

Theory of Contact and Dipolar Nuclear Magnetic Resonance Shifts in Tetrahedral Nickel(II) Complexes

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Received April 22, 1971

Abstract: The theory for the contact shift and pseudocontact shift in the nmr spectra of tetrahedral and distorted tetrahedral complexes of Ni(II) is developed. It is shown that both the contact shift and the pseudocontact shift depart markedly from the T^{-1} behavior previously assumed for tetrahedral Ni(II) complexes. The affect of this deviation upon published values of ΔH and ΔS for the "planar-tetrahedral" equilibrium is estimated. It is further shown that the pseudocontact shift may in some cases be quite large and should not be neglected in any analysis of nmr shifts. Finally, it is shown that the spin densities obtained from contact shifts are a weighted average of spin densities in more than one ligand π orbital rather than the spin density in only one molecular orbital as is commonly assumed in comparison with HMO calculations.

Extensive investigations have been made¹ of the paramagnetic shifts in the nmr spectra of tetrahedral complexes of nickel(II). The planar-tetrahedral equilibrium in many of these complexes has been investigated²⁻¹² primarily by measuring deviations of the nmr shifts from the T^{-1} dependence predicted by the McConnell equations.^{13,14} Further, in the analysis of spin densities in the ligands as determined by the nmr shifts, it has been customary to assume that the pseudocontact term is negligible in the tetrahedral Ni(II) complexes.

Kurland and McGarvey¹⁵ have recently shown that the assumptions made in deriving the McConnell equations are violated in complexes with nearly degenerate T_1 or T_2 ground states and have derived general equations for calculating contact and pseudocontact shifts in complexes of this type. These equations were applied¹⁶ to the cobalt(II) poly(1-pyrazoyl)borate complexes which have a distorted 4T_1 ground state with considerable success. These calculations showed that in these complexes the contact shift approximates T^{-1} in the experimental region of temperatures but the large pseudocontact term deviates markedly from T^{-1} behavior. This prediction has recently been verified experimentally.¹⁷

In this work the results of calculations of nmr shifts using the theory of Kurland and McGarvey¹⁵ are presented for Ni(II) in both tetrahedral and distorted tetrahedral ligand fields.

3T_1 States of Ni(II) in a Distorted Tetrahedral Field

In the following calculations we have assumed a weak crystal field in which we can use the 3F wave functions for the free ion.¹⁸ We further assume a distortion from tetrahedral symmetry to the D_{2d} symmetry appropriate to the tetrahedral forms of the aminotroponeimines^{2,3,5-7} and pyrromethenes¹⁹ of Ni(II). The coordinate system chosen is shown in Figure 1.

In the absence of spin-orbit coupling, the 3T_1 state of tetrahedral symmetry yields the following states in D_{2d} symmetry

$$\begin{aligned} A_2(M_s) &= |0, M_s\rangle \\ E_{\pm}(M_s) &= c|\pm 3, M_s\rangle + d|\mp 1, M_s\rangle \end{aligned} \quad (1)$$

$|M_L, M_s\rangle$ represents the 3F state of orbital magnetic quantum number M_L and spin quantum number M_s . In tetrahedral symmetry $c = (5/8)^{1/2}$. The excited 3T_2 state yields in D_{2d} symmetry the states

$$\begin{aligned} B_2(M_s) &= (1/\sqrt{2})[|2, M_s\rangle + |-2, M_s\rangle] \\ E_{\pm}'(M_s) &= d|\pm 3, M_s\rangle - c|\mp 1, M_s\rangle \end{aligned} \quad (2)$$

and the 3A_2 state becomes in D_{2d}

$$B_1(M_s) = (1/\sqrt{2})[|2, M_s\rangle - |-2, M_s\rangle] \quad (3)$$

For purposes of calculation, we will assume the E_{\pm} state of eq 1 to be lower in energy than the A_2 state and the separation between them to be δ in the absence of any spin-orbit interaction.

