Interpretation of Electron Spin Resonance Parameters for Transition Metal Complexes

Jeffrey I. Zink and Russell S. Drago*

Contribution from the William A. Noyes Laboratory,
University of Illinois, Urbana, Illinois 61801. *Received August 2, 1971*

Abstract: The variations of the hyperfine coupling constants and g values caused by varying the solvent and the ligand substituents are interpreted for a series of substituted acetylacetonate complexes of copper(II). The change in energy separation between a given ligand molecular orbital and the particular antibonding metal d orbital containing the unpaired spin varies in a manner directly opposite to the change in separation between the center of gravity of all of the metal orbitals and the energy of the given ligand orbital. The overall bonding in complexes cannot be reliably interpreted from esr parameters which depend on antibonding molecular orbitals.

In a recent publication from this laboratory,[1] trends in covalency between a metal ion and a constant ligand were investigated in a series of complexes of the type *trans*-Ni(*meso*-stilbenediamine)$_2$-(anion)$_2$ where the anions (the variable ligands) were acetate, chlorosubstituted acetate, benzoate, and substituted benzoate anions. It was found that the covalency trend deduced from a naive interpretation of the nmr isotropic shifts was opposite to that expected from our knowledge of the inductive properties of the substituent groups. The effect of varying the axial anionic ligand on the stilbenediamine pmr isotropic shifts was an increase in the observed isotropic shift as the axial ligand strength increased. The magnitude of the isotropic shifts of specific protons can be related to the amount of mixing of the ligand and metal ion's atomic orbitals in the molecular orbital containing the unpaired electron. The observed trend is opposite to the expected trend in metal–ligand covalency predicted on the basis of charge donated to the metal *via* the inductive properties of the axial ligands, *i.e.*, strong donor axial ligands decrease the formal charge on nickel(II) which results in a less covalent metal–stilbenediamine bond.

A model explaining the unexpected (on the basis of covalency effects) trend in isotropic shifts was presented and justified. The basic idea behind the model is that the change in energy separation between *a particular metal d orbital* and a given ligand molecular orbital of appropriate symmetry in a series of complexes may occur in a manner directly opposite to the change in separation between the energy of the center of gravity of *all* of the metal d orbitals and the energy of this ligand orbital. For example, in our earlier study, the change in the magnitude of the tetragonal splitting of the nickel d orbitals was greater than the change in energy of the center of gravity of the d orbitals arising from changing the nickel formal charge. Hence, as the axial ligand became stronger, the tetragonal splitting decreased and the energy of the $d_{x^2-y^2}$ orbital decreased even though the center of gravity of the d orbitals increased in energy. The magnitude of the isotropic shift of the stilbenediamine protons which is inversely proportional to the separation between the ligand σ and the metal $d_{x^2-y^2}$ orbital energies thus increases as the axial ligand becomes stronger. On the other hand, the total metal–ligand interaction which is dependent upon all of the metal orbitals (3d, 4s, and 4p) decreased because of the larger energy separation between the total average metal orbital energy and the constant ligand σ orbital energy. Quantitative support for this model was provided from the electronic absorption spectrum by crystal-field calculations.[2,3]

This model suggests that any interpretation of metal–ligand covalency which is based solely upon a physical method measuring properties of nonbonding or antibonding complex molecular orbitals could produce unreliable results. Consequently, we investigated the literature to find parallel experiments in which unusual trends in covalency were reported in order to extend the range of applicability of our model and shed new light upon the meaning of the previous studies. Several such studies involving interpretation of the esr parameters of copper(II) acetylacetonate complexes seemed suspect,[4–6] so the results and conclusion of these studies were reexamined in terms of our model.

Theory

In an esr experiment, the observables which are interpreted in terms of covalency are the electron spin resonance frequency, the metal hyperfine coupling, and the ligand hyperfine coupling. Before we discuss the application of our model to esr studies, we shall first show how the observables mentioned above have been related to molecular orbital (MO) theory parameters.

