearly exhibits a narrowing trend and now δT remains constant. This finding closely parallels observations made for tris nickel(II) complexes of ethylenediamine and *meso*-2,3-butanediamine, both of which were attributed to averaging of the axial and equatorial environments of the α protons on these chelate rings by racemization about the metal ion.[4b,23] These data (Figure 4) support the operation of a similar process in $Ni(tn)_3^{2+}$; however, the second resonance engaged in the apparent coalescence of the α protons is not visible. From the observed Curie behavior above 345°K, it can be estimated that the other resonance involved in this temperature-dependent process should be found at −40 ppm (from TMS*) at 300°K. The possibility exists that this unobserved proton, predominantly axial in ring character, is oriented in close proximity to the metal ion and experiences extreme dipolar broadening such that it is not visible.

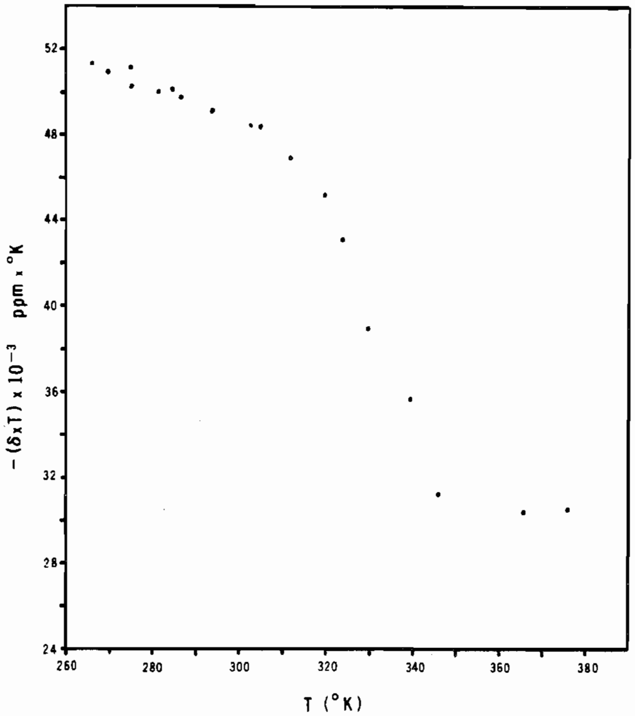

Figure 4. Temperature dependence of δT for α-proton resonance of $Ni(tn)_3^{2+}$. Shift (δ) of resonance measured against TMS*.

One can extrapolate the data in Figure 4 to estimate a value for the shift difference (Δ) between the two α-proton resonances (2 × 2440 Hz) at the coalescence temperature ∿345°K. With this value the rate of exchange ($1/\tau_c$) for the α protons at coalescence can be calculated using eq 13 to be

$$1/\tau_c = \pi\Delta/\sqrt{2} \qquad (13)$$

1.1×10^4 sec^{-1}. Using eq 14, one can calculate a free energy

$$1/\tau_c = (k/h)Te^{-\Delta G^{\ddagger}/RT} \qquad (14)$$

of activation of 14 kcal/mol for this process at 345°K. This energy barrier is quite similar to that established for racemization in the other tris(1,2-diamine)nickel(II) complexes[4b,23] thus far investigated and supports the spectral assignment proposed here.

Further Consideration of the Contact Shifts. In our initial paper in this series,[1] we drew attention to the dramatic similarity between the dihedral angle dependence of the contact shifts that we observed in the Ni-N-C-H fragment in ethylenediamine chelates and the well-known nuclear spin-spin coupling relationships in similar vicinal moieties in diamagnetic systems.[43] A number of other reports[44-47] whose ^1H nmr findings for contact shifts in paramagnetic nickel(II) complexes parallel *J-J* coupling in model diamagnetic units are now available in the literature. The data accumulated in this present effort reinforce the general operation of an orientational behavior of contact shifts in the Ni-N-C-H fragment (^3A)[48] as proposed earlier[1] and further demonstrate quite convincingly the existence of a conformational depend-

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(42) E. DeBoer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 117 (1967).

(43) A. A. Bothner-By, *Progr. Nucl. Magn. Resonance Spectrosc.*, **1**, 195 (1965).

(44) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, **54**, 3238 (1971).

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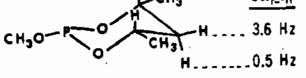
(47) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969).

ence of the contact shift across four bonds (^{4}A) in the nickel(II) complexes. Although $^4J_{H-H}$ data are difficult to obtain because of the diminished magnitudes of such interactions, available evidence confirms the existence of a conformational dependence in these long-range couplings.[49]

Theoretical formulations[50] of the nuclear spin-spin coupling phenomenon usually presume that the major contribution to the observed *J-J* interaction arises from electron-mediated Fermi contact coupling—that is, that magnetic dipole-dipole and orbital-dipole interactions are negligible. Evidence is available which asserts that the observed resonance shifts experienced in pseudooctahedral nickel(II) complexes arise by Fermi contact coupling of electron and nuclei, with any pseudocontact contributions being negligible.[27] The similarity in orientational properties associated with *J-J* coupling in diamagnetic systems and electron-nuclear hyperfine coupling in paramagnetic nickel(II) chelates is therefore not surprising. The relatively large magnitudes of the contact shifts in these 1,3-diaminenickel(II) chelates and their associated signs of coupling constants by direct spectral observation make these systems intriguing as models to provide a further understanding of long-range *J-J* coupling interactions.