To evaluate the effect of the spin-orbit interaction, we use the spin-orbit operator

$$\mathcal{H}_{LS} = -\lambda \mathbf{L} \cdot \mathbf{S} \quad (4)$$

in which the negative sign is chosen to make λ a positive parameter in our equations for Ni(II). To a first-order approximation in \mathcal{H}_{LS} the energies and wave

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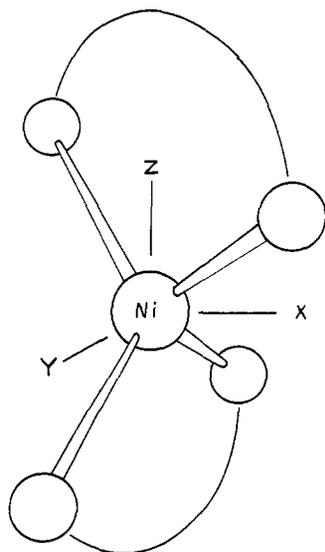


Figure 1. Coordinate system used in computations on D_{2d} symmetry complexes.

functions for seven of the nine states of 3T_1 are obtained by solving the two determinants shown in eq 5 and 6.

$$\begin{vmatrix} A_2(\pm 1) & E_{\mp}(0) \\ A_2(\pm 1) & \delta - E & -\alpha'\lambda \\ E_{\mp}(0) & -\alpha'\lambda & -E \end{vmatrix} = 0 \quad (5)$$

$$\begin{vmatrix} A_2(0) & E_+(1) & E_-(-1) \\ A_2(0) & \delta - E & -\alpha'\lambda \\ E_+(1) & -\alpha'\lambda & -\alpha\lambda - E & 0 \\ E_-(-1) & -\alpha'\lambda & 0 & -\alpha\lambda - E \end{vmatrix} = 0 \quad (6)$$

The other two states are $E_{\pm}(\mp 1)$ with energy $E = \alpha\lambda$.

$$\begin{aligned} \alpha &= 3c^2 - d^2 \\ \alpha &= \sqrt{6d} \end{aligned} \quad (7)$$

The solution of eq 5 and 6 gives the energies E_n^0 and wave functions ϕ_n which are the starting point in using the equations of Kurland and McGarvey^{15,16} to calculate the contact and pseudocontact shifts. As will be demonstrated further on, the small crystal field in tetrahedral Ni(II) makes the second-order contribution from the 3A_2 and 3T_2 states of Ni(II) sizable and these must be included in the computations. For the tetrahedral Ni(II) complexes previously studied by nmr we have no reliable information as to the values of δ , α , and α' . It will be necessary, therefore, to make computations for a range of possible values for these parameters to see what, if any, is the dependence of the computed result on these parameters.

Theory of the Contact Shift of Ni(II) in a Tetrahedral Field

Kurland and McGarvey^{15,16} have shown that the contact shift $\Delta H_F/H_0$ is given by

$$\frac{\Delta H_F}{H_0} = (3\gamma_N \hbar q)^{-1} \sum_{i=x,y,z} \sum_n \left(a_{ni}^{(1)} - \frac{a_{ni}^0 E_{ni}^{(1)}}{kT} \right) \times \exp(-E_n^0/kT) \quad (8)$$

$$q = \sum_n \exp(-E_n^0/kT) \quad (9)$$

$$E_{ni}^{(1)} = \langle \phi_n | \beta(L_i + 2.0023S_i) | \phi_n \rangle \quad (10)$$

$$a_{ni}^0 = \langle \phi_n | \mathcal{H}_{CF}(i) | \phi_n \rangle \quad (11)$$

$$a_{ni}^{(1)} = \sum_m [\langle \phi_n | \mathcal{H}_{CF}(i) | \phi_m \rangle \langle \phi_m | \beta(L_i + 2.0023S_i) | \phi_n \rangle + \langle \phi_n | \beta(L_i + 2.0023S_i) | \phi_m \rangle \langle \phi_m | \mathcal{H}_{CF}(i) | \phi_n \rangle] / (E_n^0 - E_m^0) \quad (12)$$

$$\mathcal{H}_{CF}(i) = (8\pi/3)(2.0023)\gamma_N \hbar \beta \sum_j \delta(r_j) s_{ij} \quad (13)$$

where γ_N is the nuclear magnetogyric ratio, β the Bohr magneton, and r_j the position coordinates of electron j .

