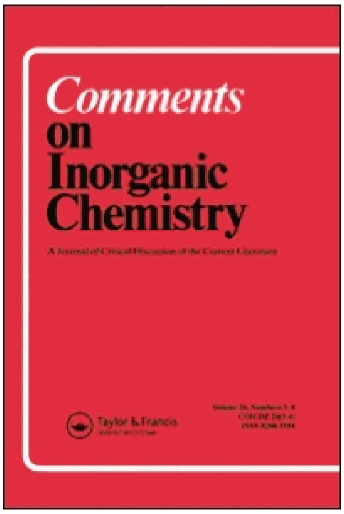
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Inorganic Spectroscopy: High Resolution

To cite this Article (1984) 'Inorganic Spectroscopy: High Resolution', Comments on Inorganic Chemistry, 3: 5, 288 — 300
To link to this Article: DOI: 10.1080/02603598408080078
URL: http://dx.doi.org/10.1080/02603598408080078

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PART 2. INORGANIC SPECTROSCOPY: HIGH RESOLUTION

VII. EPR—HYPERFINE INTERACTIONS

As observed in Section II, Figure II-5, the metal ion can also have a nuclear spin which couples to the electron spin to produce a hyperfine splitting of the EPR spectrum.[1] This coupling requires an additional term in the electron spin Hamiltonian which is given by:

$$H_{\text{hyperfine}} = \mathbf{A}\, \vec{I} \cdot \vec{S} \qquad \text{(VII-1a)}$$

Here I is the nuclear spin quantum number which has $(2I + 1)$ z components, $M_I = I, I - 1, \ldots -I$. Throughout this section we assume the reasonable limit of $H_{\text{Zeeman}} >> H_{\text{hyperfine}}$. Therefore Eq. VII-1a produces a perturbation correction to each Zeeman level given by

$$E_{M_I, M_S} = AM_I M_S \qquad \text{(VII-1b)}$$

For the simplest example of $S = 1/2$, $I = 1/2$, Figure II-1 must be expanded to include the effects of Eqs. VII-1, resulting in Figure VII-1.

The selection rules for the EPR experiment are $\Delta M_S = \pm 1$, $\Delta M_I = 0$, therefore only two transitions are allowed which are indicated as 1 and 2 in Figure VII-1. As discussed in Section II, if no hyperfine coupling is present, the resonance condition for EPR absorption is $h\nu = g\beta H$ and an EPR transition is observed at the magnetic field value, $H_0 = h\nu/g\beta$ (Figure VII-2A). When the hyperfine coupling of Figure VII-1 is turned on, the resonance conditions for EPR absorption becomes:

$$\begin{aligned} &\text{transition 1: } h\nu = g\beta H_1 - A/2, \\ &\text{therefore } H_1 = \frac{h\nu}{g\beta} + \frac{A}{2g\beta} \\ &\text{transition 2: } h\nu = g\beta H_2 + A/2, \\ &\text{therefore } H_2 = \frac{h\nu}{g\beta} - \frac{A}{2g\beta}. \end{aligned} \qquad \text{(VII-2)}$$

