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Configuration Interaction Studies on Contact Shift and Contact Nuclear Spin-Spin Coupling in Paramagnetic Transition Metal Complexes

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The magnitude of the contact shift for hydrogen nuclei is directly related to the unpaired electron density, $\rho_{\rm H}$, on the proton. The mechanism by which the unpaired electrons transfer from the transition metal *d*-orbitals to the ligand orbitals is studied on the basis of the method of intergroup (ligand and metal) configuration interaction. The $\rho_{\rm H}$ is given as a sum of two terms, $\rho_{\rm H}^{\rm P}$ and $\rho_{\rm H}^{\rm D}$, due to the spin-polarization mechanism and the spin-delocalization mechanism respectively. When the interaction between metal and ligand is restricted to a localized bond N–M, such as nickel(II)-benzylamine, $\rho_{\rm H}^{\rm P}\simeq-(C_{\rm M}^{\rm m})^2|\chi_{\rm H}^{(0)}|^2\pi_{\rm HN}\langle{\rm NM}|{\rm NM}\rangle/3\simeq0.001-0.0001$ (Here $\pi_{\rm HN}$ is the mutual atom(H)-atom(N) polarizability.). When the interaction between metal and ligand is not restricted to a special localized bond, as in metalocene, $\rho_{\rm H}^{\rm P}\simeq-(C_{\rm M}^{\rm m})^2|\chi_{\rm H}^{(0)}|^2\ \pi_{\rm HH}\langle{\rm HM}|{\rm HM}\rangle/3\simeq0.01-0.001$. The spin delocalization term has the order of magnitude of: $\rho_{\rm H}^{\rm P}\simeq-(C_{\rm M}^{\rm m})^2(\beta_{\rm MN})^2|\chi_{\rm H}^{(0)}|^2(P_{\rm HN})^2/2(\delta{\rm E})^2$ (Here $P_{\rm HN}$ is the bond order between the H and N atomic orbitals.). If the proton H is not directly bonded to the atom N, $\rho_{\rm H}^{\rm D}\simeq0.0001$. If the proton H is directly bonded to the atom N, $\rho_{\rm H}^{\rm D}\simeq0.001$. By disregarding the contributions smaller than the order of magnitude $O(S^2)$, the formulation of the contact nuclear spin-spin coupling constant is derived. The most dominant term is identical with the formula which was derived by Pople and Santry for singlet free-ligand molecules.

The purpose of this paper is to report a study of the contact shift and the contact nuclear spin-spin coupling in paramagnetic transition metal complexes. The unpaired electrons which are formally in *d* orbitals of the transition metal are partly delocalized to the ligands. The mechanism by which the spin reaches the nuclei on the ligand is closely related to the geometry of the complex and the details of the metal-ligand bonding. Hence, a study of the mechanism of the contact shift and the contact nuclear spin-spin coupling will give us information about the metal-ligand bonding. The present study is based on the method of intergroup (ligand and metal) configuration interaction. This method has the advantage of fixing the attention on the dominant mechanism of the transfer of the unpaired electrons.

The effects of paramagnetism on nuclear resonance shifts have been recognized since the discovery of the nuclear magnetic resonance(NMR).[1] Resonance shifts in paramagnetic molecules can arise from certain electron-nucleus interactions.[2–4] The shifts in the NMR arising from electron spin-nuclear spin coupling are called contact shifts. The pseudocontact shift can arise when the complex is not magnetically isotropic.[2,3] We shall ignore the pseudocontact contribution for the sake of simplicity. The isotropic contact shift arises principally from the Fermi contact term,[5] which is proportional to the odd electron density at the nucleus.[6–8] The magnitude of the contact shift for hydrogen nuclei is thus directly related to the unpaired electron density in the hydrogen $1s$ orbital. For a paramagnetic system of spin, S, contact interactions between the spin of the unpaired electron and the nuclear spin of the proton lead to the shift of the NMR frequency given by[9,10]

$$\frac{\delta \mathbf{H}_{\mathrm{H}(i)}}{\mathbf{H}} = -A_{\mathrm{H}(i)} \frac{\gamma_e}{\gamma_{\mathrm{H}}} \frac{g\beta S(S+1)}{3kT}, \tag{1}$$

where $A_{\mathrm{H(i)}}$ is the electron spin-nuclear spin coupling constant for the ith hydrogen atom. A_{H} is related to the unpaired spin density, ρ_{H}, by[11]:

$$A_{\mathrm{H}} = a \times \rho_{\mathrm{H}} \qquad (\text{here } a = 1596[\text{gauss}])$$

In Eq. (1), $\mathbf{H}$ is the resonance field, $\delta\mathbf{H}_{\mathrm{H}(i)}$ is the resonance field shift for the ith proton, γ_e and γ_{H} are, respectively, magnetogyric ratios of the electron and the resonating proton, g is the electronic g factor, and β is the Bohr magneton.