It has been shown^{15,16} that the contact interaction is not the same for all the states summed over in eq 8. It is reasonable to assume that the contact shift is different for the A_2 and E_{\pm} states and, therefore, to assume the following relationships hold

$$\langle A_2(M_s) | \mathcal{H}_{CF} | A_2(M_s) \rangle = A(A_2) \langle A_2(M_s) | S | A_2(M_s) \rangle \quad (14)$$

$$\langle E_{\pm}(M_s) | \mathcal{H}_{CF} | E_{\pm}(M_s) \rangle = A(E) \langle E_{\pm}(M_s) | S | E_{\pm}(M_s) \rangle$$

We can further assume that cross terms such as

$$\langle A_2(M_s) | \mathcal{H}_{CF} | E_{\pm}(M_s) \rangle$$

are very small or zero. The magnitudes of $A(A_2)$ and $A(E)$ depend on the mechanism for producing the contact shift. The mechanism generally assumed for the aminotroponeimines, pyrrromethene, and salicylaldehyde imine complexes of Ni(II) supposes that covalency interactions occur between the d orbitals of the nickel ion and the π orbitals of the aromatic ligand causing some of the spin density to be transferred into the π orbitals of the ligand. A contact interaction between this spin density and ring protons can then occur through the mechanism which gives contact interactions in aromatic free radicals.²⁰⁻²³

The π molecular orbitals of the aromatic bidentate ligand can be classified into two types; those which have an even number of nodes, and therefore have parallel p orbitals on the two atoms adjacent to the metal ion, and those which have an odd number of nodes with antiparallel p orbitals. The $d_{\pm 1}$ metal orbitals form MO's only with the π orbitals with parallel p orbitals. Thus we can write for the contact term of an electron in the $d_{\pm 1}$ orbital

$$a_+ = Q\rho_+$$

where ρ_+ is density of electron in p orbital adjacent to the hydrogen atom for MO's with an even number of nodes. The $d_{\pm 2}$ orbitals form MO's only with the π orbitals having antiparallel p orbitals and would have a contact term

$$a_- = Q\rho_-$$

The d_0 orbital does not form a MO with π orbitals of the ligand. Using wave functions for the F state we can show that

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$$A(A_2) = \frac{2}{5}a_+ + \frac{1}{10}a_-$$

$$A(E) = \frac{1}{4}a_+ + \frac{1}{40}[7 + \alpha - p]a_- \quad (15)$$

$$p = [15(1 + \alpha)(3 - \alpha)]^{1/2}$$

Equation 15 reveals that both types of ligand π orbitals will contribute to the contact interaction but the major contribution must come from molecular orbitals with an even number of nodes. In much of the literature on the contact interactions of aromatic ligands attached to paramagnetic ions, it is assumed implicitly that the unpaired electrons use only one ligand MO in any given complex. The preceding analysis shows this simplistic notion to be incorrect.

To calculate the contact shift to first order in tetrahedral Ni(II) we take $\delta = 0$, $\alpha = \alpha' = 1.5$, and ignore all second-order terms. Equation 8 and 15 then give for the contact shift

$$\Delta H_F/H_0 = -F(a_+ + \frac{1}{5}a_-)/(\gamma_N \hbar) \quad (16)$$

$$F = (\beta/30q) \left[\frac{3.5023}{\lambda} (9 - q) + \frac{9(0.5023)}{2kT} (v + 5v^3) \right] \quad (17)$$

$$q = 1 + 3v + 5v^3 \quad (18)$$

$$v = \exp(-3\lambda/2kT) \quad (19)$$

To make use of these equations we need to estimate a value of λ . A value of 315 cm^{-1} has been determined¹⁸ for the gaseous Ni^{2+} ion from optical data but covalency effects in the nickel(II) complexes will require a much smaller value be used in our equations. The magnetic susceptibility as a function of temperature has been measured for Ni^{2+} in tetrahedral sites of ZnS ,²⁴ CdS ,²⁵ and ZnO .²⁵ These data have been successfully fitted to a theory of the susceptibility in which the only adjustable parameter was λ . Values of λ found were 150 cm^{-1} in ZnS , 170 cm^{-1} in CdS , and 175 cm^{-1} in ZnO . From this it would seem that a reasonable value of λ which will take into account the effects of covalent bonding would be 200 cm^{-1} and this will be the value used in calculations reported in this paper.

A plot of F vs. T^{-1} is given in Figure 2. Also included in Figure 2 is the result of a calculation which includes the second-order terms and the Curie law behavior predicted by the McConnell equation.¹⁴ In the second-order calculations, it was assumed that

$$\Delta E(^3T_2) = 3500 \text{ cm}^{-1}$$

$$\Delta E(^3A_2) = 8000 \text{ cm}^{-1}$$

where $\Delta E(^3T_2)$ and $\Delta E(^3A_2)$ are the energy differences between the ground state and the 3T_2 and 3A_2 states.