The analogy between *J-J* coupling and the contact shifts in the nickel(II) chelates can be utilized to assign the β-CH_2 resonances found in conformationally rigid six-membered rings of Ni(*meso*-1,3-Me_2tn)$^{2+}$ and Ni(*cis,cis*-tach)$^{2+}$, **4** and **5**. Data for $^4J_{^{31}P-^1H}$ in a rigid molecular framework, **9**, which is quite analogous to that under study here illustrate quite well the conformational dependence of long-range coupling.[51] In a series of such heterocyclics studied by Albrand, *et al.*,[51] $^4J_{^{31}P-^1H}$ was invariably found to be greater for the equatorially oriented proton in these chair structures. In the analogous six-membered chelate rings of **4** and **5**, the β proton with the larger upfield shift is, therefore, assigned to the equatorial environment. This assignment receives support from the rather unusual feature exhibited by the β-proton resonance half-bandwidths wherein the one of smaller shift shows the larger breadth. Resonance broadening arising from a contact interaction is given[26] by the second term of the relaxation expression



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$$\frac{1}{T_2} = \frac{1}{15}S(S+1)g^2\beta^2\gamma_I^{\,2}r^{-6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s^{\,2}\tau_c^{\,2}}\right] + \frac{1}{3}S(S+1)\frac{A^2}{h^2}\left[\tau_e + \frac{\tau_e}{1+\omega_s^{\,2}\tau_e^{\,2}}\right] \qquad (15)$$

and requires the breadth of a resonance to increase as the square of its observed shift. For nickel(II) complexes, bandwidth generally increases with increasing contact shift; however, in **4** and **5**, the β-proton resonances do not obey this relationship, the most upfield resonance being significantly sharper. This unusual feature is also manifested in the spectrum of Ni(1-Metn)$^{2+}$, Figure 2a (insert) and suggests the presence of a dipolar contribution[52] to broadening in the β-CH_2 resonances. From an inspection of molecular models, the axial β proton is observed to be conspicuously nearer to the paramagnetic center. Since the dipolar contribution to broadening by the paramagnetic ion (eq 15, first term) includes an inverse sixth-power dependence on internuclear distance, *r*, the axial proton might undergo significantly more dipolar broadening than its equatorial counterpart, thus giving rise to the apparently anomalous relationship of half-bandwidths.

One additional piece of information obtained in the nmr spectrum (Figure 1D) of Ni(2-Ettn)$^{2+}$ lends support to the proposed assignment of β protons. From the α-CH_2 shifts the ethyl substituent is seen to introduce a conformational preference for the equatorially substituted species. This requires the β proton to reflect a predominantly axial time-averaged environment, and indeed the β proton shows an upfield shift which is very similar to the resonance assigned to the axial β proton in Ni(*meso*-1,3-Me_2tn)$^{2+}$.

With the data amassed here for the frozen α- and β-proton shifts in the chair species and other data for ^{13}C and ^{14}N shifts in Ni(tn)$_2^{2+}$ already in the literature,[53] a complete map of the electron delocalization in the six-membered 1,3-diamine chelate ring can be prepared. Interestingly, the sign of the electron density located on the ring is found to obey strictly an alternating relationship such as would be required by a spin-polarization mechanism of delocalization[2] (the presence of direct delocalization of electron density onto the ligand-bonding framework in these chelates is not precluded). Significantly, the upfield shifts of the β protons are in agreement with the results of a recent INDO calculation performed for the 1,3-diaminopropane radical cation.[54] On the basis of previously reported, incorrect data for the β protons in Ni(tn)$^{2+}$ which quoted these resonances to be shifted downfield,[2] these authors[54] were misled in judging their INDO results. The recent successes of such INDO calculations in describing nuclear-nuclear[55] and electron-nuclear hyperfine coupling[56-58] are now well documented and would seem to provide a very useful probe into the origins of the contact shifts in these complexes.

It is noteworthy that frozen axial and equatorial α-proton shifts in the 1,2- and 1,3-diamine chelates are found to be exceedingly different: -6 and -188 ppm in Ni(en)$^{2+}$ and -37 and -324 ppm in Ni(tn)$^{2+}$. This may partially manifest a slightly greater covalency in the Ni-N bonds in the latter species as data for Ni(en)$_3^{2+}$ and Ni(tn)$_3^{2+}$ indicate that the

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(48) Contact shifts in a Ni-N-C-H moiety (α) can be viewed as electron-nuclear hyperfine coupling interactions across three bonds—hence, ^{3}A. ^{4}A is used to represent the Ni-N-C-C-H fragment (β) in this coupling.

(49) M. Barfield, *J. Amer. Chem. Soc.*, 93, 1066 (1971).

(50) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, 1, 149 (1965).