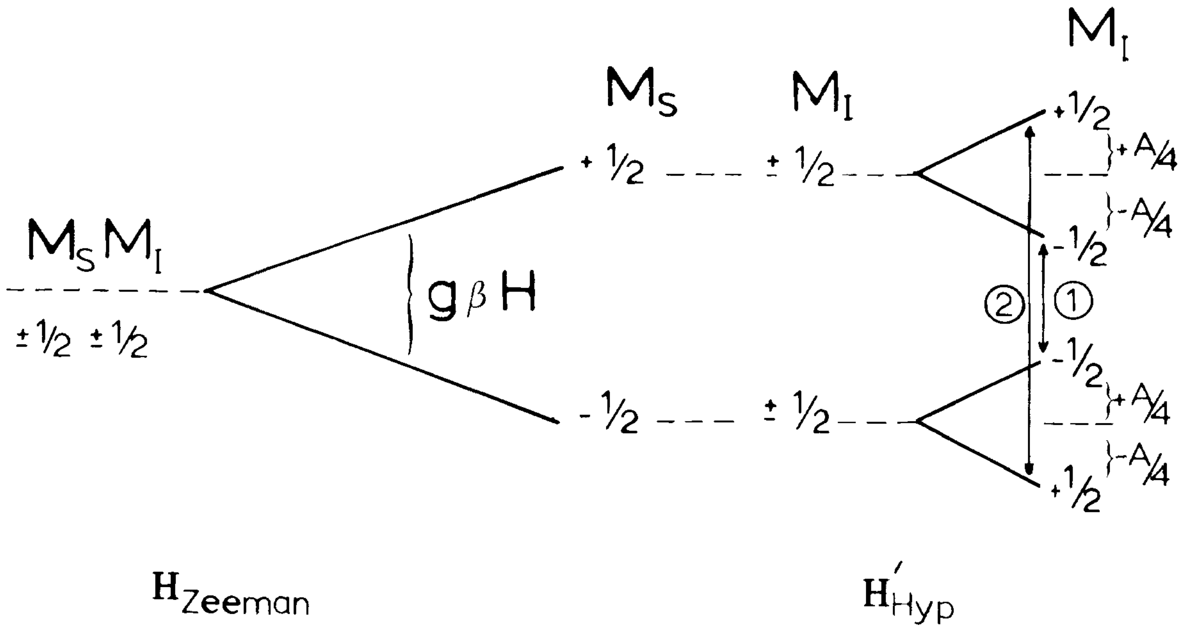


FIGURE VII-1 Effects of hyperfine interaction on Zeeman splitting of $S = 1/2$, $I = 1/2$.

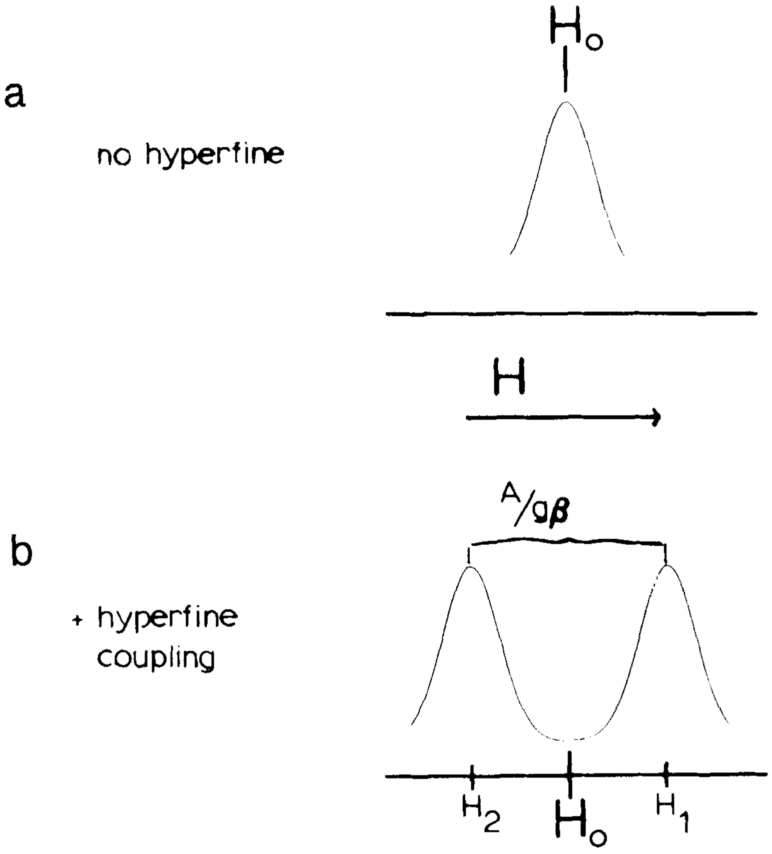


FIGURE VII-2 EPR absorption spectrum (a) without, and (b) with hyperfine splitting from $I = ½$.

Two transitions will thus be observed; they are split by the value $(H_1 - H_2) = A/g\beta$ at an average field $(H_1 + H_2)/2 = h\nu/g\beta = H_0$, as shown in Figure VII-2B. The hyperfine coupling constant A can then be obtained from the EPR spectrum by use of

$$A(\text{cm}^{-1}) = [(H_1 - H_2)\ \text{gauss}] \cdot g \cdot (4.67 \times 10^{-5}\ \text{cm}^{-1}/\text{gauss}). \tag{VII-3}$$

The above treatment demonstrates that the EPR signal associated with the Zeeman splitting is further split into two components due to hyperfine coupling to $I = ½$. In general, one will observe $(2I + 1)$ hyperfine lines, each pair split by $A/g\beta$. For copper, two isotopes are naturally occurring, ^{63}Cu and ^{65}Cu (natural abundance = 69% and 31% respectively) both with $I = 3/2$. Therefore four hyperfine levels are expected. As observed in Figure II-5, the copper hyperfine splitting is clearly aniostropic $(A_{\parallel} \neq A_{\perp})$, meaning that the hyperfine coupling constant is dependent on the orientation of the external magnetic field relative to the molecular axes. An EPR spectrum such as the one in Figure II-5 is normally described in terms of an effective spin Hamiltonian as given by

$$H = \beta \mathrm{H}\,[g_{\parallel}\hat{S}_z + g_{\perp}(\hat{S}_x + \hat{S}_y)] + A_{\parallel}\hat{I}_z\hat{S}_z + A_{\perp}[\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y]. \qquad \text{(VII-4)}$$