Intergroup Configuration Interaction

In paramagnetic-transition-metal complexes, the unpaired electrons which are formally located in the transition metal are partly delocalized to the ligands. The discussion below is based on the method of intergroup (ligand and metal) configuration interaction. We will consider the self-consistent-field molecular orbitals (SCF MO's) for an individual group.

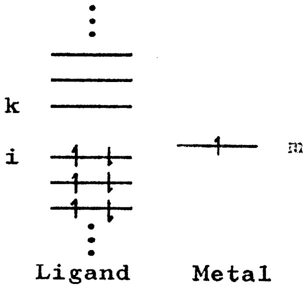

Fig. 1

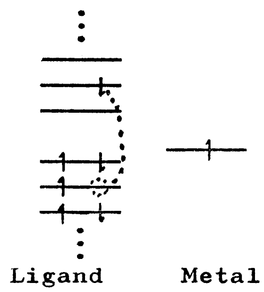

Fig. 2

Fig. 1. Configuration diagram for the lowest energy configuration.

Fig. 2. Configuration diagram for spin polalization mechanism.

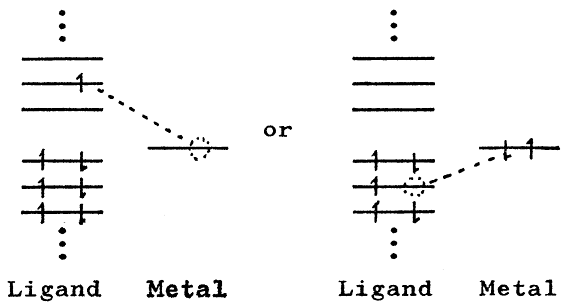

Fig. 3. Configuration diagrams for spin delocalization mechanism.

As an approximation to the configuration interaction problem for the paramagnetic transition metal complexes, we take the lowest energy state to be as shown in the configuration diagram (Fig. 1). The normalized wavefunction for this state is represented by:

$$\Phi_0 = |i\,\bar{i}\,m|, \tag{2}$$

where i denotes the occupied ligand orbitals and where m denotes the metal orbitals, hereafter, k denotes the vacant ligand orbitals. In these approximations, the charge-transferred states,

$$\Phi_{im} = |i\,\bar{m}\,m|, \tag{3}$$

$$\Phi_{mk} = |i\,\bar{i}\,k|, \tag{4}$$

and the singly-excited doublet states:

$$\Phi_{ik}(1) = (2|i\,k\,\bar{m}| - |i\,\bar{k}\,m| - |\bar{i}\,k\,m|)/\sqrt{6}, \tag{5}$$

$$\Phi_{ik}(2) = (|i\,\bar{k}\,m| - |\bar{i}\,k\,m|)/\sqrt{2}, \tag{6}$$

arise the delocalization of the unpaired electrons and spin polarization in the ligand. The doublet-state functions, Φ_o, Φ_{im}, Φ_{mk}, $\Phi_{ik}(1)$, and $\Phi_{ik}(2)$, are taken here as the basis of a variational calculation of the wavefunctions.

By the first-order perturbation approximation, the ground state wavefunction, ${}^2\Phi_g$ is found to be:

$$\begin{aligned} {}^2\Phi_g = \Phi_0 &+ \sum_i^{occ} \lambda_{im}\Phi_{im} + \sum_k^{vac} \lambda_{mk}\Phi_{mk} \\ &+ \sum_i^{occ}\sum_k^{vac} \lambda_{ik}^{(1)}\Phi_{ik}(1) + \sum_i^{occ}\sum_k^{vac} \lambda_{ik}^{(2)}\Phi_{ik}(2), \end{aligned} \tag{7}$$

where:

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1) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

2) N. Bloembergen and W. C. Dickenson, *ibid.*, **79**, 179 (1950).

3) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

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TABLE 1. THE MATRIX ELEMENTS OF $\langle {}^2\Phi_g | \rho_H | {}^2\Phi_g \rangle$ AND THE ORDER OF MAGNITUDE (O) ON S

