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Theory of the NMR Paramagnetic Shift of Pseudotetrahedral Complexes of Nickel(II) and Cobalt(II)

Bruce R. McGarvey

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

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The theory of the NMR paramagnetic shift in pseudotetrahedral complexes for Ni(II) and Co(II) has been developed and applied to experimental results for complexes using the same ligands. The theory used the atomic overlap method, AOM, for the ligand field and included the P as well as the F states. It specifically allowed for different spin delocalization from different d orbitals. It has been shown that the shifts in Ni(II) complexes is sensitive to delocalization of spin only from the metal $d_{\pm 1}$ orbitals. For Co(II) complexes, the shift is mainly due to the $d_{\pm 1}$ orbitals but there could be a measurable effect from the $d_{\pm 2}$ orbitals. It has been further shown that the failure to recognize the differing spin delocalization of different metal d orbitals in previous analyses of paramagnetic shifts has led to estimates of spin density in the ligands to be too small by a factor of 2.5 in Ni(II) complexes and 3.0 in Co(II) complexes. It has also been discovered that the so-called contact shift is not isotropic, particularly for Ni(II) complexes, and this leads to a dipolar contribution for the average contact shift that could be significant for paramagnetic shifts that are primarily due to delocalization of spin in π aromatic MOs. The theory has been used to examine experimental paramagnetic shifts for Co(II) and Ni(II) complexes having the same ligands. Spin delocalization into the ligands is significantly higher for the Ni(II) complexes.

Introduction

In the treatment of the paramagnetic NMR shift in transition metal complexes and lanthanide shift reagents, most researchers have used a simplified set of equations to analyze their experimental results. There are two contributions to the paramagnetic shift, $(\Delta H/H_0)$:

$$\begin{aligned}(\Delta H/H_0) &= (\Delta H/H_0)_C + (\Delta H/H_0)_D \\ &= \text{contact shift} + \text{dipolar shift}\end{aligned} \qquad (1)$$

The paramagnetic shift ΔH is the difference between the resonant field of the ligand in the paramagnetic complex and the resonant field of the diamagnetic ligand. The dipolar shift has also been called the pseudocontact shift in the literature. For axially symmetric complexes (the type of complex treated in this paper) this term is normally given in the form[1−3]

$$(\Delta H/H_0)_D = -\mathrm{DP}(3\cos^2\theta - 1)R^{-3} \qquad (2)$$

$$\mathrm{DP} = (\chi_{\parallel} - \chi_{\perp})/3 \qquad (3)$$

where χ is the atomic susceptibility, R is the distance between the paramagnetic ion and the nucleus, and θ is the angle between the vector R and the z axis. Equation 2 is the first term in a multipole expansion and is correct only if R is much larger than the size of the metal d orbital of the electron. When R is not large enough the expression for the dipolar term becomes more complex as has been shown in the work of Golding.[4−6] In this paper, eq 2 is adequate because R was greater than 4.0 Å and we will be using this form for only the contribution from the metal ion d orbital. Golding and Stubbs[6] claim eqs 2 and 3 to be inadequate for R values much larger than 4.0 Å in their consideration of a covalent case, but this calculation included spin and angular momentum dipolar terms from ligand atomic orbitals, which we will consider separately in this work. In much of the earlier literature on the subject, DP was rewritten using the following equation for the magnetic susceptibility:

$$\chi_i = g_i^2 \beta_e^2 S(S+1)/3kT = \mu^2/3kT \qquad (4)$$

Here β_e is the Bohr magneton, S is the spin in the ground state of the metal ion, and g_i is the g value for the ground state of the metal ion in the ith direction. Equation 4 is adequate for non orbitally degenerate ground states such as the $^4A_2$ ground state of tetrahedral Co(II) but is completely inadequate for T_1, T_2 states such as the ^3T ground state of tetrahedral Ni(II) where the spin−orbit interaction produces a non-degenerate ground state with no g value. Equation 4 is also inadequate for all lanthanide ions with the exception of the Gd^{3+} ion.

For the contact term the equation generally used is[8]

$$(\Delta H/H_0)_C = -F \cdot A \qquad (5)$$

$$F = g\beta_e S(S+1)/3kT \qquad (6)$$

where A is the average hyperfine interaction parameter expressed in G as measured by the nuclear magnetic moment, presumably due to the Fermi contact interaction between the unpaired electrons in a metal ion-ligand MO and the appropriate nucleus, and g is an average g value for the metal ion orbitals. For proton NMR, it has been customary to use the McConnell[9] equation

$$A = Q\rho_i \qquad (7)$$

for complexes in which it is assumed that spin is transmitted by conjugated π MOs. In eq 7, ρ_i is the spin density on the adjacent carbon atom in the relevant MO and Q is the

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(1) Horrocks, W. D.; Fischer, R. H.; Hutchison, J. R.; LaMar, G. N. *J. Am. Chem. Soc.* **1966**, *88*, 2436.

(2) McGarvey, B. R.; Pearlman, J. *J. Magn. Reson.* **1969**, *1*, 178.

(3) Kurland, R. J.; McGarvey, B. R. *J. Magn. Reson.* **1970**, *2*, 286.

(4) Golding, R. M.; Pascual, R. O.; Vrbanich, J. *Mol. Phys.* **1976**, *31*, 731.

(5) Golding, R. M.; Pascual, R. O.; Stubbs, L. C. *Mol. Phys.* **1976**, *31*, 1933.

(6) Golding, R. M.; Stubbs, L. C. *Proc. R. Soc. London* **1977**, A354, 223; *J. Magn. Reson.* **1979**, *33*, 627.

(7) McConnell, H. M.; Robertson, R. E. *J. Chem. Phys.* **1958**, *27*, 1361.

(8) McConnell, H. M.; Chestnut, D. B. *J. Chem. Phys.* **1958**, *28*, 107.

(9) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 764; *Proc. Natl. Acad. Sci. U.S.A.* **1957**, *43*, 721.