Here, the g and A tensors are assumed to be colinear (i.e., $A_{\parallel}$ along $g_{\parallel}$) and the g and A values are obtained from experiment. For D_{4h}–$\mathrm{CuCl_4^{=}}$, $A_{\parallel} = |113| \times 10^{-4}$ cm^{-1} and $A_{\perp} = 0 \pm 4 \times 10^{-4}$ cm^{-1}.[2] It should be noted that the EPR spectrum gives the magnitude but not the sign of the hyperfine coupling constant.

We now consider the theoretical origins of the hyperfine coupling tensor in Eq. (VII-1). Three contributions to the hyperfine coupling to the metal ion need to considered. These are (A) Fermi contact, which is purely isotropic, (B) dipolar coupling, which is purely anisotropic, and (C) the indirect dipolar coupling which contributes to both the isotropic and anisotropic parts of the hyperfine constant.

A. Fermi Contact

The Fermi contact contribution to the hyperfine constant derives from the Dirac equation and is given by

$$A^{\text{Fermi}} = \frac{8\pi}{3}\, g_e\beta_e g_n\beta_n\, |\psi(0)|^2. \qquad \text{(VII-5)}$$

Here $g_n\beta_n$ are the nuclear g value and nuclear magneton $(= \beta_e/1836)$ and $|\psi(0)|^2$ is the unpaired electron density at the nucleus. Since electron density at the nucleus can only occur for an electron in an

s orbital, and the unpaired electron in $CuCl_4^=$ is in a $d_{x^2-y^2}$ orbital which has no electron density at the nucleus, one might expect there to be no Fermi contact contribution. However, there is still an indirect Fermi contact term which arises from spin polarization of the $(1s)^2$, $(2s)^2$, and $(3s)^2$ core electrons by the unpaired electron in the $d_{x^2-y^2}$ orbital. This is caused by the exchange interaction between the d and core electrons. Reciprocally, this produces a multiplet splitting in the XPS spectra of core s electrons (see Section VI). The effect of this exchange interaction is to produce a net spin density at the nucleus which can be either of the same spin (positive) or opposite spin (negative) as that of the unpaired electron. For a $3d$ electron, the $1s$ and $2s$ filled subshells contribute negative spin density while the $3s$ filled subshell gives a positive spin density, the total being negative as the $2s$ contribution dominates. For D_{4h}-$CuCl_4^=$ a reasonable estimate for an unpaired electron in pure $d_{x^2-y^2}$ orbital is $A^{\text{Fermi}} \cong -155 \times 10^{-4}\ \text{cm}^{-1}$. It should be noted that if the symmetry of the complex is lowered such that the $4s$ orbital has the same symmetry as the $3d_{x^2-y^2}$ orbital, these can mix, producing a direct Fermi contact contribution which will have a large positive spin density ($A^{\text{Fermi}}\ (\text{Cu}4s) \cong 1680 \times 10^{-4}\ \text{cm}^{-1}$).

B. Dipolar Coupling

This term is due to the classical interaction of the dipoles associated with the electron and nuclear spins ($\vec{\mu}_e = g_e\beta_e\vec{S}, \vec{\mu}_n = g_n\beta_n\vec{I}$) interacting at a distance r. The Hamiltonian associated with this interaction is given in Eq. (VII-6a)

$$H_{\text{dipolar}} = -g_e\beta_e g_n\beta_n\left[\frac{\hat{S}\cdot\hat{I}}{r^3} - \frac{3(\hat{S}\cdot r)(\hat{I}\cdot r)}{r^5}\right] \qquad \text{(VII-6a)}$$

$$= \underbrace{g_e\beta_e g_n\beta_n\left[\frac{3\cos^2\theta - 1}{r^3}\right]}_{A^{\text{dipolar}}} M_S M_I. \qquad \text{(VII-6b)}$$

If we consider the limiting case of a strong external magnetic field, $\vec{S}$ and $\vec{I}$ will both orient along $\vec{H}$ and we need only include $\hat{S}_z$, $\hat{I}_z$, and $z = r\cos\theta$ (θ is the angle between the axis of the dipoles and