Matrix elements	:the order of magnitude O
$\langle \Phi_0 \| \rho_H \| \Phi_0 \rangle = \langle m \| \rho_H \| m \rangle$	$:O(0)$
$\langle \Phi_0 \| \rho_H \| \Phi_{im} \rangle = -\langle i \| \rho_H \| m \rangle$	$:O(S_{im})$
$\langle \Phi_0 \| \rho_H \| \Phi_{mk} \rangle = \langle m \| \rho_H \| k \rangle$	$:O(S_{mk})$
$\langle \Phi_0 \| \rho_H \| \Phi_{ik}^{(1)} \rangle = 2\langle i \| \rho_H \| k \rangle/(6)^{1/2}$	$:O(1)$
$\langle \Phi_0 \| \rho_H \| \Phi_{ik}^{(2)} \rangle = 0$	$:O(0)$
$\langle \Phi_{im} \| \rho_H \| \Phi_{mk} \rangle = -\mathrm{S}_{mk}\langle m \| \rho_H \| i \rangle + \mathrm{S}_{mi}\langle m \| \rho_H \| k \rangle$	$:O(S_{mi}S_{mk})$
$\langle \Phi_{im} \| \rho_H \| \Phi_{i'm} \rangle = \langle i \| \rho_H \| i' \rangle$	$:O(1)$
$\langle \Phi_{im} \| \rho_H \| \Phi_{ik}^{(1)} \rangle = -\langle m \| \rho_H \| k \rangle/(6)^{1/2}$	$:O(S_{mk})$
$\langle \Phi_{im} \| \rho_H \| \Phi_{ik}^{(2)} \rangle = -\langle m \| \rho_H \| k \rangle/(2)^{1/2}$	$:O(S_{mk})$
$\langle \Phi_{mk} \| \rho_H \| \Phi_{mk'} \rangle = \langle k \| \rho_H \| k' \rangle$	$:O(1)$
$\langle \Phi_{mk} \| \rho_H \| \Phi_{ik}^{(1)} \rangle = \langle i \| \rho_H \| m \rangle/(6)^{1/2}$	$:O(S_{im})$
$\langle \Phi_{mk} \| \rho_H \| \Phi_{ik}^{(2)} \rangle = -\langle i \| \rho_H \| m \rangle/(2)^{1/2}$	$:O(S_{im})$
$\langle \Phi_{i'k'}^{(1)} \| \rho_H \| \Phi_{ik}^{(1)} \rangle : (i'=i,\ k'\neq k) = 2\langle k' \| \rho_H \| k \rangle/3$	$:O(1)$
$: (i'\neq i,\ k'=k) = 2\langle i' \| \rho_H \| i \rangle/3$	$:O(1)$
$: (i'=i,\ k'=k) = 2(\langle i \| \rho_H \| i \rangle + \langle k \| \rho_H \| k \rangle)$	$:O(1)$
$: (i'\neq i,\ k'\neq k) = 0$	$:O(0)$
$\langle \Phi_{i'k'}^{(1)} \| \rho_H \ \Phi_{ik}^{(2)} \rangle : (i'=i,\ k'\neq k) = \langle k' \| \rho_H \| k \rangle/(3)^{1/2}$	$:O(1)$
$: (i'\neq i,\ k'=\ ) = -\langle i \|{}_H\| i \rangle/(3)^{1/2}$	$:O(1)$
$: (i'=i,\ k'=k) = (\langle k \| \rho_H \| k \rangle - \langle i \| \rho_H \| i \rangle)/(3)^{1/2}$	$:O(1)$
$: (i'\neq i,\ k'\neq k) = 0$	$:O(0)$
$\langle \Phi_{i'k'}^{(2)} \| \rho_H \ \Phi_{ik}^{(2)} \rangle : (i'=i,\ k'\neq k) = 0$	$:O(0)$
$: (i'\neq i,\ k'=k) = 0$	$:O(0)$
$: (i'=i,\ k'=k) = 0$	$:O(0)$
$: (i'\neq i,\ k'\neq k) = 0$	$:O(0)$

$$\lambda_{im} = \frac{\langle \Phi_{im} | H | \Phi_0 \rangle}{\delta E_{im}}, \quad \lambda_{mk} = \frac{\langle \Phi_{mk} | H | \Phi_0 \rangle}{\delta E_{mk}},$$

$$\lambda_{ik}^{(1)} = \frac{\langle \Phi_{ik}^{(1)} | H | \Phi_0 \rangle}{\delta E_{ik}}, \quad \lambda_{ik}^{(2)} = \frac{\langle \Phi_{ik}^{(2)} | H | \Phi_0 \rangle}{\delta E_{ik}}.$$

Here,

$$\delta E_{im} = \langle \Phi_{im} | H | \Phi_{im} \rangle - \langle \Phi_0 | H | \Phi_0 \rangle, \tag{8}$$

$$H = H_L + H_M + H_{LM}. \tag{9}$$

H_L and H_M are Hamiltonians in an average effective field, which are due to the electrons in the ligand and the metal respectively. Since the wavefunctions, (φ_i, φ_k) and (φ_m, $\varphi_{m'}$), are taken to be SCF MO for H_L and H_M respectively, the molecular integrals, $\langle i | H_L | k \rangle_{i \neq k}$ and $\langle m | H_M | m' \rangle_{m \neq m'}$, are equal to zero. H_{LM} represents the term corresponding to the electron-electron and electron-core interaction over the ligand and the metal.

Contact Shifts and Unpaired Electron Distribution.