An examination of Figure 2 reveals significant deviations from T^{-1} dependence of the contact shift even in the experimental range of 200–400°K. This is not surprising when one examines the relative magnitudes of the two terms in eq 17. At room temperature ($kT \sim 200 \text{ cm}^{-1}$) the T^{-1} term makes only a 2–3% contribution to the total shift. Thus $(\Delta H_F/H_0)$ is determined primarily by the second-order Zeeman term which one would not expect to follow the Curie law.

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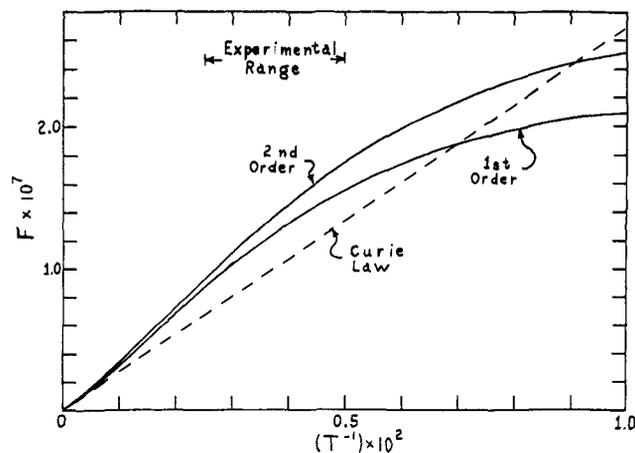


Figure 2. First- and second-order computations of contact shift parameter F as a function of reciprocal temperature. Curie law line was computed from the McConnell equation (ref 14) assuming $g = 2.0023$ and $S = 1$.

It is also seen from Figure 2 that F is some 30% greater in the experimental range than predicted by the McConnell equation and hence contact terms calculated using this equation are 30% too large. The second-order terms are seen to be significant, being more than 10% of the first-order term in the range of 200–400°K.

Theory of the Contact and Pseudocontact Shift in a Distorted Tetrahedral Field

For a distorted tetrahedral field, the calculation of the contact shift is identical with that used for a tetrahedral field except that δ is no longer zero and α and α' are no longer 1.5. The pseudocontact shift which must be zero for a purely tetrahedral field can be calculated by use of the following equations^{15, 16, 26, 27}

$$\Delta H^M/H_0 = -\frac{1}{3}(\chi_{\parallel} - \chi_{\perp})(3 \cos^2 \Omega - 1)R^{-3} = -D(3 \cos^2 \Omega - 1)R^{-3} \quad (20)$$

$$\chi_{\parallel} = (kTq)^{-1} \sum_n \exp(-E_n^0/kT) \{ [E_{nz}^{(1)}]^2 - 2kT \sum_{m \neq n} E_{nmz}^{(2)} \} \quad (21)$$

$$E_{nmz}^{(2)} = |\langle \phi_n | \beta(L_z + 2.0023S_z) | \phi_m \rangle|^2 / (E_n^0 - E_m^0) \quad (22)$$

Ω is the angle between the main symmetry axis (z axis in Figure 1) and the direction vector between the metal atom and the nucleus whose nmr is being measured and R is the distance between the metal atom and this nucleus. Equation 21 is just Van Vleck's²⁸ equation for paramagnetic susceptibility along the symmetry axis. A similar equation applies for χ_{\perp} .

To make reasonable calculations of the effect of changing δ on the contact and pseudocontact shifts, we must estimate how the values of α and α' change with δ . The crystal field parameters for the tetragonal component V_T of the crystal field can be written²⁹ as

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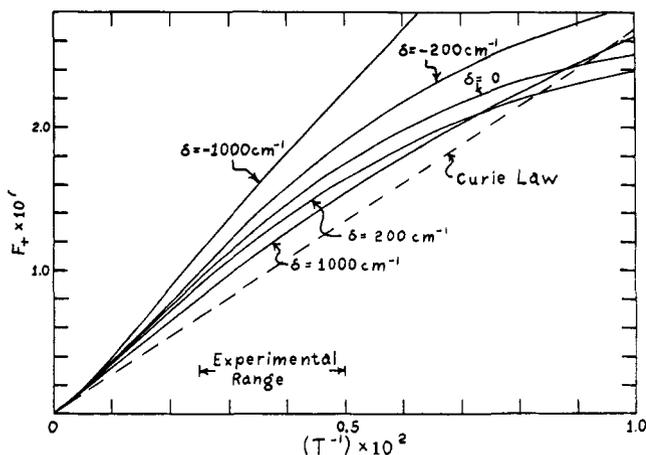