The specific applications to be considered here will be square-planar copper(II) complexes (D_{4h} symmetry). The following antibonding MO's can be formed from the copper 3d orbitals and the orbitals of the ligand donor atom

$$\mathrm{B_{1g}} = \alpha \mathrm{d}_{x^2-y^2} - \alpha'(-\sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^3 - \sigma_y{}^4)/2 \quad (1)$$

$$\mathrm{B_{2g}} = \beta_1 \mathrm{d}_{xy} - \beta_1'(P_y{}^1 + P_x{}^2 - P_y{}^3 - P_x{}^4)/2 \quad (2)$$

$$\mathrm{A_{1g}} = \alpha_1 \mathrm{d}_{z^2} - \alpha_1'(\sigma_x{}^1 + \sigma_y{}^2 - \sigma_x{}^3 - \sigma_y{}^4)/2 \quad (3)$$

$$\mathrm{E_g} = \begin{Bmatrix} \beta \mathrm{d}_{xz} - \beta'(P_z{}^1 - P_z{}^3)/2^{1/2} \\ \beta \mathrm{d}_{yz} - \beta'(P_z{}^2 - P_z{}^4)/2^{1/2} \end{Bmatrix} \quad (4)$$

---

(1) J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, 92, 5339 (1970).

(2) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967).

(3) D. A. Rowley and R. S. Drago, *ibid.*, 7, 795 (1968).

(4) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 43, 1744 (1965).

(5) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, 71, 109 (1967).

(6) H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Jap.*, 43, 1078 (1970).

where

$$\sigma^{(i)} = np^{(i)} \mp (1 - n^2)^{1/2} S^{(i)} \tag{5}$$

The notation, which follows that of Maki and McGarvey,[7] represents four ligands on the x and y axes. The superscripts label the appropriate ligand orbitals and start with one on the $+x$ axis and proceed counterclockwise. The orbitals are given in order of increasing energy. The unpaired electron occupies the B_{1g} orbital. The coefficients in that orbital are related by

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \tag{6}$$

where the overlap integral S is

$$S = (d_{x^2-y^2}|-\sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^3 + \sigma_y{}^4)/2 \tag{7}$$

Our goal is to find the energy of the magnetic interactions important in the interpretation of covalency by using the ligand field eigenfunctions as the basis set and using second-order perturbation theory. The expression for the perturbing part of the total Hamiltonian containing the magnetic effects of interest for the case of a $3d^9$ configuration is[8]

$$W' = \lambda \mathbf{L}\cdot\mathbf{S} + \beta_0 \mathbf{H}\cdot(\mathbf{L} + 2\mathbf{S}) + P/7[(4\mathbf{S}\cdot\mathbf{I}) - (\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{I}) - (\mathbf{L}\cdot\mathbf{I})(\mathbf{L}\cdot\mathbf{S})] - Pk\mathbf{S}\cdot\mathbf{I} \tag{8}$$

The first term is the spin–orbit coupling; the second, the magnetic Zeeman interaction; the third, the electron-nuclear dipolar coupling; and the last, the scalar (Fermi contact) coupling. As is usually done, we abbreviate $2\lambda\beta\beta_N\langle r^{-3}\rangle$ as P where $\langle r^{-3}\rangle$ is the average value of $1/r^3$ for a free copper ion, and we use k to represent the isotropic Fermi interaction. Several important assumptions concerning k will be discussed later. The energy to second order is found[9] to be

$$\begin{aligned} E_{\text{total}} = E^{(1)} + E^{(2)}{}_{\text{Zeeman}} = {} & \beta_0 H_z S_z\left[2 - \frac{8\lambda\alpha\beta_1}{E_{xy}}\left(\alpha\beta_1 - \frac{\alpha'(1-\beta_1{}^2)^{1/2}}{2}T(n)\right)\right] + \\ & \beta_0 H_x S_x\left[2 - \frac{2\lambda\alpha\beta}{E_{xz}}\left(\alpha\beta - \frac{\alpha'(1-\beta^2)^{1/2}}{2^{1/2}}T(n)\right)\right] + \\ & \beta_0 H_y S_y\left[2 - \frac{2\lambda\alpha\beta}{E_{yz}}\left(\alpha\beta - \frac{\alpha'(1-\beta^2)^{1/2}}{2^{1/2}}T(n)\right)\right] \end{aligned} \tag{9}$$