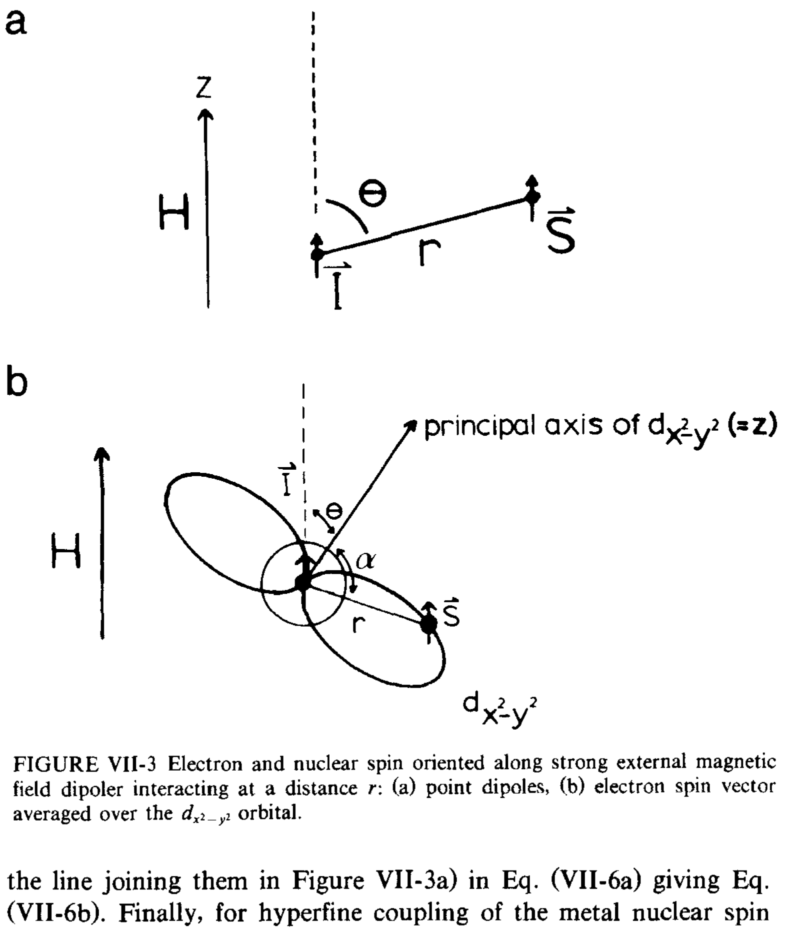


FIGURE VII-3 Electron and nuclear spin oriented along strong external magnetic field dipoler interacting at a distance r: (a) point dipoles, (b) electron spin vector averaged over the $d_{x^2-y^2}$ orbital.

the line joining them in Figure VII-3a) in Eq. (VII-6a) giving Eq. (VII-6b). Finally, for hyperfine coupling of the metal nuclear spin with the unpaired electron, the electron is in an orbital centered at the nucleus so one needs to average over the position of the electron spin vector in this orbital. This leads to the expression for the dipolar contribution to the hyperfine coupling given by

$$A^{\text{dipolar}} = \frac{g_e\beta_e g_n\beta_n}{\langle r^3\rangle_d}\langle 3\cos^2\alpha - 1\rangle_d \frac{(3\cos^2\theta - 1)}{2}, \qquad \text{(VII-7)}$$

where θ is now the angle between the principal axis of the orbital (z in the case of the $d_{x^2-y^2}$ orbital) and the nuclear moment vector and

α is the angle between r and the principal axis. $\langle\,\rangle_d$ indicates averages over the position of the unpaired electron in the occupied d orbital (Figure VII-3B). For an electron in the $d_{x^2-y^2}$ orbital, $\langle 3\cos^2\alpha - 1\rangle = -4/7$. Defining $g_e\beta_e g_n\beta_n/\langle r^3\rangle_d$ as P_d, Eq. (VII-7) becomes $A^{\text{dip}}(d_{x^2-y^2}) = -2/7 \times P_d(3\cos^2\theta - 1)$. Therefore when the complex is oriented with the molecular z axis parallel to $\vec{H}$, $\theta = 0°$ and $A_{\parallel}^{\text{dip}} = -4/7\ P_d$. When the complex is oriented with z perpendicular to $\vec{H}$, $\theta = 90°$ and $A_{\perp}^{\text{dip}} = +2/7\ P_d$ (see Figure VII-4). A reasonable estimate for P_d for Cu is $\cong 350 \times 10^{-4}\ \text{cm}^{-1}$. This term produces a large anisotropic contribution to the hyperfine coupling constant which averages to zero $((A_{\parallel} + 2A_{\perp})/3 = 0)$ and thus does not have an isotropic component.