The present formulation is primarily intended for the estimation of the contact shift of the transition-metal complexes. Since the contact shifts are proportional to the unpaired electron density at the proton, it is necessary to evaluate the molecular integral $\langle {}^2\Phi_g | \rho_H | {}^2\Phi_g \rangle$. ρ_H is the spin density operator at the ligand proton, H. The orders of the magnitude of λ_{im}, λ_{mk}, λ_{ik}, and λ_{ik}, are $O(S_{mi})$, $O(S_{km})$, $O(S_{km}S_{mi})$ and $O(S_{km}S_{mi})$ respectively.[12] The other matrix elements in $\langle {}^2\Phi_g | \rho_H | {}^2\Phi_g \rangle$ have also been evaluated; they are shown in Table 1. By disregarding the contributions smaller than the $O(S^3)$ order, we obtain

$$\rho_H = \langle {}^2\Phi_g | \rho_H | {}^2\Phi_g \rangle = {\rho_H}^{\Gamma} + {\rho_H}^{D}, \tag{10}$$

where:

$${\rho_H}^{P} = \frac{4}{\sqrt{6}} \sum_i^{occ} \sum_k^{vac} \lambda_{ik}^{(1)} \langle i | \rho_H | k \rangle, \tag{11}$$

and

$$\begin{aligned} {\rho_H}^{D} = (&-2\sum_i^{occ} \lambda_{im} \langle i | \rho_H | m \rangle + 2\sum_k^{vac} \lambda_{mk} \langle m | \rho_H | k \rangle \\ &+ \sum_i^{occ} \sum_{i'}^{occ} \lambda_{im} \lambda_{i'm} \langle i | \rho_H | i' \rangle \\ &+ \sum_k^{vac} \sum_{k'}^{vac} \lambda_{mk} \lambda_{mk'} \langle k | \rho_H | k' \rangle). \end{aligned} \tag{12}$$

ρ_H^P is the contribution due to the spin-polarization mechanism (see Fig. 2), while ρ_H^D is the contribution due to the spin-delocalization mechanism (see Fig. 3).

Spin-polarization Mechanism. In this section, we will discuss the spin-polarization mechanism. The (ik)-element of the spin polarization term in Eq. (10) is:

$$({\rho_H}^{P})_{ik} = \frac{4}{\sqrt{6}} \lambda_{ik}^{(1)} \langle i | \rho_H | k \rangle. \tag{13}$$

The molecular orbital, $|i\rangle$, is expressed as a linear combination of atomic orbitals:

$$|i\rangle = \sum_\mu {C_\mu}^i \chi_\mu. \tag{14}$$

Since the one-center term is the most dominant in $\langle i | \rho_H | k \rangle$, $(\rho_H^P)_{ik}$ is, approximately:

$$({\rho_H}^{P})_{ik} = \frac{4}{\sqrt{6}} \lambda_{ik}^{(1)} {C_H}^i {C_H}^k |\chi_H^{(0)}|^2, \tag{15}$$

where:

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[12] K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

$$\lambda_{ik}^{(1)} = -\frac{2}{\sqrt{6}}\sum_{\mu,\nu} C_\mu{}^k C_\nu{}^i \frac{\langle \mu m | \nu m\rangle}{\delta E_{ik}}. \tag{16}$$

Hence,

$$(\rho_{\mathrm{H}}{}^{\mathrm{P}})_{ik} = -\frac{4}{3}\frac{1}{\delta E_{ik}}\sum_{\mu,\nu} C_\mu{}^k C_\nu{}^i C_{\mathrm{H}}{}^k C_{\mathrm{H}}{}^i |\chi_{\mathrm{H}}^{(0)}|^2 \langle \mu m | \nu m\rangle. \tag{17}$$

Let us denote the atomic orbitals of the transition metal, of the adjacent atom in the ligand, of the ligand proton, H, and of the proton-attached nucleus as M, N, H, and C respectively. Then, the spin density at the proton H due to the spin polarization mechanism, $\rho_{\mathrm{H}}^{\mathrm{P}}$, may be writtern as:

$$\begin{aligned}\rho_{\mathrm{H}}{}^{\mathrm{P}} &= \sum_i^{occ}\sum_k^{vac}(\rho_{\mathrm{H}}{}^{\mathrm{P}})_{ik}\\ &= -\{(C_{\mathrm{M}}{}^m)^2/3\}(\pi_{\mathrm{HN}}\langle \mathrm{NM}|\mathrm{NM}\rangle + \pi_{\mathrm{HH}}\langle \mathrm{HM}|\mathrm{HM}\rangle\\ &\quad + \sum_{t\neq \mathrm{N,H}}\pi_{\mathrm{H}t}\langle t\mathrm{M}|t\mathrm{M}\rangle + \sum_{t,u(t\neq u)}\pi_{\mathrm{H},tu}\langle t\mathrm{M}|u\mathrm{M}\rangle),\end{aligned} \tag{18}$$

where π_{NN}' is completely analogous to the mutual atom-atom polarizability associated with the atoms N and N′[13]:

$$\pi_{\mathrm{NN'}} = 4\sum_i^{occ}\sum_j^{vac}\frac{C_{\mathrm{N}}{}^i C_{\mathrm{N'}}{}^i C_{\mathrm{N}}{}^j C_{\mathrm{N'}}{}^j}{\delta E_{ij}}, \tag{19}$$