Figure 3. Second-order computations of contact shift parameter F_+ as a function of reciprocal temperature for different values of distortion parameter δ . α is computed from eq 25.

$$V_T = Ds(L_z^2 - 4) - Dt(35/12L_z^4 - 335/12L_z^2 + 30) \quad (23)$$

for F state ions. From this it can be shown that in the limit of $Ds, Dt \ll 10Dq$

$$\alpha = \frac{3}{2} \left\{ 1 - \frac{25}{2} (Ds - \frac{5}{4}Dt) / (10Dq) \right\} \quad (24)$$

From a point charge model it can be estimated that for small distortions from tetrahedral symmetry $Ds/Dt \sim 4.5$. From this it appears reasonable to estimate α as a function of δ from the equation

$$\alpha = \frac{3}{2} (1 + 0.900(\delta/10Dq)) \quad (25)$$

In using eq 25 a value of $10Dq = 4500 \text{ cm}^{-1}$ was used to calculate α . α' can always be obtained from α by use of the normalization condition.

In Table I are given values of F and D at 300°K for

Table I. Contact and Pseudocontact Parameters for Distorted Tetrahedral Ni(II) at 300°K

Order of calcn	α	δ, cm^{-1}	$F_+ \times 10^7, \text{G/erg}$	$F_- \times 10^7, \text{G/erg}$	$D \times 10^{27}, \text{cm}^3$
First	1.500	0	1.1355	0.1892	0.0
Second	1.500	0	1.2494	0.2083	0.0
First	1.500	100	1.0989	0.1722	0.5447
Second	1.500	100	1.2102	0.1892	0.7814
Second	1.530	100	1.2078	0.1926	1.0000
First	1.500	200	1.0707	0.1583	1.0946
Second	1.500	200	1.1771	0.1728	1.4966
Second	1.560	200	1.1733	0.1806	1.9552
First	1.500	400	1.0254	0.1368	2.0504
Second	1.500	400	1.1251	0.1480	2.7133
Second	1.620	400	1.1218	0.1677	3.6663
First	1.500	1000	0.9567	0.1074	3.7338
Second	1.500	1000	1.0516	0.1161	4.7575
Second	1.800	1000	1.0662	0.1855	7.0315
First	1.500	-100	1.1647	0.2060	-0.6080
Second	1.470	-100	1.2911	0.2271	-0.9307
First	1.500	-200	1.1999	0.2247	-1.1496
Second	1.440	-200	1.3359	0.2477	-1.7980
First	1.500	-400	1.2657	0.2610	-2.0028
Second	1.380	-400	1.4179	0.2888	-3.1005
First	1.500	-1000	1.3520	0.3200	-2.4295
Second	1.200	-1000	1.5214	0.3553	-3.8279

different values of δ . In addition to the second-order calculation using eq 25 values of F and D for $\alpha = 1.5$

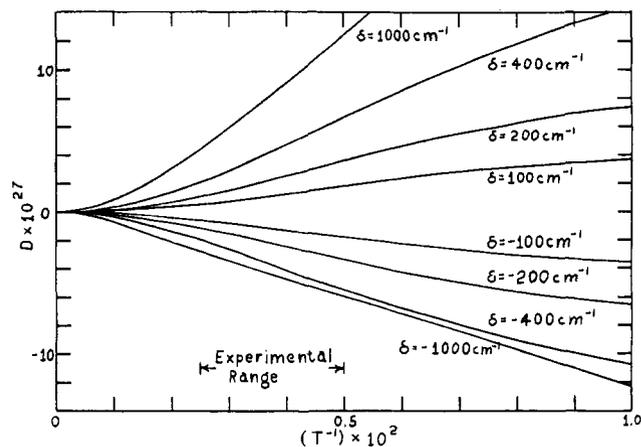


Figure 4. Second-order computations of pseudocontact parameter D as a function of reciprocal temperature for different values of distortion parameter δ . α is computed from eq 25.

are given for both first- and second-order calculations to show the dependence upon α . F_{\pm} 's are defined by the equation

$$\frac{\Delta H_F}{H_0} = -F_+(a_+/\gamma_N \hbar) - F_-(a_-/\gamma_N \hbar) \quad (26)$$

For the tetrahedral complex, to first order, $F_+ = 6F_-$ but this relation does not hold exactly to second order or for the distorted systems.