C. Indirect Dipolar Coupling

The nuclear spin of the metal can also dipolar couple with the orbital angular momentum of the electron. Abragam and Pryce[3] have obtained an expression for this interaction using the method of operator equivalents which is given by

$$H_{\text{indirect dipolar}} = P_d\left[(\hat{L}\cdot\hat{I}) - \frac{1}{7}(\hat{L}\cdot\hat{S})(\hat{L}\cdot\hat{I}) - \frac{1}{7}(\hat{L}\cdot\hat{I})(\hat{L}\cdot\hat{S})\right]. \qquad \text{(VII-8)}$$

Here, the $P_d(\hat{L}\cdot\hat{I})$ term dominates. For $\text{CuCl}_4^{=}$, as discussed in Section II, the ${}^2B_{1g}(x^2 - y^2)$ ground state contains no orbital angular momentum, therefore Eq. (VII-8) cannot contribute to the hyperfine coupling in first order. However, as with the g values deviating from 2.00 in Section II, spin-orbit coupling $(H_{\text{s.o.}} = \lambda\vec{L}\cdot\vec{S})$ mixes excited states into the ground state wavefunction as given in Eq. (II-5). Equation (VIII-8) can then contribute indirectly to the hyperfine coupling through this second-order effect. For ${}^2B_{1g}\ (d_{x^2-y^2})$ the relevant expressions are

$$A_{\parallel}^{\text{indirect dipolar}} = P_d\left[\frac{-8\lambda}{E_{x^2-y^2} - E_{xy}} + \frac{3}{7}\left(\frac{-2\lambda}{E_{x^2-y^2} - E_{xz,yz}}\right)\right] \qquad \text{(VII-9a)}$$

$$= P_d\left[(g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2)\right] \qquad \text{(VII-9b)}$$

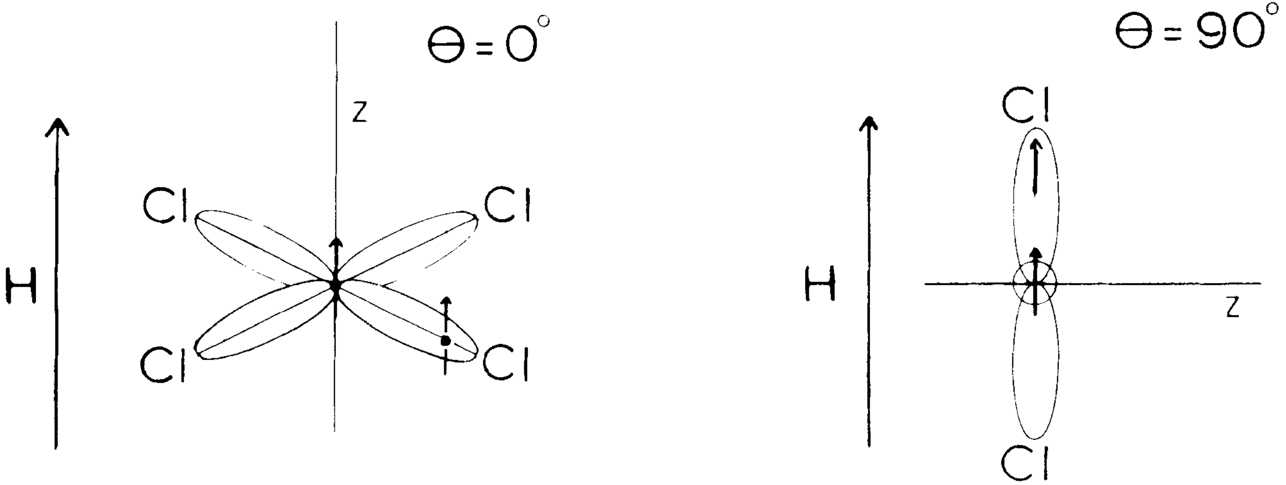


FIGURE VII-4 Anisotropy in the dipolar contribution of the nuclear hyperfine coupling to an electron spin vector averaged over the $d_{x^2-y^2}$ orbital.

$$A_{\perp}^{\text{indirect dipolar}} = P_d\left[\frac{-2\lambda}{E_{x^2-y^2} - E_{xz,yz}} - \frac{3}{14}\left(\frac{-2\lambda}{E_{x^2-y^2} - E_{xz,yz}}\right)\right] \qquad \text{(VII-9c)}$$

$$= P_d\,[(g_{\perp} - 2) - \frac{3}{14}(g_{\perp} - 2)] \qquad \text{(VII-9d)}$$

The first term on the right in Eqs. (VII-9) derives from evaluating the $\hat{L} \cdot \hat{I}$ part of Eq. (VII-8) over the spin-orbit mixed $^2B_{1g}$ ground state wavefunction, and the parallel of this treatment to that for the g values is emphasized by substituting Eqs. (II-7a,b) into (VII-9a,c). Clearly $A^{\text{indirect dipolar}}$ is anisotropic. However, it should be noticed that $A_{\text{ave}}^{\text{indirect dipolar}} = (A_{\parallel} + 2A_{\perp})/3 = P_d[(g_{\parallel} - 2) + 2(g_{\perp} - 2)]/3$. Therefore the indirect dipolar term also has an isotropic component which is referred to as the pseudo-contact term. General expressions for $A^{\text{indirect dipolar}}$ for other d orbital ground states are given in Ref. 3.