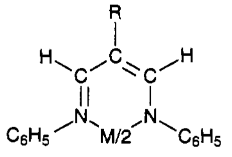
0020-1669/95/1334-6000$09.00/0

appropriate McConnell coefficient. To account for systems with a thermal population of multiple spin states as the lanthanides and transition metal ions with T_1, T_2 ground states, Golding *et al.*[10,11] have proposed using the following equation for the contact shift:

$$(\Delta H/H_0)_C = (A/H_0)\langle S_z\rangle \tag{8}$$

Here $\langle S_z\rangle$ is a computed average of the S_z spin operator over all thermally populated states of the ion. The problam with eqs 5–8 is 3-fold. First, it is assumed that the F parameter is isotropic so that only the isotropic portion of the hyperfine interaction constant makes a contribution to the contact shift. It will be shown in this work that this is not true for the systems considered, and it will be shown below that in certain situations the proton contact shift could have a dipolar contribution as large as 25% of the Fermi contact term for Ni(II) complexes. Second, it is assumed that all orbitals and states occupied by the unpaired spins have the same hyperfine parameter A. It will be shown in this work that this is a seriously flawed assumption which has led to underestimates of spin delocalization in π systems by factors as large as 3. Third, eq 8 ignored the possibility of the effect of Zeeman mixing of the states, which has been shown in the case of Yb^{3+} to make the major contribution to the paramagnetic shift and cannot be related to hyperfine parameters of individual states.[12]

This work is the result of a request from Professor R. Knorr of the University of Munich to develop a theory for the paramagnetic shift of tetrahedral cobalt(II) complexes similar to our earlier treatment of the tetrahedral nickel(II) complexes[13] so that they could be applied to his extensive NMR studies of both nickel and cobalt pseudotetrahedral complexes of type **I**.[14–16] The earlier treatment had used a crystal field treatment of the orbital energies and a first- and second-order perturbation approach to the spin-orbit interaction. The results were presented as a function of the energy splitting δ of the T_1 ground state into A_2 and E states. Examination of the old computer program revealed several errors in the second order terms which had little effect on the final results but serious errors were found in the treatment of the different contact interactions in the various states of the system. We did recognize the earlier errors in treating all orbitals as having the same hyperfine interaction but did not do the proper analysis for all the states.



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Since present-day PCs are far superior to the main frame computer used in the earlier work, it was decided to repeat the calculation for Ni(II) and extend it to Co(II) without resorting to perturbation theory to include the spin–orbit mixing of excited states into the ground state. We also decided to use the atomic overlap method (AOM)[17,18] instead of the crystal field theory to relate the paramagnetic shift to the bite angle of the bidentate ligands.

Theory of Paramagnetic NMR Shift

We will use the approach of Kurland and McGarvey[3] to calculate the paramagnetic NMR shift. The shift in resonance magnetic field from that for the diamagnetic ligand, ΔH, for the ith direction of the magnetic field is given by the equations

$$\begin{aligned}(\Delta H/H_0)_i = (kTq)^{-1}\{&\textstyle\sum_{\Gamma n,\Gamma m}\exp(-\epsilon_\Gamma/kT)\langle\Gamma n|\mu_i|\Gamma m\rangle\\ &\langle\Gamma m|A_{\mathrm{Ni}}|\Gamma n\rangle - kT\textstyle\sum_{\Gamma n,\Gamma' m(\Gamma\neq\Gamma')}Q_{\Gamma\Gamma'}\langle\Gamma n|\mu_i|\Gamma' m\rangle\\ &\langle\Gamma' m|A_{\mathrm{Ni}}|\Gamma n\rangle\}\end{aligned} \tag{9}$$

$$Q_{\Gamma\Gamma'} = [\exp(-\epsilon_\Gamma/kT) - \exp(-\epsilon_{\Gamma'}/kT)]/(\epsilon_\Gamma - \epsilon_{\Gamma'}) \tag{10}$$

$$q = \textstyle\sum_{\Gamma n}\exp(-\epsilon_\Gamma/kT) \tag{11}$$

where

$$\mu_i = -\beta_e(L_i + 2S_i) \tag{12}$$

$$A_N = A_F + A_D + A_L \tag{13}$$

$$A_F = (8\pi/3)2\beta_e\textstyle\sum_k\delta(r_k)s_k \tag{14a}$$

$$A_D = 2\beta_e\textstyle\sum_k[3(s_k\cdot r_k)r_k - {r_k}^2 s_k]{r_k}^{-5} \tag{14b}$$

$$A_L = 2\beta_e\textstyle\sum_k {r_k}^{-3} l_k \tag{14c}$$

ϵ_Γ is the energy of the multiplet state $|\Gamma n\rangle$, and the other symbols have their usual meaning. In this paper we will be only considering systems with axial symmetry, which will necessitate making calculations for the z, parallel, orientation and for the x, perpendicular, orientation.

In principle, the dipolar shift, sometimes referred to as the pseudocontact shift, arises from the A_D and A_L terms above and the contact term comes from the A_F term. In practice, however, most attempts to separate contact and dipolar shifts in the literature assume the dipolar shift comes only from the central metal ion and use eqs 2 and 3 along with geometrical arguments to make the separation. This means that any contributions from the ligand atom orbitals to the A_D and A_L terms will be mostly lumped in with the reported contact shift. Thus, experimentally, it would appear that the operational definition of the dipolar shift should be that portion of the shift due to the unpaired electrons in the metal ion orbitals and the contact shift should be defined as that portion of the shift due to electrons in the ligand part of the molecular orbital. *We shall be using this operational definition to make comparison between experiment and theory easier.* In some instances therefore, the label "contact shift" may be inaccurate but we will continue to use it in this paper. This definition of the two terms will not necessarily bring experiment and theory perfectly together, however, since the experimental separation into contact and dipolar shifts assumes the only geometrical dependence to be that of the position of the nucleus relative to the central metal ion, whereas the ligand atoms contribution to the shift from the A_D and A_L terms will have a dependence upon the position of the nucleus relative to the ligand rather than to the central metal ion.

The contact shift arises from the hyperfine interaction terms coming from the antibonding molecular orbitals, MOs, that

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(10) Golding, R. M. *Mol. Phys.* **1964**, *8*, 561.
(11) Golding, R. M.; Halton, M. P. *Aust. J. Chem.* **1972**, *25*, 2577.
(12) McGarvey, B. R. *J. Chem. Phys.* **1976**, *65*, 962.
(13) McGarvey, B. R. *J. Am. Chem. Soc.* **1972**, *95*, 1103.
(14) Knorr, R.; Polzer, H.; Bischler, E. *J. Am. Chem. Soc.* **1975**, *97*, 643.
(15) Knorr, R.; Weiss, A.; Polzer, H.; Bischler, E. *J. Am. Chem. Soc.* **1975**, *97*, 644.
(16) Knorr, R. Institute for Organic Chemistry, University of Munich, private communication.
(17) Schäffer, C. E. *Struct. Bonding*, **1968**, *5*, 68; *Theor. Chim. Acta* **1966**, *4*, 166.
(18) Gerloch, M.; Manning, M. R. *Inorg. Chem.* **1981**, *20*, 1051.