The integrals over the normalized radial 2p and 2s ligand functions are abbreviated as Q. R is the central ion–ligand internuclear distance. It is a good approximation to consider the term $T(n) = (n + {}^1/_2(1 - n^2)^{1/2}RQ)$, a constant in the series of ligands we will consider here. Kivelson and Neiman[9] calculate its value to be 0.22 for $R = 1.9$ Å for acetylacetonate, one of the ligands in our series. E_n is the energy between state n and the B_{1g} ground state. If we had originally set up our total Hamiltonian to be the familiar spin Hamiltonian

$$\mathcal{H} = \beta_0[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] \tag{10}$$

direct comparison shows that

$$\begin{aligned} g_{\parallel} &= 2 - \frac{8\lambda\alpha\beta_1}{E_{xy}}\left(\alpha\beta_1 - \frac{\alpha'(1-\beta_1{}^2)^{1/2}}{2}T(n)\right) \\ g_{\perp} &= 2 - \frac{2\lambda\alpha\beta_1}{E_{xz},E_{yz}}\left(\alpha\beta - \frac{\alpha'(1-\beta^2)^{1/2}}{2^{1/2}}T(n)\right) \end{aligned} \tag{11}$$

The expressions for A and B, respectively the parallel and perpendicular components of the hyperfine coupling constant, may be found in the same manner. When the Hamiltonian W' is applied to the ground electronic state wavefunction B_{1g}, the first-order energy is

$$E^{(1)} = (B_{1g}|W'|B_{1g}) = 2\beta_0 \mathbf{H}\cdot\mathbf{S} + P\alpha^2[-4/7 S_z I_z + 2/7(S_x I_x + S_y I_y)] - kP\mathbf{S}\cdot\mathbf{I} \tag{12}$$

This result is easily obtained since matrix elements of the type $(B_{1g}|L_i|B_{1g})$ all vanish because a singlet orbital state has no angular momentum. Hence, spin–orbit coupling does not contribute in first order. In second order, however, it gives rise to extremely important magnetic effects. The matrix elements of the dipolar Hamiltonian are tabulated by Griffith.[8] Direct comparisons of eq 12 with the general hyperfine Hamiltonian for Cu(II) in a tetragonal crystal field

$$\mathcal{H} = AS_z I_z + B(S_x I_x + S_y I_y) \tag{13}$$

gives (to first order)

$$A = P(-4\alpha^2/7 - k) \tag{14}$$

$$B = P(2\alpha^2/7 - k) \tag{15}$$

In order to find the expressions for A and B to second order, matrix elements involving excited states must be evaluated. The calculation involves no new assumptions and for reasons of brevity will not be repeated here. The result to second order is[9]

$$\begin{aligned} A = P[&-4/7\alpha^2 - k + (g_{\parallel} - 2) + 3/7(g_{\perp} - 2) - \frac{\lambda 4\alpha\alpha'\beta_1}{E_{xy}}(1 - \beta_1{}^2)^{1/2}T(n) - \\ & \frac{(3\sqrt{2}/7)\alpha\alpha'\beta}{E_{xz},E_{yz}}(1 - \beta^2)^{1/2}T(n)] \end{aligned} \tag{16}$$

$$B = P[2/7\alpha^2 - k + 11/14(g_{\perp} - 2) - \frac{(11\sqrt{2}/14)\alpha\beta\alpha'}{E_{xz},E_{yz}}(1 - \beta^2)^{1/2}T(n)] \tag{17}$$

The terms involving integrals are small, as discussed previously, and have a value of approximately 0.04.

The covalency is defined in terms of the quantity α appearing in the equations we have discussed and derived. If $\alpha = 1$, the bond would be completely ionic. If the overlap integral S were vanishingly small and $\alpha = 0.5$, the bond would be completely covalent. However, because $S \neq 0$, these absolute definitions are not used and, instead, one must speak of trends. The smaller the value of α, the greater the assumed covalent nature of the bond. A crucial assumption has been made in deriving these equations, *i.e.*, the ratio of s to d character is unchanged by the presence of ligands.[9] In this way, the Fermi contact coupling of electron and copper spins is treated as the coupling observed in the free ion ($k = 0.43$ with $\alpha^2 = 1.0$) weighted by the depletion of unpaired spin due to covalency. We will examine this crucial assumption more fully later. The

---

(7) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

(8) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, England, 1964.