Combining the three contributions to the hyperfine coupling constant discussed above for an unpaired electron in a Cu($d_{x^2-y^2}$) orbital, one obtains

$$\begin{aligned} A_{\parallel} &= P_d\left[-\kappa - \frac{4}{7} + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2)\right] \\ A_{\perp} &= P_d\left[-\kappa + \frac{2}{7} + \frac{11}{14}(g_{\perp} - 2)\right] \end{aligned} \qquad \text{(VII-10)}$$

where A^{Fermi} is rewritten as $P_d(-\kappa)$ with κ for Cu(II) being $\cong$ 0.43. Substituting experimental[2] values for $g_{\parallel}$ and $g_{\perp}$ for D_{4h}-$\text{CuCl}_4^{=}$ into Eqs. (VII-10) gives $A_{\parallel} = 220 \times 10^{-4}\ \text{cm}^{-1}$, $A_{\perp} = -31.5 \times 10^{-4}\ \text{cm}^{-1}$. The experimental values are[2] $A_{\parallel} = |113| \times 10^{-4}\ \text{cm}^{-1}$ and $A_{\perp} = 0 \times 10^{-4}\ \text{cm}^{-1}$. An additional feature must then be included[4] to make theory agree with experiment: covalent delocalization of the unpaired electron onto the ligands. While the indirect dipolar term already includes covalency in that experimental g values have been used, both the Fermi contact and dipolar contributions have assumed that the electron occupies a pure Cu(II) $d_{x^2-y^2}$ orbital. However, as has been discussed, $\Phi(b_{1g}) = C_{\text{M}}\phi_{x^2-y^2} + C_{\text{L}}\chi_{\text{L}}$. Thus, the first two terms in Eq. (VII-10) should be written as $[-\kappa - 4/7](C_{\text{M}})^2$ and $[-\kappa + 2/7](C_{\text{M}})^2$. Using the expression for $A_{\parallel}$, a value of $(C_{\text{M}})^2 = 0.69$

gives reasonable agreement with experiment, consistent with the value determined from the experimental g values in Section II. It should be noted, however, that the dependence of κ on covalency is more complicated[5] than indicated above and is best obtained from a fit to the data. Thus metal hyperfine coupling can also provide an estimate of electron delocalization onto the ligands. At still higher resolution electron delocalization can be probed through the ligand superhyperfine structure contained in the EPR spectrum.

The ligands can also have a nuclear spin. This spin will couple to the electron spin to produce a superhyperfine splitting of each hyperfine line as shown[2] for $CuCl_4^=$ in Figure VII-5. One ligand will

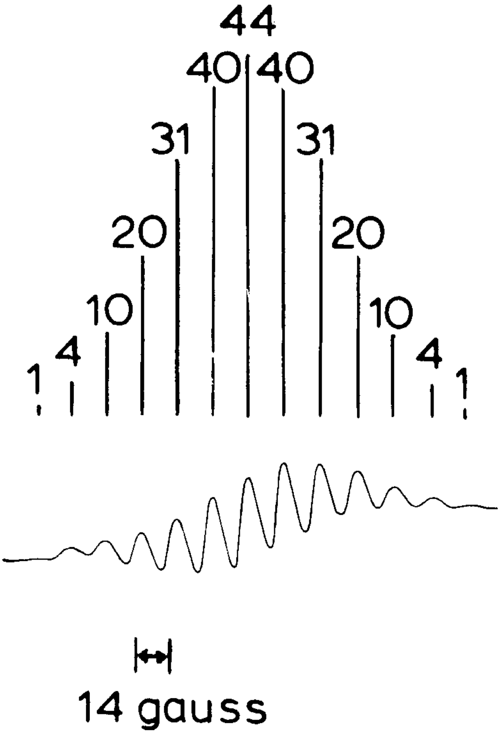


FIGURE VII-5 Experimental superhyperfine splitting of a given hyperfine line in the EPR spectrum. D_{4h}–$CuCl_4^=$ orientation is with $\vec{H}$ 45° to x in the xy plane, therefore all chlorides are equivalent with respect to $\vec{H}$. (Taken from Ref. 2.) Intensity pattern predicted for four equivalent Cl($I = 3/2$) at top (see Section II, Ref. 1e, Table II).