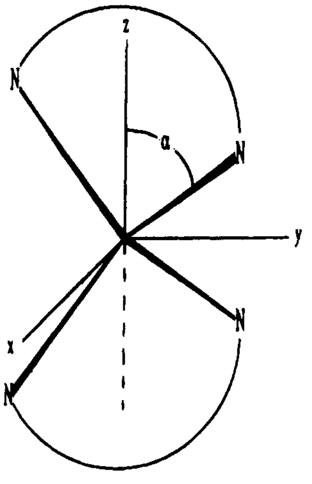

Figure 1. Coordinate system used for pseudotetrahedral complexe with D_{2d} symmetry.

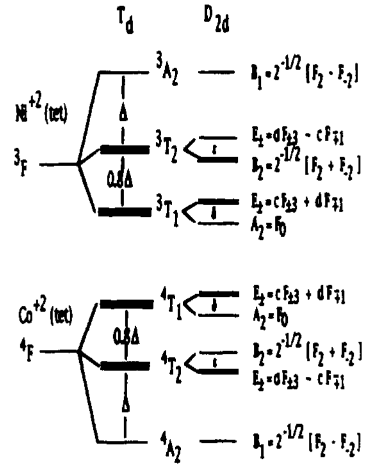

Figure 2. Ligand field energy levels for Ni^{2+} (d^8) and Co^{2+} (d^7) in T_d and D_{2d} symmetries before application of the spin–orbit interaction.

contain delocalized spin from the metal atom. Earlier treatments made the untenable assumption that unpaired spin in every d orbital was equally transferable to any molecular orbital in the ligand and therefore underestimated the spin density in a particular MO. In the distorted tetrahedral system we shall demonstrate that there are three types of d orbitals (d_0, $d_{\pm1}$, and $d_{\pm2}$) all of which interact in both the σ and π fashion but with different ligand molecular orbitals, MOs. Thus there are three types of π interaction for the D_{2d} bidentate complexes we are considering. When calculating the contact shift, we must sum over the three types of spin transfer to obtain the total contact shift.

Since the d orbitals have differing hyperfine interaction constants as well as differing Zeemann matrix elements, we must write for the ith orientation of the magnetic field

$$(\Delta H/H_0)_{Ci} = -\sum_n F_{ni}A_{ni} \tag{15a}$$

in which the summation is over the five d orbitals. The average shift in solution is

$$(\Delta H/H_0)_C = -\sum_n (F_{nx}A_{nx} + F_{ny}A_{ny} + F_{nz}A_{nz})/3 \tag{15b}$$

Equation 6 was obtained by assuming (1) that the hyperfine interaction term A_{ni} was identical for all d orbitals and could be factored out in eq 15a and (2) the hyperfine interaction was isotropic, so that $F = \sum_n(F_{nx} + F_{ny} + F_{nz})/3$. Actually, in most papers it was further assumed that $\sum_n F_{ni}$ was isotropic, because only the z component was ever calculated. We shall see in the following sections, that the hyperfine term is not isotropic for even the ligand protons and, since the F_{ni}'s are not isotropic for the distorted complexes we are discussing, the anisotropic portion of the hyperfine constant can contribute to the average shift observed. Thus the so-called "contact shift" can have anisotropic contributions.

Ni(II) D_{2d} Distorted Tetrahedral Complexes. Most of the complexes studied involve conjugated bidentate ligands for which we will assume a D_{2d} symmetry, and the coordinate system chosen is that given in Figure 1. Because we are in the weak field case, the starting wave functions will the ionic $|LM_LSM_S\rangle$ functions. In tetrahedral symmetry the ^3F state is split into three states, $^3A_2$, $^3T_1$, and $^3T_2$, with the ground state being $^3T_1$. For a D_{2d} distortion the $^3T_1$ and $^3T_2$ states are further split as shown in Figure 2. Our earlier calculation used a crystal field approach, which appeared appropriate for tetrahedral complexes which have rather small values of $10Dq$, using first and second order perturbation methods to calculate the effect of the spin–orbit interaction. This time we shall do an almost complete crystal field plus spin–orbit calculation over all the ^3F and ^3P states of the d^8 configuration of Ni(II). In the earlier work a traditional crystal field approach, which assumes an electric potential generated by point charges, was used. This time we will use the AOM (Atomic Overlap Method)[17–19] semiempirical approach to assign individual orbital energies. This approach allows us to use parameters more directly related to the ligand field method and to recognize the nonpointlike symmetry about the bonding ligand atoms due to asymmetries in the π bonding. This will not be a complete calculation because there are matrix cross terms from the spin–orbit interaction between the triplet states and some singlet states which we will be ignoring. For this calculation we will use the hole formalism to simplify our equations. In this formalism, the d^8 Slater determinants are replaced by d^2 holes which are considered to have a positive charge which changes the sign of the crystal field parameter. Thus the $|LM_LSM_S\rangle = |3311\rangle$ function of the ^3F state which has the Slater determinant function of $d_2^+d_2^-d_1^+d_1^-d_0^+d_0^-d_{-1}^+d_{-2}^+$ is represented by $d_2^+d_1^+$, which gives the same sign for M_L and M_S but the wrong sign for the spin–orbit terms. Thus we must change the sign for the crystal field and spin–orbit terms but can keep the same sign for the spin and angular momentum terms in the calculation.

The starting basis set for the calculation are the $|LM_LSM_S\rangle$ functions for ^3F and ^3P states. The ^3F functions for $M_S = 1$ are

$$\begin{aligned}
|3, 3, 1, 1\rangle &= d_2^+d_1^+ \\
|3, 2, 1, 1\rangle &= d_2^+d_0^+ \\
|3, 1, 1, 1\rangle &= \sqrt{0.4}\, d_1^+d_0^+ + \sqrt{0.6}\, d_2^+d_{-1}^+ \\
|3, 0, 1, 1\rangle &= \sqrt{0.8}\, d_1^+d_{-1}^+ + \sqrt{0.2}\, d_2^+d_{-2}^+ \\
|3, -1, 1, 1\rangle &= \sqrt{0.4}\, d_0^+d_{-1}^+ + \sqrt{0.6}\, d_1^+d_{-2}^+ \\
|3, -2, 1, 1\rangle &= d_0^+d_{-2}^+ \\
|3, -3, 1, 1\rangle &= d_{-1}^+d_{-2}^+
\end{aligned} \tag{16}$$

and for the ^3P state the functions are

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(19) Larsen, E.; LaMar, G. N. *J. Chem. Educ.* **1974**, *51*, 633.