To put the numbers in Table I in perspective it should be noted that for $\bar{g} = 2.2$, McConnell's equation^{13,14} predicts at 300°K that $F = 0.9852 \times 10^{-7} \text{ G/erg}$ and for $g_{\parallel} = 2.2, g_{\perp} = 2.0$ that $D = 0.3876 \times 10^{-27} \text{ cm}^3$. A value of $1.0 \times 10^{-27} \text{ cm}^3$ for D means an nmr shift of 480 Hz at 60 MHz for a proton with $R = 5.0 \text{ \AA}$ and $(3 \cos^2 \Omega - 1) = 1$. An examination of Table I reveals that the second-order term is 10% of the first-order term in F and 30–40% of the first-order term in D . The larger contribution to D from the second-order term is not surprising if we note that D is primarily a difference in two larger terms. We further note from Table I that D is much more dependent on α than F , the changes in F being less than 1% while changes in D vary from 30 to 50%. The ratio F_+/F_- varies from 4.3 to 6.7 in Table I.

Plots of F_+ and D vs. T^{-1} are given in Figures 3 and 4. Examination of Figure 3 reveals that deviations from T^{-1} dependence are quite marked when δ is small in magnitude but become less so for larger magnitudes of δ . When E_{\pm} is the ground state, large deviations from tetrahedral symmetry bring the shift closer to that predicted by the McConnell equation using $\bar{g} = 2.0023$, but for the A_2 ground state large deviations produce a Curie law temperature dependence with a slope nearly double that predicted from the McConnell equation. Figure 4 reveals that the pseudocontact shift mimics T^{-1} dependence in the experimental range 200–400°K but extrapolating this dependence to $T = \infty$ produces errors in the intercept whose magnitude is 50–100% of the shift at room temperature. Thus those protons having sizable pseudocontact shifts could be expected to follow a T^{-1} dependence experimentally but have an extrapolated shift at $T = \infty$ considerably different than the corresponding diamagnetic ligand. Examination of Figure 4 further reveals that large dis-

tortions for the E_{\pm} ground state produce larger pseudocontact shifts than for the A_2 ground state.

Discussion

In any discussion of the application of these calculations to measurements on tetrahedral nickel(II) complexes we must consider three things: (A) the planar-tetrahedral equilibrium, (B) the pseudocontact shift, and (C) the interpretation of the contact shifts in terms of MO theory.

A. Planar-Tetrahedral Equilibrium. Large deviations from T^{-1} dependence in the aminotroponeimines, ^{2,3,5-7} salicylaldehyde imines, ^{4,10} β -keto amines, ⁸ pyrrole-2-aldimines, ⁹ and dihalobisphosphines ^{11,12} of Ni(II) have been attributed to an equilibrium between the tetrahedral configuration of the complex and a diamagnetic planar configuration. In many instances the deviations are very large and can only be accounted for by assuming an equilibrium between a diamagnetic and paramagnetic species. Recently in the case of some dihalobisphosphines, ^{11,12} the rate of interconversion has been found to be slow enough to allow detection at low temperatures of both the paramagnetic and diamagnetic species separately.

To determine the values of ΔH and ΔS for the reaction (diamagnetic form \rightarrow paramagnetic form) it has been assumed that the paramagnetic species has a T^{-1} dependence, and therefore the observed shift can be fitted to an equation of the form

$$\Delta H/H_0 = -A/T(1 + e^{\Delta G/RT}) \quad (27)$$

If the paramagnetic species is a tetrahedral complex, as assumed, then the calculations in this paper show that use of eq 27 will yield values of ΔH and ΔS that are in error. To evaluate the magnitude of such errors, eq 27 has been fitted to the calculated values of F for a pure tetrahedral Ni(II) in the temperature range of 200–400°K. The best fit (shown in Figure 5) is obtained for $\Delta H = 1180$ cal/mol and $\Delta S = 10.2$ cal/(deg mol). This is close to the values of $\Delta H = 1250$ cal/mol and $\Delta S = 11.3$ cal/(deg mol) found³ for nickel(II) *N,N'*-bis-(ethyl)aminotroponeimineate except in our calculation there is no assumption of a diamagnetic species.