(9) D. Kivelson and R. Nieman, *J. Chem. Phys.*, **35**, 149 (1961).

desired expression for α^2 may be found by rearranging eq 16. The last two terms of that expression are approximated by the number 0.04, giving

$$\alpha^2 = 7/4[-A/P - k + (g_{\parallel} - 2) + 3/7(g_{\perp} - 2) + 0.04] \quad (18)$$

In principle, α, β, and β' could be calculated from eq 11, 12, 16, and 17 if E_{xy}, E_{xz}, $g_{\parallel}$, $g_{\perp}$, A, and B were all known. However, E_{xy}, E_{xz}, and B usually cannot be accurately measured. Consequently, eq 18 is often used to obtain a first approximation to α. Examples of the applications of the procedure outlined here may be found in the papers by Kivelson, *et al.*,[9] Gersmann, *et al.*,[10] and Maki, *et al.*[7] For completeness, we should note that eq 16 and 17 are often written as

$$A = P[-\alpha^2(4/7 + K) + (g_{\parallel} - 2) + 3/7(g_{\perp} - 2) + 0.04] \quad (19)$$

$$B = P[\alpha^2(2/7 - K) + 11/14(g_{\perp} - 2) + \text{small terms}] \quad (20)$$

where K is related to k through the definition $K\alpha^2 = k$. Also, using the definitions $A_{\text{ave}} = {}^1/_3A + {}^2/_3B$ and $g_{\text{ave}} = {}^1/_3g_{\parallel} + {}^2/_3g_{\perp}$, and using eq 19 and 20 we find

$$A_{\text{ave}} = P[(-\alpha^2K + (g_{\text{ave}} - 2.0023) + \text{small terms}]$$

or

$$\alpha^2 = -A_{\text{ave}}/PK + (g_{\text{ave}} - 2.0023)/K + \text{small terms} \quad (21)$$

Discussion

In the study by Rogers, *et al.*,[4,5] on square-planar acetylacetonato and substituted acetylacetonato complexes of copper(II), the trend in covalency of the unpaired electron was directly related to the expected covalency in the metal–ligand bond. An opposite trend was deduced from the values of α^2 compared to that expected from ligand basicity (see Table I). As more electron-withdrawing substituents are placed on the ligand, the metal–ligand σ bond is expected to become weaker and less covalent. As can be seen from eq 18, decreasing values of $g_{\parallel}$ and $g_{\perp}$ correspond to smaller values of α^2 which indicate more extensive mixing in of the ligand orbitals in the MO containing the unpaired electron. The trend in the average g values (Table I) is seen to parallel the expected trend in metal–ligand covalency (as the bonding becomes more covalent g approaches 2.0023).

Table I. Esr Data for $Cu(R^1\text{–}CO\text{–}CHR^2\text{–}COR^3)_2$

R_1	R_2	R_3	$10^4 \cdot A_{\parallel}$, cm^{-1}	$10^4 \cdot A_{\perp}$, cm^{-1}	$g_{\parallel}$	$g_{\perp}$	Solvent
CF_3	H	CF_3	173	24.5	2.306	2.051	$CHCl_3$
CF_3	H	CH_3	167	25.2	2.308	2.040	$CHCl_3$
Phenyl	H	CH_3	176	26.6	2.281	2.046	$CHCl_3$
CH_3	H	CH_3	175	28.2	2.285	2.042	$CHCl_3$
CH_3	H	CH_3			2.256	2.056	Toluene
CH_3	H	CH_3	160		2.304	2.060	10% pyridine 90% toluene
CH_3	H	CH_3	163		2.297	2.062	20% pyridine 40% $CHCl_3$ 40% EtOH
CH_3	H	CH_3	172	13:1	2.293	2.061	DMF
CH_3	H	CH_3	164	3.5	2.302	2.071	Pyridine