$$|1,1,1,1\rangle = \sqrt{0.6}\mathrm{d}_1{}^+\mathrm{d}_0{}^+ - \sqrt{0.4}\mathrm{d}_2{}^+\mathrm{d}_{-1}{}^+$$

$$|1,0,1,1\rangle = \sqrt{0.2}\mathrm{d}_1{}^+\mathrm{d}_{-1}{}^+ - \sqrt{0.8}\mathrm{d}_2{}^+\mathrm{d}_{-2}{}^+ \qquad (17)$$

$$|1,-1,1,1\rangle = \sqrt{0.6}\mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+ - \sqrt{0.4}\mathrm{d}_1{}^+\mathrm{d}_{-2}{}^+$$

To calculate the AOM energies and the individual F_n terms in eq 15 we must consider how each d_m orbital bonds and transfers spin to the ligand MOs. First, we consider the $d_{\pm1}$ orbitals which are an equal mixture of d_{xz} and d_{yz} orbitals, each of which is in the plane of one ligand and perpendicular to the plane of the other ligand. Thus $d_{\pm1}$ is equally effective in σ bonding and π bonding. In aromatic ligands the MO must have the p orbitals on the two bonding ligand atoms pointing in the same direction. Hence the π MOs must have an even number of nodes and we label these the (+) symmetry MOs. Conversely the σ MOs interacting with $d_{\pm1}$ must have an odd number of nodes. The $d_{\pm1}$ orbitals, therefore, are significant σ and π donors to the ligand MOs. Second, we consider the $d_{\pm2}$ orbitals, which are equal mixtures of the d_{xy} and $d_{x^2-y^2}$ orbitals. The first can form bonds with both ligands in which the σ MOs have an even number of nodes in the ligand and the second can form π bonds with MOs having an odd number of nodes which we will label as (−) type MOs in both ligands. The $d_{\pm2}$ orbitals, therefore, can be σ and π donors to a different set of ligand MOs. This classification of π MOs in conjugated bidentate ligands has been proposed before in our earlier paper[3] and by Orgel.[20] Orgel and others designated the (+) orbitals by the symbol ψ and the (−) orbitals by χ. We found these symbols to be confusing, since χ is normally used for magnetic susceptibility, and have not used them in this paper.

Finally, we consider the d_0 orbital. This orbital can contribute to the in-plane π bonding and to a σ bonding, if the bond angles are not close to the tetrahedral values. In-plane π bonding is not considered to be important in these complexes and σ bonding becomes important only at angles far from tetrahedral, so we might assume that this orbital is unimportant for calculating spin delocalization. More to the point, we will show below that this orbital does not contribute in a significant manner to the paramagnetic shift in either nickel(II) or cobalt(II) tetrahedral complexes, even if there were a sizable covalent interaction between this orbital and the ligand MOs.

We therefore set out to calculate the F term for contact shifts separately for the $d_{\pm1}$, $d_{\pm2}$, and d_0 orbitals assuming for the $d_{\pm1}$ and $d_{\pm2}$ orbitals that half went to some sort of π antibonding MOs and half to σ antibonding MOs. These will be labeled F_+ for $d_{\pm1}$, F_- for $d_{\pm2}$, and F_0 for d_0, respectively. In addition, we also have calculated an F_A term in which it was assumed all five d orbitals are equally efficient in transferring spin into the ligand orbitals, which is what previous treatments have assumed. The value of F_A will differ from what eq 8 will give because we have included the Zeeman mixing terms which were ignored in earlier work using this equation. F_A should be equal to $(2F_+ + 2F_- + F_0)$.

The Hamiltonian operator is

$$\mathcal{H} = \mathcal{V}_L + \mathcal{H}_{LS} \qquad (18)$$

where $\mathcal{V}_L$ is the crystal field operator and $\mathcal{H}_{LS} = -\lambda L\cdot S$ is the spin−orbit interaction with λ a positive parameter. Using AOM, the $\mathcal{V}_L$ matrix elements for d_m orbitals are

$$\langle d_0|\mathcal{V}_L|d_0\rangle = (3\cos^2\alpha - 1)e_\sigma + 12\sin^2\alpha\cos^2\alpha\, e_\pi\text{(in-plane)} \qquad (19a)$$

$$\langle d_{\pm1}|\mathcal{V}_L|d_{\pm1}\rangle = 6\sin^2\alpha\cos^2\alpha\, e_\sigma + (8\cos^4\alpha - 6\cos^2\alpha + 1)e_\pi(+) \qquad (19b)$$

$$\langle d_{\pm2}|\mathcal{V}_L|d_{\pm2}\rangle = 1.5\sin^4\alpha\, e_\sigma + 2\sin^2\alpha\, e_\pi(-) + 2\sin^2\alpha\cos^2\alpha\, e_\pi\text{(in-plane)} \qquad (19c)$$

$$\langle d_{\pm2}|\mathcal{V}_L|d_{\mp2}\rangle = -1.5\sin^4\alpha\, e_\sigma + 2\sin^2\alpha\, e_\pi(-) - 2\sin^2\alpha\cos^2\alpha\, e_\pi\text{(in-plane)} \qquad (19d)$$

The angle α shown in Figure 1 is half the bite angle of the bidentate ligand, e_σ is the σ bonding parameter in AOM, e_π(in-plane) is the π bonding parameter for the ligand p orbitals in the plane of the bidentate ligand, $e_\pi(+)$ is the π bonding parameter for ligand π MOs with an even number of nodes, and $e_\pi(-)$ is the π bonding parameter for ligand π MOs with an odd number of nodes. In the calculation the 30 × 30 matrix for the ^3F and ^3P functions separates into two 8 × 8 and two 7 × 7 matrices. The diagonalization of these matrices give the energies and wave functions that are used in eqs 9−14 to calculate the paramagnetic shifts. A crude approximation to covalency is added by introduction of reduction factor k such that $\lambda = k\lambda_0$ and $\mu_i = -\beta_e(kL_i + 2S_i)$ with λ_0 being the free ion value.