produce $(2I^{L} + 1)$ superhyperfine lines of equal intensity, adjacent pairs being separated by $A^{L}/g\beta$. I^{L} is the nuclear spin of the ligand and A^{L} is the ligand superhyperfine coupling constant. For a complex with more than one ligand having a nuclear spin, each superhyperfine line is further split, producing a total of $(2I^{L_1} + 1)(2I^{L_2} + 1) \cdots$ lines. For n equivalent ligands related by symmetry and with the same M-L orientation relative to the magnetic field [*vide infra* Eq. (VII-11)] each hyperfine line will split into $(2nI^{L} + 1)$ superhyperfine lines again separated by $A_{L}/g\beta$. For D_{4h}–$CuCl_4^{=}$, naturally abundant ^{35}Cl and ^{37}Cl both have $I^{Cl} = 3/2$, thus 13 superhyperfine lines are predicted with the intensity ratio given at the top of Figure VII-5. The superhyperfine coupling constant will in general be anisotropic, requiring a new term in the effective spin Hamiltonian for each ligand L_i

$$H_{\text{superhyperfine}} = A_{\parallel}^{L_i}\hat{I}_{z}^{L_i}\hat{S}_{z}^{L_i} + A_{\perp}^{L_i}(\hat{I}_{x}^{L_i}\hat{S}_{x}^{L_i} + \hat{I}_{y}^{L_i}\hat{S}_{y}^{L_i}). \qquad \text{(VII-11)}$$

It should be emphasized that in Eq. (VII-11) the z axis for each ligand refers to the M-L_i axis and not the molecular axis of the complex. Therefore $A_{\parallel}^{L_i}$ is the superhyperfine splitting observed from ligand L_i with the magnetic field along the M-L_i axis and $A_{\perp}^{L_i}$ is the splitting observed due to L_i with the magnetic field perpendicular to M-L_i.

Several factors contribute to the ligand superhyperfine coupling constant. Even in the absence of overlap of the metal orbital with the ligand orbitals, the electron spin in the Cu $d_{x^2-y^2}$ orbital can dipole couple with the nuclear spin I^{L_i} of the ligands. This coupling is described by Figure VII-3A and Eq. (VII-6b), where for a M-L_i distance $r \geqslant 2$ Å, $\vec{S}$ and $\vec{I}^{L_i}$ can be treated as point dipoles with no averaging over the position of the electron in the d orbital. From Eq. (VII-6b), this ligand dipole contribution to the superhyperfine coupling is anisotropic $A_{\parallel}^{L_i,\,\mathrm{dip}} = -2A_{\perp}^{L_i,\,\mathrm{dip}}$ where parallel and perpendicular refer to the orientation of $\vec{H}$ relation to the M-L_i axis ($\theta = 0°$ and $90°$, respectively). If r is known, this contribution can be subtracted from the experimental superhyperfine coupling constants to obtain the overlap-related contributions to the superhyperfine constant.

As has been discussed, bonding interactions with the ligands produce a molecular orbital for the half-occupied $^{2}B_{1g}$ ground state of the form $\Phi(b_{1g}) = C_M\phi_{x^2-y^2} + C_L\chi_L$. C_M and C_L are related by the normalization condition $(C_M)^2 + (C_L)^2 + 2(C_M)(C_L)S_{x^2-y^2,\chi_L} = 1$, and from Figure IV-1, $\chi_L = 1/\sqrt{4}\,(p_z\sigma_1 - p_z\sigma_2 + p_z\sigma_3 - p_z\sigma_4)$. Therefore, covalent interactions with the ligands result in unpaired electron density equal to $(C_L)^2\,(1/\sqrt{4})^2$ in each Cl $3p_z\sigma$ orbital. Further, sigma bonding to the copper will result in a small fraction (n^2) of Cl $3s$ mixed into the Cl $3p_z$, hence the Cl "$3p_z\sigma$" orbital is actually equal to $(1 - n^2)$Cl $3p_z$ + n^2Cl $3s$. One unpaired electron in a Cl $3p_z\sigma$ orbital will have two contributions to its hyperfine splitting: $(n^2)A^{\mathrm{L}}_{\mathrm{iso}}$ due to direct Fermi contact associated with the $3s$ mixing; and $(1 - n^2)A^{\mathrm{L}}_{\mathrm{aniso}} \times (3\cos^2\theta - 1)/2$ due to dipolar coupling of the chloride nuclear spin with the unpaired electron averaged over the Cl $3p_z$ orbital [Eq. (VII-7)]. Thus the total covalent contributions to the superhyperfine coupling constants for the D_{4h}-$\mathrm{CuCl_4}^{=}$ $^2B_{1g}$ ground state are given by

$$
\begin{aligned}
A_{\parallel}^{\mathrm{Cl}} &= (C_L)^2\left(\frac{1}{4}\right)\left[(n^2)\,A_{\mathrm{iso}}^{\mathrm{Cl}} + (1 - n^2)\,A_{\mathrm{aniso}}^{\mathrm{Cl}}\right] \\
A_{\perp}^{\mathrm{Cl}} &= (C_L)^2\left(\frac{1}{4}\right)\left[(n^2)\,A_{\mathrm{iso}}^{\mathrm{Cl}} - \frac{1}{2}(1 - n^2)\,A_{\mathrm{aniso}}^{\mathrm{Cl}}\right].
\end{aligned}
\qquad \text{(VII-12)}
$$