The A values for these complexes are negative. As can be seen from eq 18, a more negative A corresponds to a larger α^2 which corresponds to less mixing of the metal ion orbital and the ligand in the molecular orbital containing the unpaired electron. The trend in A values does not parallel the expected trend of covalency in the metal–acetylacetonato bonds. Furthermore, interpretation of the parameters obtained from the spectra of the complexes dissolved in different solvents in terms of covalency would cause one to conclude that the more basic the solvent, the greater the covalency in the metal–acetylacetonato bond deduced from the A values and the smaller the covalency deduced from the g values.[4] These observations were the first reported inconsistencies of trends in covalency when these two different esr parameters (A and g) were interpreted this way. Recently, other workers[6] also found a trend in covalency as interpreted from g values to be opposite to that found from the A values in a solvent effect study of some copper(II) acetylacetonates. They did not attempt to explain their results.[6] Table I summarizes the data obtained by the two groups of workers.

Rogers, *et al.*,[5] rationalized this apparent inconsistency by postulating a changing fraction of metal 4s character in the ground state. The derivation outlined in the theory section assumed a constant ratio of 3d to 4s character in the orbital containing the unpaired spin in all of the complexes and explained changes in A by a changing the metal coefficient in the B_{1g} molecular orbital. Rogers introduced a new parameter, f^2, defined as the fraction 3d character in the copper B_{1g} orbital. Following Rogers,[5] eq 25 may be written

$$\alpha^2 = -A_{\text{ave}}PK + (1 - f^2)0.0975/PK + (g_{\text{ave}} - 2.0023)/K \quad (22)$$

where an electron in a 4s orbital is assigned a Fermi coupling constant of 0.0975 cm^{-1}. An analogous expression may be derived using the anisotropic components of the coupling constants

$$\alpha^2f^2 = 7/4(A_{\parallel}/P - A_{\text{ave}}/P + 2g_{\parallel}/3 - 5g_{\perp}/21 - 6/7) \quad (23)$$

The data in Table II was calculated by Rogers, *et al.*,[5] using these equations. Obviously, the use of another parameter allows the α^2 values to follow the expected covalency order. The additional parameter is in effect a correction to A for changing 4s character in B_{1g}. It has complicated the interpretation by introducing another factor which cannot be tested or rigorously solved.

When applied to the data in Table II, the interpretation of the f^2 factor indicates that the amount of 4s character increases as the metal–ligand bond becomes more ionic contrary to the reported[5] mechanism of vibronic mixing. Furthermore, it was possible to obtain the correct trend in α^2 using eq 23 and omitting the parameter f^2 entirely as indicated in Table II. Thus, introduction of the parameter f^2 for the 4s interpreta-

---

(10) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, 36, 3221 (1962).

Table II. Values of α^2 and f^2

R_1	R_2	R_3	Solvent	α^2 (from isotropic data)	α^2 (from anisotropic data $f = 1$)	α^2 (from eq 15, 16)	f^2
CF_3	H	CF_3	$CHCl_3$	0.757	0.840	0.853	0.985
CF_3	H	CH_3	$CHCl_3$	0.763	0.802	0.808	0.993
Phenyl	H	CH_3	$CHCl_3$	0.777	0.793	0.795	0.997
CH_3	H	CH_3	$CHCl_3$	0.779	0.791	0.793	0.997
CH_3	H	CH_3	DMF	0.743	0.831	0.844	0.985
CH_3	H	CH_3	Pyridine	0.706	0.843	0.865	0.975

tion has created almost as many problems as have been "solved."

Our interest in the problem arose by virtue of the close analogy between the solvent effect data (Tables I and II) and our nmr contact shift study of a series of bis(stilbenediamine)nickel(II) complexes. Our conclusion in this nmr study is directly transferrable to the esr experiment. Basically, the point is that *one cannot deduce information about the overall bonding in complexes by probing what is happening in nonbonding or antibonding molecular orbitals.* By virtue of the fact that the esr experiment is only telling us about the orbitals containing unpaired electrons, it suffers all of the disadvantages of the isotropic nmr shift in determining covalency trends. A complete bond order analysis of $d_{x^2-y^2}$, d_{z^2}, 4s, $4p_x$, and $4p_y$ interacting with ligand orbitals (ligands on the xy axis) is needed as has recently been done[11] for a series of metallocene and bisbenzene complexes. With this point in mind, we are in a position to propose an alternative explanation to the interpretation of the esr parameters which is consistent with our earlier interpretation of the isotropic shifts of the nickel(II) complexes. Unfortunately, the electronic spectrum of copper(II) is not as rich as that of nickel(II).