χ_{N} is an atomic orbital at the nucleus, N, and $\pi_{\mathrm{H},tu}$ is the atom-bond-polarizability defined by:

$$\pi_{\mathrm{H},tu} = 2\sum_i^{occ}\sum_j^{vac}\frac{C_{\mathrm{H}}{}^i C_{\mathrm{H}}{}^j(C_u{}^i C_t{}^j + C_t{}^i C_u{}^j)}{\delta E_{ij}}. \tag{20}$$

When the interaction between metal and ligand is restricted to the localized bond N–M:

$$\pi_{\mathrm{HN}}\langle \mathrm{NM}|\mathrm{NM}\rangle > \pi_{\mathrm{HH}}\langle \mathrm{HM}|\mathrm{HM}\rangle \gtrsim \pi_{\mathrm{H}t}\langle t\mathrm{M}|t\mathrm{M}\rangle.$$

Thus $\rho_{\mathrm{H}}^{\mathrm{P}}$ may be written as:

$$\rho_{\mathrm{H}}{}^{\mathrm{P}} \simeq -\frac{1}{3}(C_{\mathrm{M}}{}^m)^2|\chi_{\mathrm{H}}^{(0)}|^2\pi_{\mathrm{HN}}\langle \mathrm{NM}|\mathrm{NM}\rangle. \tag{21}$$

That is, the order of magnitude of $\langle \mathrm{AM}|\mathrm{AM}\rangle$ (A= N, H, t) is $(S_{\mathrm{AM}})^2$, $(S_{\mathrm{NM}})^2 \gg (S_{\mathrm{HM}})^2 \simeq (S_{t\mathrm{M}})^2$ in the above N–M localized bond. The order of magnitude is $C_{\mathrm{M}}^{\mathrm{m}} \simeq 1$, $\chi_{\mathrm{H}}(0) \simeq 1$, $\pi_{\mathrm{HN}} \simeq -(0.1)^2/10[(\mathrm{eV})^{-1}]$, and $\langle \mathrm{NM}|\mathrm{NM}\rangle \simeq 3$ [eV]. Accordingly, $\rho_{\mathrm{H}}^{\mathrm{P}}$ is of the order of magnitude of 0.001—0.0001. The contact shifts for the amino proton of the nickel(II)-benzylamine complex[14] can be explained by this mechanism (Table 2*a*). The alternative character of spin density (the change in the sign of the spin density) can be explained by the alternative character of $\pi_{\mathrm{NN'}}$. Further, Eq. (21) shows that the sign of $\rho_{\mathrm{H}}^{\mathrm{P}}$ is the same as the sign of J_{NH} (the I–I coupling constant between N and H AO.) of a free molecule, because $J_{\mathrm{NH}} \propto \pi_{\mathrm{NH}}$ and $\langle \mathrm{NH}|\mathrm{NH}\rangle > 0$.

When the interaction between metal and ligand is not restricted to a special localized bond, $\pi_{\mathrm{HH}}\langle \mathrm{HM}|\mathrm{HM}\rangle \geq \pi_{\mathrm{H}}\langle t\mathrm{M}|t\mathrm{M}\rangle$. Accordingly, $\rho_{\mathrm{H}}^{\mathrm{P}}$ may be written as:

$$\rho_{\mathrm{H}}{}^{\mathrm{P}} \simeq -\frac{1}{3}(C_{\mathrm{M}}{}^m)^2|\chi_{\mathrm{H}}^{(0)}|^2\pi_{\mathrm{HH}}\langle \mathrm{HM}|\mathrm{HM}\rangle. \tag{22}$$

The order of magnitude is $C_{\mathrm{M}}^{\mathrm{m}} \simeq 1$, $\chi_{\mathrm{H}}^{(0)} \simeq 1$, $\pi_{\mathrm{HH}} \simeq 1/10$ $[(\mathrm{eV})^{-1}]$, and $\langle \mathrm{HM}|\mathrm{HM}\rangle \simeq 0.1$ [eV]. Accordingly, $\rho_{\mathrm{H}}^{\mathrm{P}}$ is of the order of magnitude of 0.01—0.001. The large contact shifts and the hyperfine coupling constants for paramagnetic metallocene[15,16] can be explained by this mechanism (Table 2*b*).