Co(II) D_{2d} Distorted Tetrahedral Complexes. The approach here is much the same, since the ground state of Co(II) is ^4F which in tetrahedral symmetry splits in to $^4A_2$, $^4T_1$, and $^4T_2$ states. The main difference from Ni(II) is the $^4A_2$ ground state. The energy levels for a D_{2d} distortion of Co(II) is shown in Figure 2. As for Ni(II) the contribution of the ^4P state is included in the Co(II) calculations. The $|LM_L,{}^3/_2,{}^3/_2\rangle$ functions for the ^4F state in terms of the three-hole model are given below:

$$|3, 3, {}^3/_2, {}^3/_2\rangle = \mathrm{d}_2{}^+\mathrm{d}_1{}^+\mathrm{d}_0{}^+$$

$$|3, 2, {}^3/_2, {}^3/_2\rangle = \mathrm{d}_2{}^+\mathrm{d}_1{}^+\mathrm{d}_{-1}{}^+$$

$$|3, 1, {}^3/_2, {}^3/_2\rangle = \sqrt{0.4}\,\mathrm{d}_2{}^+\mathrm{d}_1{}^+\mathrm{d}_{-2}{}^+ + \sqrt{0.6}\,\mathrm{d}_2{}^+\mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+$$

$$|3, 0, {}^3/_2, {}^3/_2\rangle = \sqrt{0.8}\,\mathrm{d}_2{}^+\mathrm{d}_0{}^+\mathrm{d}_{-2}{}^+ + \sqrt{0.2}\,\mathrm{d}_{1+}\mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+ \qquad (20)$$

$$|3, -1, {}^3/_2, {}^3/_2\rangle = \sqrt{0.4}\,\mathrm{d}_2{}^+\mathrm{d}_{-1}{}^+\mathrm{d}_{-2}{}^+ + \sqrt{0.6}\,\mathrm{d}_1{}^+\mathrm{d}_0{}^+\mathrm{d}_{-2}{}^+$$

$$|3, -2, {}^3/_2, {}^3/_2\rangle = \mathrm{d}_1{}^+\mathrm{d}_{-1}{}^+\mathrm{d}_{-2}{}^+$$

$$|3, -3, {}^3/_2, {}^3/_2\rangle = \mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+\mathrm{d}_{-2}{}^+$$

The $|LM_LS,{}^3/_2$ functions for the ^4P state are

$$|1, 1, {}^3/_2, {}^3/_2\rangle = \sqrt{0.6}\,\mathrm{d}_2{}^+\mathrm{d}_1{}^+\mathrm{d}_{-2}{}^+ - \sqrt{0.4}\,\mathrm{d}_2{}^+\mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+$$

$$|1, 0, {}^3/_2, {}^3/_2\rangle = \sqrt{0.2}\,\mathrm{d}_2{}^+\mathrm{d}_0{}^+\mathrm{d}_{-2}{}^+ - \sqrt{0.8}\,\mathrm{d}_1{}^+\mathrm{d}_0{}^+\mathrm{d}_{-1}{}^+ \qquad (21)$$

$$|1, -1, {}^3/_2, {}^3/_2\rangle = \sqrt{0.6}\,\mathrm{d}_2{}^+\mathrm{d}_{-1}{}^+\mathrm{d}_{-2}{}^+ - \sqrt{0.4}\,\mathrm{d}_1{}^+\mathrm{d}_0{}^+\mathrm{d}_{-2}{}^+$$

In this calculation the 40 × 40 matrix for the ^4F and ^4P functions can be separated into one 20 × 20 and two 10 × 10 matrices. The only difference from our Ni(II) calculation is due to the Co(II) having an EPR active ground site, and therefore we have calculated the spin Hamiltonian parameters of this state.

Dipolar Contribution to the Contact Shift. We will show here for the proton shift that if the F term in eq 8 is anisotropic then a dipolar term in the hyperfine term A will not be averaged

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(20) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683.

Table 1. Parameters Used in the Calculations

	Ni(II)	Co(II)
e_σ (cm^{-1})	4500	4500
$e_\pi(+)$ (cm^{-1})	400	400
$e_\pi(-)$ (cm^{-1})	0	0
e_π(in-plane) (cm^{-1})	0	0
λ (cm^{-1})	315	172
k	0.6	0.9
α (deg)	47.4	48.7
B (cm^{-1})	650	900
χ(calc) × 10^{27} (emu/molecule)	7.27	12.9
χ(expt) × 10^{27} (emu/molecule)	7.5[a]	12.0[a]
DP(calc) × 10^{27} (cm^3)	−1.19	0.60
DP(expt) × 10^{27} (cm^3)	−0.8[b]	1.0[b]

[a] Reference 21. [b] Reference 16.

out and will make a contribution to the contact shift. We shall first discuss the case of delocalization in a π aromatic MO. The spin centered on the adjacent carbon atom in a aromatic π MO will generate an anisotropic hyperfine interaction constant of the form

$$A_z + Q\rho_i + Q_d(3\cos^2\beta - 1)\rho_i$$

$$A_x = Q\rho_i + Q_d(3\sin^2\beta - 1)\rho_i \tag{22}$$

$$A_y = Q\rho_i - Q_d\rho_i$$

$$Q_d = g_e\beta_e/R_{CH}{}^3$$

where β is the angle between the R_{CH} vector and the z (parallel) axis of the complex and ρ_i is the spin density in a p orbital of the carbon atom bonded to the hydrogen atom. The y direction is taken to be perpendicular to the ligand plane. The first term in the hyperfine interaction is the familiar McConnell[9] relation and the Q parameter generally has values of −22.5 to −27 G (as measured by the electron magnetic moment) while Q_d is approximately 23 to 28 G for R_{CH} = 1.08−1.00 Å. Putting the hyperfine terms of eq 22 into eq 15b we obtain for the average contact shift

$$(\Delta H/H_0)_C = -F_{av}Q\rho_i - \mathrm{FD}(3\cos^2\beta - 1)Q_d\rho_i \tag{23a}$$

$$F_{av} = \{(F_{\parallel} + 2F_{\perp})/3\} \qquad \mathrm{FD} = \{(F_{\parallel} - F_{\perp})/3\} \tag{23b}$$

If the FD term becomes appreciable compared to the F_{av} term, then the dipolar contribution to the so-called contact shift cannot be ignored. A similar dipolar term should occur for ^{13}C NMR shifts but will be more complex in form due to the spin contributions from several atom centers.

To avoid too many subscripts, we will be using in the rest of this paper the symbols F_A, F_+, F_-, and F_0 to represent the average of the respective F terms as defined in eq 23b and FD$_A$, FD$_+$, FD$_-$, and FD$_0$ to represent the respective anistropic terms.