The results of the preceding computation should not be taken as necessarily typical of possible errors in reported values of ΔH and ΔS for the planar-tetrahedral equilibrium. For systems having larger values of ΔH and hence a smaller percentage of paramagnetic species in equilibrium, the error incurred in assuming T^{-1} dependence for the paramagnetic species will become smaller. For example, if one assumes an equilibrium with $\Delta H = 1770$ cal/mol and $\Delta S = 11.2$ cal/(deg mol) and the temperature dependence calculated for tetrahedral Ni(II) for the paramagnetic species, eq 27 (fitted in the range 200–400°K) will give values of $\Delta H = 1970$ cal/mol and $\Delta S = 13.2$ cal/(deg mol). Thus we can expect, for those tetrahedral species which most likely have a small magnitude for δ , that major errors in estimating ΔH and ΔS from eq 27 will occur for those systems with small enough ΔH 's and large enough ΔS 's to make the paramagnetic species the predominate form over the temperature interval at which measurements are made. For those systems, such as the dihalobisphosphines, where δ can be expected to be large in

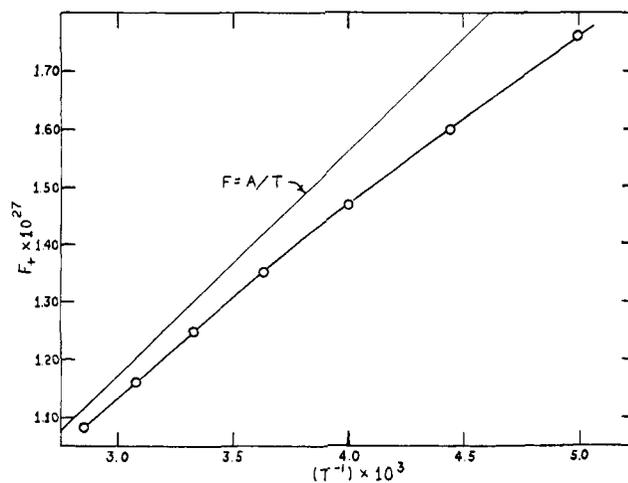


Figure 5. Comparison of theoretical values of F_+ with fitted eq 27. Solid curve is eq 27 and points are theoretical values. $\Delta H = 1180$ cal/mol; $\Delta S = 10.2$ cal/(deg mol).

magnitude, the computations indicate that errors due to assuming T^{-1} dependence are probably minimal.

B. Pseudocontact Shift. In analyzing the ligand nmr shifts in tetrahedral Ni(II), it has been customary to assume that the pseudocontact shift is negligible and, therefore, that the shifts measured are a direct measure of the contact shift. Three arguments are generally advanced³⁰ for making this assumption. The first argument points out that in the aminotroponeimines and salicylaldehyde imines the relative spin densities calculated in the ligands, assuming no pseudocontact shift, agree with HMO calculations for the free radical formed by removing one π electron from the ligand anion. This is not a particularly strong argument because the crudeness of HMO calculations would make it easy to overlook a pseudocontact term of 20–30%. Further, as will be discussed shortly, it is not necessarily correct to expect the contact shifts to give exactly the same spin distribution as found in the ligand free radical even if the assumption of delocalization of spin only into the π system is correct.

A second argument advanced for absence of a pseudocontact shift is the observation that in several ligands having the phenyl ring, the shift in a hydrogen atom attached to the ring has a magnitude similar to the shift observed for a methyl group attached at the same site but is opposite in sign. Since this behavior is found for contact interactions in free radicals, it is argued that the pseudocontact term must be small as it would contribute a shift of the same sign and magnitude for both the hydrogen and methyl groups. Unfortunately, R is generally quite large for the hydrogens in question so that the pseudocontact term would be expected to be small and again contributions of 10–20% would be easily overlooked in such a comparison.