Spin-delocalization Mechanism. In this section, we will discuss the spin-delocalization mechanism. In the LCAO form, the spin delocalization term in Eq. (10) is:

$$\begin{aligned}\rho_{\mathrm{H}}{}^{\mathrm{D}} \simeq &\Big(\sum_i^{occ}\sum_{i'}^{occ}\lambda_{im}\lambda_{i'm}C_{\mathrm{H}}{}^i C_{\mathrm{H}}{}^{i'} + \sum_k^{vac}\sum_{k'}^{vac}\lambda_{mk}\lambda_{mk'}C_{\mathrm{H}}{}^k C_{\mathrm{H}}{}^{k'}\Big)|\chi_{\mathrm{H}}^{(0)}|^2\\ &- \Big(2\sum_i^{occ}\lambda_{im}C_{\mathrm{H}}{}^i C_{\mathrm{M}}{}^m - 2\sum_k^{vac}\lambda_{mk}C_{\mathrm{M}}{}^m C_{\mathrm{H}}{}^k\Big)\chi_{\mathrm{H}}^{(0)}\chi_{\mathrm{M}}^{(0)},\end{aligned} \tag{23}$$

where $\chi_{\mathrm{M}}^{(0)}$ is the value of the metal orbital at the proton H. The value of the metal orbital at the proton H is insignificant (the order of the magnitude of $\chi_{\mathrm{H}}^{(0)}\chi_{\mathrm{M}}^{(0)}$ is calculated to be 0.001[17]), so it will be omitted. λ_{im} and λ_{mk} may be approximated in the order of magnitude as follows:

$$\lambda_{im} \simeq \frac{C_{\mathrm{M}}{}^m C_{\mathrm{N}}{}^i \beta_{\mathrm{MN}}}{\delta E_{im}}, \quad \lambda_{mk} \simeq \frac{C_{\mathrm{M}}{}^m C_{\mathrm{N}}{}^k \beta_{\mathrm{MN}}}{\delta E_{mk}},$$

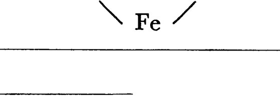
where β_{MN} is the core-resonance integral between the atomic orbitals *M* and *N*. Then,

TABLE 2. SPIN DENSITY ON THE LIGAND PROTON CALCULATED FROM THE OBSERVED CONTACT SHIFT REFERENCED AGAINST DIAMAGNETIC LIGAND BY EQ. (1)—(3)

a) $[\mathrm{Ni}\ (bz)_6]^{2+}$ $(bz = \mathrm{C_6H_5CH_2NH_2})$:
$\rho^{\mathrm{NH_2}} = -0.0003$, $\rho^{\mathrm{CH_2}} = +0.0001$, $\rho^{H_{ortho}} = -0.000004$,
$\rho^{H_{meta}} = +0.000004$,
$\rho^{H_{para}} = -0.000004$.

b) $\mathrm{Ni\ (C_5H_4\text{-}CH_3)_2}$:
$\rho^{\mathrm{H}} = -0.0008$, $\rho^{\mathrm{CH_3}} = +0.0006$.
$\mathrm{Cr\ (C_5H_4\text{-}CH_3)_2}$:
$\rho^{\mathrm{H}} = +0.002$, $\rho^{\mathrm{CH_3}} = -0.0005$.

c) (bipyridine)$_3$ $\mathrm{FeCl_3}$:
$\rho^{\mathrm{2H}} = +0.0005$, $\rho^{\mathrm{3H}} = +0.0001$,
$\rho^{\mathrm{4H}} = +0.00006$, $\rho^{\mathrm{5H}} = +0.00001$.



a) Ref. 14, b) Ref. 16, c) Ref. 18

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[15] M. F. Retting and R. S. Drago, *ibid.*, **91**, 1361, 3432 (1969).

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[17] S. E. Anderson and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 3656 (1969).

$$\rho_{\mathrm{H}}{}^{\mathrm{D}} \simeq (C_{\mathrm{M}}{}^{m})^2\beta_{\mathrm{MN}}^2|\chi_{\mathrm{H}}^{(0)}|^2\left\{\left(\sum_i^{occ}\frac{C_{\mathrm{H}}{}^{i}C_{\mathrm{N}}{}^{i}}{\delta E_{im}}\right)^2+\left(\sum_k^{vac}\frac{C_{\mathrm{H}}{}^{k}C_{\mathrm{N}}{}^{k}}{\delta E_{mk}}\right)^2\right\}. \tag{24}$$

Taking the mean excitation energy (δE) approximation, one obtains:

$$\rho_{\mathrm{H}}{}^{\mathrm{D}} \simeq (C_{\mathrm{M}}{}^{m})^2\beta_{\mathrm{MN}}^2|\chi_{\mathrm{H}}^{(0)}|^2(P_{\mathrm{HN}})^2/2(\delta E)^2, \tag{25}$$

where:

$$P_{\mathrm{HN}} = 2\sum_i^{occ}C_{\mathrm{H}}{}^{i}C_{\mathrm{N}}{}^{i}.$$

The order of magnitude is $C_{\mathrm{M}}^{\mathrm{m}}\simeq 1$, $\beta\simeq 5$ [eV], $P_{\mathrm{HN}}\simeq 0.1$, and $\delta E\simeq 10$[eV], so $\rho_{\mathrm{H}}^{\mathrm{D}}$ is of the order of magnitude of 0.0001. Thus, if the proton H is not directly bonded to the atom N, the spin-delocalization mechanism is not important. However, if the proton H is directly bonded to the atom N, $P_{\mathrm{HN}}\simeq 0.5$ and $\rho_{\mathrm{H}}^{\mathrm{D}}$ is of the order of magnitude of 0.001—0.0001. Therefore, the spin-delocalization mechanism is not negligible in this case. The bipyridine proton contact shift in α,α'-bipyridine chelates of Fe(III)[18] can be explained by this mechanism (Table 2*c*). Further, if only the integral $\langle i|H|m\rangle$ is not equal to zero, $\rho_{\mathrm{H}}^{\mathrm{D}}\simeq(\beta_{\mathrm{NH}}/E_{im})^2\times(P_{\mathrm{HN}}^{i})^2$; that is the partial bond order $(P_{\mathrm{HN}}^{i})^2$ is proportional to the spin densities of the related atoms. The total amount of odd electrons transferred to the ligand is estimated by means of the values of $(\beta_{\mathrm{NM}}/\delta E_{im})\simeq 0.1$.

Contact Nuclear Spin-Spin Coupling

Ramsey[19] has shown by the perturbation therory that the contact nuclear spin-spin coupling constant, $J_{\mathrm{NN'}}$ between the nuclei N and N′ can be written as:

$$J_{\mathrm{NN'}} = -\frac{2}{3h}\left(\frac{16\pi\beta h}{3}\right)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}} \times\sum_n\frac{\langle\Phi_0|\sum_k\delta(\mathbf{r}_{k\mathrm{N}})\mathbf{S}_k|\Phi_n\rangle\langle\Phi_n|\sum_j\delta(\mathbf{r}_{j\mathrm{N'}})\mathbf{S}_j|\Phi_0\rangle}{\delta E_{n0}}, \tag{26}$$

where Φ_0 denotes the ground state MO and where Φ_n represents the *n*th excited state MO. A theory of spin-spin coupling for a singlet molecule has been given by Pople and Santry[20] and the contact nuclear spin-spin coupling constant has been represented by:

$$J_{\mathrm{NN'}} = -\frac{1}{4h}\left(\frac{16\pi\beta h}{3}\right)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}|\chi_{\mathrm{N}}^{(0)}|^2|\chi_{\mathrm{N'}}^{(0)}|^2\pi_{\mathrm{NN'}}. \tag{27}$$

Let us assume Eq. (7) as the ground-doublet-state wavefunction. In the evaluation of the proton-proton coupling constant of the ligand molecule, the molecular integrals $\langle i|\rho_{\mathrm{N}}|m\rangle$ are insignificant and will be omitted. Neglecting any contributions smaller than the $O(S^2)$ order, we obtain:

$$J_{\mathrm{NN'}} = -\frac{2}{3h}\left(\frac{16\pi\beta h}{3}\right)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}(A+B+C+D), \tag{28}$$

where:

$$A = \sum_{i'}^{occ}\frac{1}{\delta E_{i'm}}\Big(\sum_i^{occ}\lambda_{im}\langle i|\rho_{\mathrm{N}}|i'\rangle\Big)\Big(\sum_i^{occ}\lambda_{im}\langle i'|\rho_{\mathrm{N'}}|i\rangle\Big), \tag{29}$$

$$B = \sum_{k'}^{vac}\frac{1}{\delta E_{mk'}}\Big(\sum_k^{vac}\lambda_{mk}\langle k|\rho_{\mathrm{N}}|k'\rangle\Big)\Big(\sum_k^{vac}\lambda_{mk}\langle k'|\rho_{\mathrm{N'}}|k\rangle\Big). \tag{30}$$

$$C = \sum_{i'}^{occ}\sum_{k'}^{vac}\frac{1}{\delta E_{i'k'}}\frac{2}{3}\langle i'|\rho_{\mathrm{N}}|k'\rangle\langle k'|\rho_{\mathrm{N'}}|i'\rangle, \tag{31}$$

$$\begin{aligned} D = {} & \sum_{i'}^{occ}\sum_{k'}^{vac}\frac{1}{\delta E_{i'k'}}\frac{4}{3\sqrt{6}} \\ & \times\{\langle i'|\rho_{\mathrm{N}}|k'\rangle[\sum_{k\neq k'}^{vac}\langle k'|\rho_{\mathrm{N'}}|k\rangle\lambda_{i'k}^{(1)}+\sum_{i\neq i'}^{occ}\langle i'|\rho_{\mathrm{N'}}|i'\rangle\lambda_{ik'}^{(1)} \\ & +\frac{2}{3}(\langle i'|\rho_{\mathrm{N'}}|i'\rangle+\langle k'|\rho_{\mathrm{N'}}|k'\rangle\lambda_{i'k'}^{(1)}] \\ & +\langle k'|\rho_{\mathrm{N'}}|i'\rangle[\sum_{k\neq k'}^{vac}\langle k|\rho_{\mathrm{N}}|k'\rangle\lambda_{i'k}^{(1)}+\sum_{i\neq i'}^{occ}\langle i|\rho_{\mathrm{N}}|i'\rangle\lambda_{ik'}^{(1)} \\ & +\frac{2}{3}(\langle i'|\rho_{\mathrm{N}}|i'\rangle+\langle k'|\rho_{\mathrm{N}}|k'\rangle)\lambda_{i'k'}^{(1)}]\}. \end{aligned} \tag{32}$$