Because the calculation assumed the spin to be a point dipole, there would be a similar term to the second term in eq 23a for σ delocalization except ρ_i would refer instead to the spin density in the σ orbital on the carbon atom. The effective magnitude of the Q term could be much larger for σ MOs so that the dipolar term may not be significant, in those cases where σ delocalization is evident mainly due to the rather large magnitude of the observed shift.

Results

The parameters used in the computations are displayed in Table 1. The AOM parameters were chosen after examining spectral studies of related complexes in the literature[18,21−23] and the spin−orbit parameters for the free ion were taken from Figgis.[24] The values of the orbital reduction factor were chosen to get reasonable agreement between the calculated paramagnetic susceptibility and experimental values reported in the literature[21] and this is the reason for the rather low value of k for tetrahedral Ni(II). Higher values of k gave much larger values for the susceptibility than are reported in the literature for tetrahedral Ni(II) complexes.[25−29] Much of the literature we have examined have reported their results in terms of the magnetic moment or g value of the ground state. There seems to be little recognition of the fact that the ground state of these tetrahedral complexes of Ni(II) is not degenerate and can have no magnetic moment or g value and that the main source of the magnetic susceptibility comes from Zeeman mixing of excited states with the ground state. The α values are from X-ray diffraction studies on type **I** complexes.[16] The electronic repulsion parameter B for Ni(II) was chosen smaller than the ionic value in line with the smaller value of k but the value for Co(II) was chosen to be closer to the ionic value. The results of the calculations were influenced very little by the magnitude of B chosen, particularly for the case of Co(II). Leaving out the P state in the calculation affected the results by less than 10% for Ni(II) and less than 0.5% for Co(II).

The calculated and experimental values of the average susceptibility and the dipolar shift parameter DP at 300 K are also given in Table 1. The agreement with experiment of DP, including the sign, for the Co(II) and Ni(II) complexes appears to be satisfactory, considering the errors implicit in the separation techniques used to obtain the dipolar shift from the total observed shift.

Since the ground state of the cobalt(II) is EPR active, the program also calculates the spin Hamiltonian. For the $S = {}^3/_2$ spin state the complete spin Hamiltonian is

$$\mathscr{H} = \beta_e(g_{\parallel}H_zS_z + g_{\perp}H_xS_x + g_{\perp}H_yS_y) + D[S_z{}^2 - S(S+1)/3] + u(z)T^0(z)H_z + u(x)[T^0(x)H_x + T^0(y)H_y] + u^2(x)[T^2(x)H_x + T^2(y)H_y]$$

$$T^0(z) = S_z{}^3 - (1/5)[3S(S+1) - 1]S_z \tag{24}$$

$$\mathrm{T}^2(x) = S_x(S_y{}^2 - S_z{}^2) + (S_y{}^2 - S_z{}^2)S_x$$

The calculated parameters of the spin Hamiltonian are as follows: $g_{\parallel} = 2.2477$; $g_{\perp} = 2.1569$; $D = -7.5717$ cm^{-1}; $u(z) = -0.002548$ cm^{-1}; $u(x) = -0.000773$ cm^{-1}; $u^2(x) = 0.000037$ cm^{-1}. To our knowledge, no EPR has been reported for cobalt(II) complexes of this type to which we can compare these results. We shall make use of these parameters later when we compare our results with those obtained from the earlier equations, eqs 1−6, which require a knowledge of the spin-Hamiltonian parameters.

Before we discuss the results, it is essential to understand how sensitive the various quantities we are calculating are to the N−M−N bond angle of the bidentate ligand. In Figure 3

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(21) Richard, C. P.; Webb, G. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3459.

(22) Schäffer, C. E. *Pure Appl. Chem.* **1970**, *24*, 361.

(23) Horrocks, W. D. *Inorg. Chem.* **1974**, *13*, 2775.

(24) Figgis, B. N. *Introduction to Ligand Fields*; John Wiley & Sons: New York, 1966; p 60.

(25) LaMar, G. N.; Horrocks, W. D.; Allen, L. C. *J. Chem. Phys.* **1964**, *41*, 2126.

(26) Holm, R. H.; Chakravorty, A.; Dudek, G. O. *J. Am. Chem. Soc.* **1964**, *86*, 379.

(27) Chakravorty, A., Holm, R. H. *Inorg. Chem.* **1964**, *3*, 1010.

(28) Eaton, D. R.; LaLancette, E. A. *J. Chem. Phys.* **1964**, *41*, 3534.

(29) Horrocks, W. D.; Greenberg, E. S. *Inorg. Chem.* **1971**, *10*, 2190.

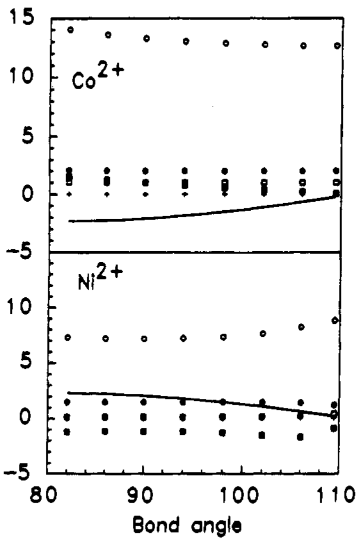

Figure 3. Various results calculated for different bite angles (2α as defined in Figure 1). Key: solid line, δ in $10^3 \times \mathrm{cm}^{-1}$; open circle: magnetic atomic susceptibility $\chi \times 10^{27}$; solid circle, $F_+ \times 10^7$; open square: $F_- \times 10^7$; plus sign, $F_0 \times 10^7$; solid square, dipolar shift parameter DP $\times 10^{27}$.