The third argument which states that the pseudocontact term must be small because $g_{\parallel} = g_{\perp}$ in a pure tetrahedral complex can be readily dismissed by the results of calculations in this work, which show that very large pseudocontact shifts can be expected for small values of δ . Since the highest symmetry for any tetrahedral Ni(II) complex studied is D_{2d} , it would be expected that

(30) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

δ would be at least several hundred reciprocal centimeters for any complex. For large negative values of δ the calculations show that we could expect small pseudocontact shifts. A small pseudocontact shift would also occur for positive δ if we had a large distortion from axial symmetry causing the E_{\pm} state to split.

Recently the pseudocontact shift for a complex with a large distortion from axial symmetry has been measured. Horrocks and Greenberg³¹ have measured the anisotropy in the magnetic susceptibility of dichlorobis(triphenylphosphine)nickel(II) in a single crystal and have calculated the expected pseudocontact shift using equations similar to eq 20. They report a D value whose magnitude is $\sim 0.5 \times 10^{-27} \text{ cm}^{-1}$ and a second term of similar magnitude for the distortion in the xy plane. It seems clear from this work and the experimental results of Horrocks and Greenberg³¹ that the pseudocontact shift may not be zero in tetrahedral Ni(II) complexes and this should be recognized in any analysis of nmr shifts in these complexes.

C. Contact Shifts and Spin Densities. In comparing contact shifts to MO calculations, the general model has been to assume a π electron is removed from the ligand anion and paired up with one of the unpaired electrons on Ni(II) leaving a neutral ligand free radical. The spin densities of this free radical are calculated and compared with spin densities calculated from the contact shift with the scaling factor representing the fraction of time the unpaired electron is delocalized into the π system of the ligand. This model is an oversimplification of what actually should be the situation in a molecular orbital picture of the complexes.

In the molecular orbital model, bonding and antibonding orbitals result from a linear combination of metal d and ligand π orbitals of appropriate symmetry. The ligand electron pairs occupy the bonding orbitals and spend some time on the metal atom while the d electrons of the metal occupy antibonding orbitals and spend some time in the π system of the ligands. Thus in the case of the d orbitals occupied by unpaired electrons, there is a net movement of electrons from the ligand to metal atom reducing the charge difference and stabilizing the bond. If Ni(II) were in a strong ligand field, the 3T_1 state of Ni(II) would have the unpaired

(31) W. D. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, 10, 2190 (1971).

electron occupying only the d_{xy} , d_{xz} , and d_{yz} orbitals. Since the d_{xy} orbital cannot mix with π orbitals and d_{xz} and d_{yz} only mix with π orbitals with an even number of nodes, the contact terms $A(A_2)$ and $A(E)$ would be $1/2a_+$ in this case. However, for a weak field (as indicated by optical studies on tetrahedral Ni(II)^{18,29}) the 3T_1 state of Ni(II) has the electron also occupying the $d_{x^2-y^2}$ and d_{z^2} orbitals a portion of the time and this gives rise to eq 15 which has two types of molecular orbitals contributing to the contact term.

Thus, a more proper model for comparing spin densities with HMO calculations on free radicals would be to consider the spin densities from nmr to be a weighted average of the spin densities in the top filled molecular orbital with an even number of nodes and the top filled orbital with an odd number of nodes. Equation 15 indicates that the weighting is toward the molecular orbital with the even number of nodes, all other factors being even.

In the aminotroponeimineates, salicylaldehyde imines, and β -keto amines the top filled π orbital has an even number of nodes so that it is not surprising that the nmr spin densities approximate that of a free radical with an unpaired electron in the top filled π orbital. In the case of the pyrromethenes the top filled orbital has an odd number of nodes while the next lower filled orbital has an even number of nodes. Thus, it is understandable that the spin densities from nmr more nearly approximate the distribution of spin in this lower orbital than the top filled molecular orbital. The fact that the unpaired spin must be distributed in a more stable orbital than in the aminotroponeimineates also accounts for the considerably smaller fraction of spin in the π system of the pyrromethenes. Eaton and Lalancette¹⁹ have interpreted the spin densities in the pyrromethenes as resulting from a transfer of spin into the first empty π orbital which also has an even number of nodes. However, this transfer would only make the ligand more negative and the nickel atom more positive and would seem to be less likely to occur.

The pyrrole-2-aldimines⁹ are also ligand anions with the top π orbital having an odd number of nodes but the low symmetry of the complex plus the uncertainties in assignment of the nmr lines makes any interpretation difficult at this time.