For Cl, $A_{\mathrm{iso}}^{\mathrm{Cl}} \cong 1500 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $A_{\mathrm{aniso}}^{\mathrm{Cl}} \cong 100 \times 10^{-4}\ \mathrm{cm}^{-1}$.[2] The experimental values for D_{4h}-$\mathrm{CuCl_4}^{=}$ obtained from a series of single crystal orientations including that reproduced in Figure VII-5 are $A_{\parallel} = 18.5 \times 10^{-4}$ and $A_{\perp} = 5 \times 10^{-4}\ \mathrm{cm}^{-1}$. Therefore the superhyperfine splitting gives[6] $n^2 = 0.07$ and $(C_L)^2 = 0.36$ which compares nicely with the ~35% mixing estimated from copper hyperfine and g values.

References

1. See Section II, Refs. 1(a)–(g).
2. J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, Proc. Phys. Soc. London **78**, 1263 (1961).

It should be noted that no hyperfine coupling is observed in the pure, single crystal D_{4h}-$\mathrm{CuCl_4}^{=}$ salt treated throughout this text due to intermolecular interactions. The hyperfine and superhyperfine values used here were obtained from the tetragonally elongated $\mathrm{CuCl_6}^{4-}$ complex doped into a $\mathrm{CdCl_2}$ lattice. The g values of this complex are $g_{\parallel} = 2.339$ and $g_{\perp} = 2.070$.

A parallel analysis of the hyperfine parameters for Cu doped into a K_2PdCl_4 lattice [C. Chow, K. Chang, and R. D. Willett, J. Chem. Phys. **59**, 2629 (1973)] gives results similar to those presented here.

3. (a) A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London), A **205**, 135, (1951).
   (b) A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London), A **206**, 164, (1951).
   (c) M. H. L. Pryce, Proc. Phys. Soc. A. **63**, 25 (1950).
4. (a) A. J. Maki, B. R. McGarvey, J. Chem. Phys. **29**, 31 (1958).
   (b) D. Kivelson, R. Neiman, J. Chem. Phys. **35**, 149 (1961).
   (c) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, J. Phys. Chem. **71**, 109, (1976).
5. B. R. McGarvey, J. Phys. Chem. **71**, 51 (1967).
6. $A^{\mathrm{L}_i,\mathrm{dip}}$ is negligible in this calculation. G. F. Kokoszka, C. W. Reimann, and H. C. Allen, Jr., J. Phys. Chem. **71**, 121 (1967).

VIII. ELECTRONIC ABSORPTION SPECTROSCOPY—VIBRONIC COUPLING AND BAND SHAPE ANALYSIS

From Section III, for D_{4h}–$\mathrm{CuCl_4}^=$, the parity forbiddenness of the $d \rightarrow d$ transitions in this centrosymmetric complex is overcome by vibronic or Herzberg-Teller coupling to odd parity vibrations of the nuclear framework. In addition, absorption bands in metal complexes can be greatly broadened (relative to the < 1 cm^{-1} expected on the basis of their lifetimes) due to coupling of the electronic transitions to distortions of the molecular framework. Both effects require two new terms in the molecular Hamiltonian which relate to nuclear motion.

For a complex with N atoms there are $3N - 6$ normal modes of vibration Q_i which are given for D_{4h}–$\mathrm{CuCl_4}^=$ by

$$Q_i(D_{4h}\text{–}\mathrm{CuCl_4^=}) = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u. \qquad \text{(VIII-1)}$$

We must then add a term to the Hamiltonian for each Q_i to account for the potential energy associated with the nuclear vibration[1]

$$H_{\text{nuc vib}} = \tfrac{1}{2}k_i(Q_i - Q_i^0)^2,\ i = 1 \cdots 3N - 6. \qquad \text{(VIII-2)}$$

The nuclei vibrate about equilibrium position Q_i^0 with a harmonic oscillator restoring force given by the force constant $k_i = 4\pi^2 m_i c^2 \nu_i^2$ where ν_i is the frequency given in cm^{-1} for a force constant expressed