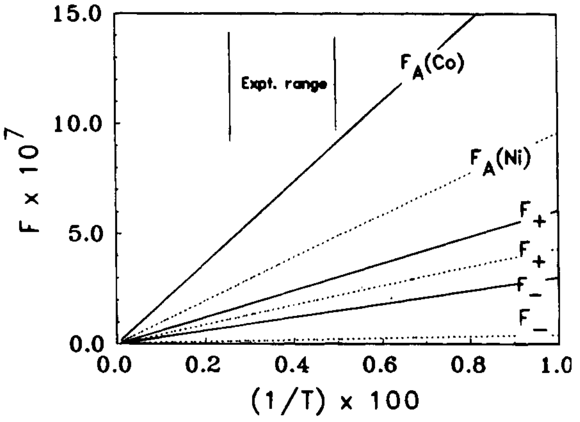

Figure 4. F parameters *vs* reciprocal temperature. Solid lines are for Co(II), and dotted lines are for Ni(II).

we present a graph of δ, $F_\pm$, F_0, χ and DP calculated for 300 K as a function of the N−M−N bite angle. As expected the electronic splitting of the T_1 state, δ, which is defined in Figure 2 varies smoothly with angle and becomes small when the angle is the tetrahedral angle of 109.74°. It should be noted that it does not go to zero due to the π anisotropy imposed by our model at the nitrogen atom, and this is very apparent for the case of nickel(II). The dipolar shift term, DP, varies smoothly toward zero as the angle approaches the tetrahedral value, but the same is not true for nickel(II). The difference in behavior is due to the large sensitivity to distortion of the $^3T_1$ ground state of Ni(II), while the $^4A_2$ ground state of Co(II) is affected only to second order by any distortions. The contact terms, $F_\pm$ and F_0, change very little with angle and the magnetic susceptibility, χ, changes only slightly over the most relevant range of 90−100°.

The calculated parameters F_A, F_+, and F_- are plotted as a function of the reciprocal Kelvin temperature in Figure 4 and the respective anisotropic parameters FD_A, FD_+, and FD_- are plotted in Figure 5. The F_0 and FD_0 terms are not plotted since they are essentially zero in these plots. The temperature dependence of the cobalt (II) terms is strictly linear with respect to T^{-1} down to low temperatures. The temperature dependence of Ni(II) appears to be nearly linear in the figure, but at even lower temperatures it tends to a constant value. This is to be expected for a system whose ground state is not magnetic. At very low temperatures, the higher magnetic states are no longer populated, the only paramagnetism comes from the Zeeman mixing of excited states with the ground state, and this term is temperature independent.

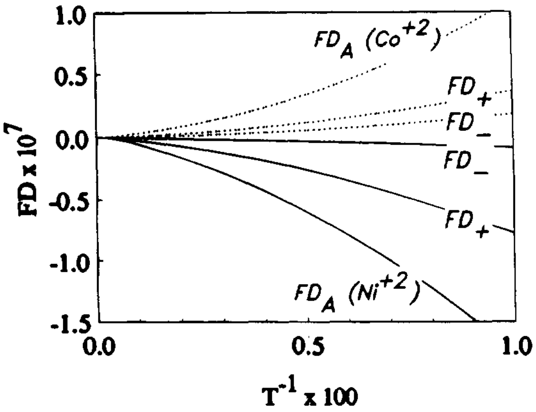

Figure 5. FD parameters *vs* reciprocal temperature. Solid lines are for Ni(II), and dotted lines are for Co(II).

It should be noted that the magnitudes of the actual delocalization parameters F_+, F_- and F_0 are smaller than the parameter F_A which assumes that delocalization takes place equally through all d orbitals. The ratio (F_+/F_A) is 0.453 for nickel(II) and 0.332 for cobalt(II). The respective values for (F_-/F_A) are 0.046 and 0.167 and for (F_0/F_A) are 0.003 and 0.001. For Ni(II) it is clear that the paramagentic shift is sensitive only to delocalization of spin through the $d_{\pm 1}$ orbital since F_- is 1 order of magnitude smaller than F_+ and F_0 is 2 orders of magnitude smaller. For Co(II), delocalization is most important for $d_{\pm 1}$ as it is for Ni(II) but since F_- is about one-half of F_+, delocalization through $d_{\pm 2}$ orbitals will also have some influence on the paramagnetic shift. Again the F_0 parameter is too small to be of any importance.

It is of interest to see how our value of F_A compares to that predicted by eq 6, which is the one most often used in the literature. At 300 K $F_A = 6.107 \times 10^{-7}$ for cobalt(II) and eq 6 gives 6.12×10^{-7} for $g = 2.187$ (average of calculated g values listed above) and for nickel(II) $F_A - 3.288 \times 10^{-7}$ and eq 6 gives 3.28×10^{-7} for a fictitious $g = 2.2$ and $S = 1$. The agreement for cobalt(II) is not surprising since the $^4A_2$ ground state of cobalt(II) is just the type of state for which the equation was derived, but the agreement for nickel(II) appears to be fortuitous.

The anisotropic term FD is plotted in Figure 5. The magnitude of FD for nickel(II) is more than double that of cobalt(II) and, since F for nickel(II) is half that found for cobalt(II), the dipolar contribution to the proton contact shift in π MOs as given by eq 12 is much more important for nickel(II) complexes. If the angle β is 0°, we estimate the magnitude of the dipolar contribution could be 20−25% that of the Fermi contact term. This is not a term to be ignored for those protons for which β is near 0° or 90°. Although we have not set up the equations, it seems clear that a similar dipolar contribution should be important for ^{13}C shifts. It is of interest to note that the temperature dependence of FD is not T^{-1} even though the temperature dependence of F is T^{-1}.

The dipolar shift parameter DP is plotted as a function of the reciprocal Kelvin temperature in Figure 6. The predicted signs of DP are confirmed experimentally for both nickel(II) and cobalt(II). The temperature dependence is definitely not linear for either cobalt(II) or nickel(II). The nonlinear dependence for cobalt(II) is mainly due to the large zero-field parameter D and was predicted by Kurland and McGarvey.[3]

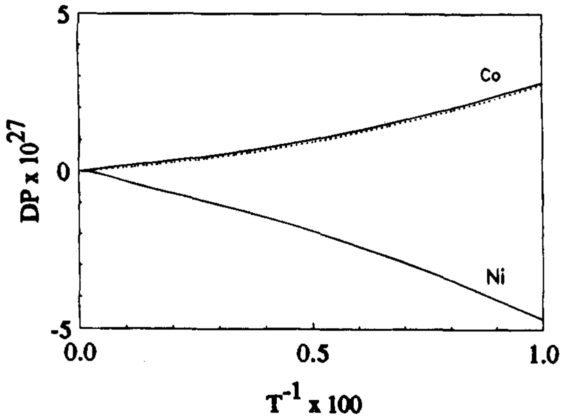

Figure 6. Dipolar shift parameter DP *vs* reciprocal temperature. Dotted line was calculated from equations in ref 3 using zero-field parameters calculated in this work.

Included in Figure 6 is a plot of DP as predicted by their equations. The small difference is due to the inclusion of contributions of the higher electronic states in the present calculation. Since the bulk of the measured shifts is due to the contact shift, this nonlinearity with respect to T^{-1} will not be detected experimentally.