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(52) It should be pointed out that the presence of dipolar broadening contributions here does not conflict with earlier findings[27] of negligible pseudocontact shifts in nickel(II) complexes; for, although dipolar contributions to isotropic shifts are averaged to zero, the dynamic influence of molecular reorientation on local magnetic fields experienced at individual nuclei may still effect relaxation.

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(54) M. J. Scarlett, A. T. Casey, and R. A. Craig, *Aust. J. Chem.*, 23, 1333 (1970).

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latter exerts a slightly stronger nephelauxetic effect;[59] hence slightly greater electron transmission to the ligand might be expected. A part of this difference may also arise from dihedral angle origins; the six-membered ring axial proton has an Ni-N-C-H angle (70°) more conducive to electron delocalization than that of its $Ni(en)^{2+}$ analog which was found to be 80°. At the same time, the equatorial proton of $Ni(tn)^{2+}$ also has a more favorable orientation for spin transmission. The conformational dependence elucidated for ^4A coupling in the six-membered chelate rings in this paper suggests the possibility of another source for some of the large observed difference. By virtue of the ring structure in $Ni(en)^{2+}$ each α proton can be visualized to experience electron delocalization from the nickel atom through each nitrogen atom, *i.e.*, *via* an ^3A and an ^4A coupling route. Our data indicate that these coupling paths will produce oppositely sensed spins at the proton nucleus and may produce some coupling decrease by a net cancelation effect. The $Ni(tn)^{2+}$ structure, on the other hand, would provide ^3A and ^5A coupling contributions for its α protons and purely ^4A coupling at the β proton nuclei. The α proton shifts would then be virtually fully determined by ^3A coupling, the influence of ^5A interaction (also negative on spin-polarization grounds) expected to be greatly diminished. Multipath coupling considerations would then predict an α proton in $Ni(en)^{2+}$ to exhibit slightly less contact shift than $Ni(tn)^{2+}$, all other factors being equal. In view of the substantial ^4A coupling for $Ni(tn)^{2+}$ demonstrated here, Cramer's recent HMO analysis[60] of $Ni(N\text{-}Meen)^{2+}$ proton contact shifts which neglected multipath coupling may require further consideration. It is noteworthy that such multipath coupling schemes are supported by theoretical calculations (INDO) for carbon-13 internuclear coupling in cyclic organic systems.[61] The enhanced magnitude of electron-nuclear coupling in these nickel(II) systems makes them extremely attractive as models for such phenomena.

The contact shift information for six-membered ring chelates presented here can prove exceedingly useful in conformational studies. For example, the proton nmr spectrum of the 1:1 nickel(II)-histidine system reported by Milner and Pratt[2] can be reinterpretated. From their spectrum and resonance assignment which seems correct, it appears likely that the ligand is bound in a tridentate fashion requiring the six-membered ring formed between the nitrogen donors to be rigidly maintained. This structure can account for the large shift obtained for the glycinate methine proton and the upfield appearance of two distinct resonances for the methylene group.

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Registry No. $Ni(tn)^{2+}$, 24669-45-2; $Ni(1,3\text{-}Me_2tn)^{2+}$, 50601-08-6; $Ni(1\text{-}Metn)^{2+}$, 50601-09-7; $Ni(2,2\text{-}Me_2tn)^{2+}$, 50601-10-0; $Ni(N\text{-}Metn)^{2+}$, 50601-11-1; $Ni(2\text{-}Ettn)^{2+}$, 50790-64-2; $Ni(tn)_2{}^{2+}$, 45843-82-1; $Ni(tn)_3{}^{2+}$, 18347-71-2; $Ni(rac\text{-}1,3\text{-}Me_2tn)_2{}^{2+}$, 50600-58-3.

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Synthesis and Reactivity of Five-Coordinate Nickel(II) and Copper(II) Complexes with a Pentadentate Ketoamine Ligand

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A general method for the synthesis of hitherto unreported pentadentate fluorinated Schiff base ligands is presented. Two new five-coordinate metal complexes, Ni(tfacDPT) and Cu(tfacDPT), where H_2(tfacDPT) is the pentadentate Schiff base derived from trifluoroacetylacetone and bis(3,3′-aminopropyl)amine, have been prepared and characterized by various physical techniques. Data for the Cu(II) complex indicate that it is square pyramidal while electronic spectra for the high spin Ni(II) complex suggest that it may possess a geometry intermediate between square pyramidal and trigonal bipyramidal. Ni(tfacDPT) coordinates with pyridine to produce a pseudooctahedral adduct, Ni(py)(tfacDPT), which releases pyridine *in vacuo* or on gentle heating of the complex.

Introduction

While numerous five-coordinate transition metal complexes have been described in recent years, only a limited number have contained linear pentadentate ligands.[1,2] The most common ligands of this type are Schiff bases derived from substituted salicylaldehydes[3,4] or 2-pyridinecarboxaldehyde[5] and tridentate polyamines. Until now, no complexes containing pentadentate ketoamine ligands have been reported although many with tetradentate[6] and a few with sexadentate ketoamine ligands[7,8] have been well studied.

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