Only the third term, *C*, in Eq.(28) is of the order of magnitude of $O(1)$; the other terms, *A*, *B*, and *D*, are of the order of magnitude of $O(S^2)$. Accordingly, Eq. (28) may be written approximately by only the *C*-term. Then;

$$\begin{aligned} J_{\mathrm{NN'}} &= -\frac{1}{h}\left(\frac{16\pi\beta h}{3}\right)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}} \\ &\quad\times\sum_{i'}^{occ}\sum_{k'}^{vac}C_{\mathrm{N}}{}^{i'}C_{\mathrm{N}}{}^{k'}C_{\mathrm{N'}}^{i'}C_{\mathrm{N'}}^{k'}|\chi_{\mathrm{N}}^{(0)}|^2|\chi_{\mathrm{N'}}^{(0)}|/\delta E_{i'k'} \\ &= -\frac{1}{4h}\left(\frac{16\pi\beta h}{3}\right)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}\pi_{\mathrm{NN'}}|\chi_{\mathrm{N}}^{(0)}|^2|\chi_{\mathrm{N'}}^{(0)}|^2, \end{aligned} \tag{33}$$

where we have considered the contribution from only the atomic orbital of the nucleus N in the evaluation of the molecular integral, $\langle k'|\rho_{\mathrm{N}}|k\rangle$. Eq. (33) is identical with Eq. (27), which was derived by Pople and Santry for a singlet free molecule.[20] From this result, we can conclude that: the proton-proton coupling constant of the ligand molecule in paramagnetic transition metal complexes is approximately identical with that of a singlet free ligand molecule and that the effect of a paramagnetic metal on $J_{\mathrm{NN'}}$ is of the order of magnitude of $(S_{\mathrm{LM}})^2$. The spin-spin couplings observed for the ligand quinoline of the nickel(II) aminotropone-imineate[21] is $J_{23}=4.0\pm0.2$ Hz, $J_{34}=7.9\pm0.2$ Hz, and $J_{78}=7.9\pm0.2$ Hz, and for a free quinoline[22] $J_{23}=4.1\pm0.2$ Hz, $J_{34}=8.5\pm0.3$ Hz, and $J_{78}=8.2\pm0.3$ Hz. These observed results are in good agreement with the above conclusion.

Summary

When the interaction between metal and ligand is restricted to the localized bond N–M, as in nickel(II)-benzylamine,

$$\rho_{\mathrm{H}}{}^{\mathrm{P}} \simeq -(C_{\mathrm{M}}{}^{m})^2|\chi_{\mathrm{H}}^{(0)}|^2\pi_{\mathrm{HN}}\langle\mathrm{NM}|\mathrm{NM}\rangle/3 \simeq 0.001\text{—}0.0001.$$

When the interaction between metal and ligand is not restricted to a special localized bond, as in metallocene,

$$\rho_{\mathrm{H}}{}^{\mathrm{P}} \simeq -(C_{\mathrm{M}}{}^{m})^2|\chi_{\mathrm{H}}^{(0)}|^2\pi_{\mathrm{HH}}\langle\mathrm{HM}|\mathrm{HM}\rangle/3 \simeq 0.01\text{—}0.001.$$

The spin-delocalization term has the order of magnitude of $\rho_{\mathrm{H}}^{\mathrm{D}}\simeq-(C_{\mathrm{M}}^{\mathrm{m}})^2(\beta_{\mathrm{MN}})^2|\chi_{\mathrm{H}}^{(0)}|^2(P_{\mathrm{HN}})^2/2(\delta E)^2$. If the proton H is directly bonded to the atom N, $\rho_{\mathrm{H}}^{\mathrm{D}}\simeq 0.001$. If

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the H proton is not directly bonded to the atom N, $\rho_H^D \simeq 0.0001$. The mechanism by which the spin reaches the nuclei on the ligand is closely related to the geometry of the complex and the details of the metal-ligand bonding. The magnitude of the contact shift gives us information about the mechanism and the metal-ligand bonding.

The most dominant term in $J_{NN'}$ derived for a transition metal complex, is identical with the formula which was derived for a singlet free-ligand molecule by Pople and Santry.[20] This implies that the proton-proton coupling constant of the ligand molecule in paramagnetic-transition metal complexes is nearly equal to that of the singlet free-ligand molecule and that the effect of the paramagnetic metal on $J_{NN'}$ is of the order of magnitude of $(S_{LM})^2$.

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