Discussion

The standard method of spin delocalization is for the ligand to donate a pair of electrons into a covalent bonding MO made up of the appropriate ligand and d orbitals with the unpaired electrons on the metal going into the related antibonding MO. One would expect the HOMO MO to be most involved in this transfer with lesser delocalization involving the more stable lower energy MOs. Back-donation into the LUMO orbital is a lesser possibility since this transfer would make the metal ion higher in charge rather than lower and should only occur where there is excessively large charge transfer from the filled ligand orbitals to the metal ion. We have found that the paramagnetic shift of Ni(II) is sensitive only to π MOs with an even number of nodes, which we have designated with the (+) symbol. It is not surprising, therefore that early investigations[26,30-32] of the paramagnetic shift in tetrahedral Ni(II) complexes of the aminotroponeimineates, salicylaldehydeamines, and β-keto amines found that the shifts for nuclei several bonds away from the nickel ion, where only π delocalization of spin would be important, were proportional to the spin distribution of an unpaired electron in the HOMO MO. All of these ligands have a (+) HOMO state. Eaton and LaLancette[33] in their study of the pyrromethenes, which have a (−) HOMO, interpreted the results in terms of spin delocalization into the LUMO orbital. More likely we can interpret the smaller shifts as coming from delocalization involving one of the lower filled (+) MOs, since the paramagnetic shift is insensitive to the delocalization in the (−) HOMO. One important feature coming from our analysis is that *the spin densities reported in the earlier literature are too small by a factor greater than two* since F_+ is less than half of the F_A value that they used in their calculations.

For tetrahedral Co(II) complexes the situation is similar to Ni(II) in that F_0 is negligible and F_+ is largest, but F_- in this case is half that of F_+. Thus the paramagnetic shift in the tetrahedral Co(II) complexes is more sensitive to spin delocalization in (+) symmetry MOs, but is also influenced by spin delocalization in (−) symmetry MOs to a greater extent than is the case for Ni(II) complexes. It is noteworthy that F_A, F_+, and F_- are all larger for Co(II), so one would expect larger shifts in Co(II) complexes than Ni(II) complexes if spin delocalization were equivalent. The Co(II)/Ni(II) ratios are 1.858, 1.364, and 6.797, respectively, for F_A, F_+, and F_- at 300 K.

The Co(II) and Ni(II) complexes of type **I** have a HOMO π MO of (+) symmetry for the ligand. This is the expected MO for spin delocalization in the outer rings of the ligand, but σ delocalization could be important in the inner ring, which includes the metal ion, itself. The average reported shift[16] at 300 K for the proton situated para to the metal ion is reported to be 105 ppm for Ni(II) and 108 ppm for Co(II), while the corresponding proton shifts for the meta position are −382 and −456 ppm, respectively. If we were to assume that only π spin delocalization were present in this inner ring, we could use eq 23 to calculate the spin densities ρ_i at each site. Assuming $Q = -22.5$ G and $Q_d = 28$ G and using our calculated values of F_+ and FD_+ we obtain for the para position ρ_i values of 0.038 and 0.034 for Ni(II) and Co(II), respectively. For the meta position the same calculation gives ρ_i values of −0.192 and −0.158 for Ni(II) and Co(II), respectively, which are unrealistic and must indicate that σ delocalization must dominate at the meta position in the inner ring.

The results for the calculated values of ρ_i for the para position are reasonable, and we shall argue here that indeed only π delocalization should be detected at the para position. We have shown that for Ni(II) complexes, only delocalization from the $d_{\pm 1}$ orbitals will affect the paramagnetic shift and for Co(II) complexes this delocalization will dominate the shift. We have further shown that the symmetry of the σ ligand MOs must have an odd number of nodes. An odd number of nodes requires no spin density at the para position, so it is unlikely that σ delocalization will cause any paramagnetic shift for the proton at the para position in the ring. This can be confirmed by using the proton shifts of the methyl group attached at the para position. The reported CH_3 shifts at 300 K are −94 ppm for Ni(II) and −83 ppm for Co(II). Using $Q = 25$ G for methyl groups and assuming FD_+ is not important due to the larger distances gives ρ_i for Ni(II) of 0.038 and for Co(II) of 0.025. These values are essentially identical to the values found from the proton shifts and support our contention that the para shifts are influenced only by π delocalization.

The Co(II)/Ni(II) ratio for the paramagnetic shift is predicted to be 1.18 for the para proton and 1.36 for the meta proton if spin delocalization is identical in the two complexes. The experimental values are 1.0 for the para position and 1.19 for the meta position. In general the ratio is found to be 1.1 ± 0.1 for the proton shifts in all complexes observed.[16] The same ratio was observed for ^{13}C shifts also. The larger delocalization for the Ni(II) complexes is consistent with the fact that we had to assume a smaller orbital reduction coefficient for the Ni(II) complexes. The difference in delocalization of spin, however, suggests a difference in covalency of the two complexes that is less than that suggested by the *k* values. It is of course true that the paramagnetic shift is only measuring spin delocalization in certain MOs.

Conclusions

The theory of the NMR paramagnetic shift of pseudotetrahedral complexes for Ni(II) and Co(II) has been developed and applied to experimental results for complexes using the same

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(30) Benson, R. E.; Eaton, D. R.; Josey, A. D.; Phillips, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 3714.

(31) Holm, R. H.; Chakravorty, A.; Dudek, G. O. *J. Am. Chem. Soc.* **1963**, *85*, 821.

(32) LaLancette, E. A.; Eaton, D. R.; Benson, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1962**, *84*, 3468.

(33) Eaton, D. R.; LaLancette, E. A. *J. Chem. Phys.* **1964**, *41*, 3534.

ligands. It has been shown that the shifts in the Ni(II) complexes are sensitive to delocalization of spin only from the metal $d_{\pm 1}$ orbitals. For Co(II) complexes, the shift is mainly due to the $d_{\pm 1}$ orbitals, but there could be a measurable effect from the $d_{\pm 2}$ orbitals. It has been further shown that the failure to recognize the differing spin delocalization of different metal d orbitals in previous analyses of paramagnetic shifts has lead to estimates of spin density in the ligands to be too small by a factor of 2.5 in Ni(II) complexes and 3.0 in Co(II) complexes.

It has also been discovered that the so-called contact shift is not isotropic, particularly for Ni(II) complexes, and this leads to a dipolar contribution for the average contact shift that could be significant for paramagnetic shifts that are primarily due to delocalization of spin in π aromatic MOs.

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