First, we consider the solvent effect data. Figure 1a illustrates the d-orbital splittings in D_{4h} symmetry. The energy of the σ acetylacetonate orbitals has been arbitrarily placed and labeled ligand. In Figure 1b, we have indicated the expected changes in the d-orbital energies which would accompany solvation of d_{z^2}. The crux of the argument is that the tetragonal distortion and hence the d_{z^2} and $d_{x^2-y^2}$ separation decreases from the crystal field of the ligand on the z axis much more rapidly than the energy of the entire d manifold is raised. Thus, even though the charge on the metal is decreasing and the overall covalency in the metal-acetylacetonate bond is decreasing as the solvent becomes more basic, the mixing of $d_{x^2-y^2}$ with the ligand orbitals is increasing because of the smaller energy separation between them. However, the total covalency decreases due to the total net raising of all the metal orbital energies. The $g_{\parallel}$ values increase as the solvent becomes more basic because they are dominated by the coupling between the d_{xy} and $d_{x^2-y^2}$ orbitals which is directly proportional to the spin-orbit coupling constant and inversely proportional to the energy separation between the two orbitals, E_{xy}. The latter quantity has been found to decrease by 800 cm^{-1} when the solvent is changed from $CHCl_3$ to pyridine.[5] The $g_{\parallel}$ values will also reflect changes in the coefficients. As the energy of the $d_{x^2-y^2}$ orbital decreases, α will always decrease, α' increases, and β either increases or decreases depending on the relative energies of the d_{z^2} orbital and ligand B_{2g} orbitals. On the other hand, the value of A decreases as the solvent becomes more basic. It is dominated by the α coefficient and reflects the more extensive mixing of $d_{x^2-y^2}$ with the ligand because of the decreased tetragonal distortion.

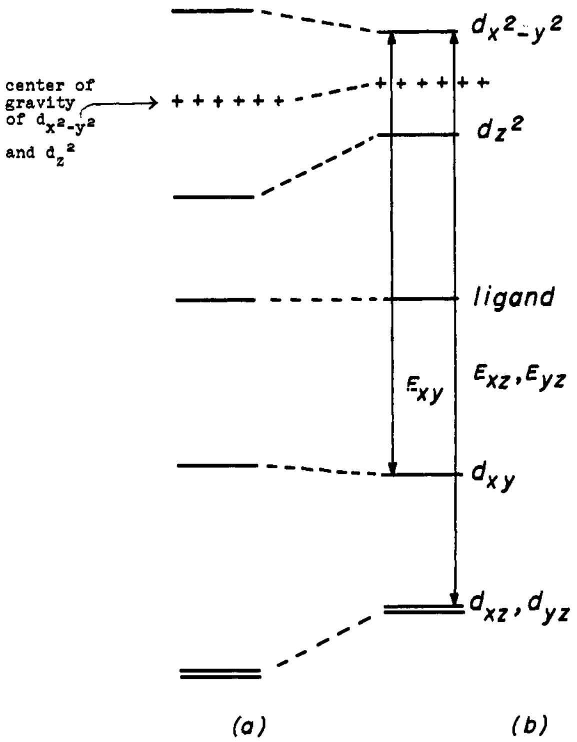

Figure 1. The effect of changing the solvent on the relative energies of the d orbitals of a square-planar complex. The unsolvated complex is indicated in (a) and the solvated complex in (b).

The effect of substituents on the acetylacetonate data may be interpreted using Figure 2. The application of our model to this case is not as unambiguous since we are not considering the trends in metal-ligand covalency for a ligand which is held constant in the series. The cautions discussed previously concerning a variable ligand and its changing molecular orbital must be considered. In particular, we cannot assume that the ligand σ orbitals remain constant in energy. However, the metal $d_{x^2-y^2}$ and the ligand σ orbital energy difference can increase as we substitute less electron-withdrawing substituents, since now both transfer of elec-

---

(11) S. Anderson, Jr., and R. S. Drago, submitted for publication.

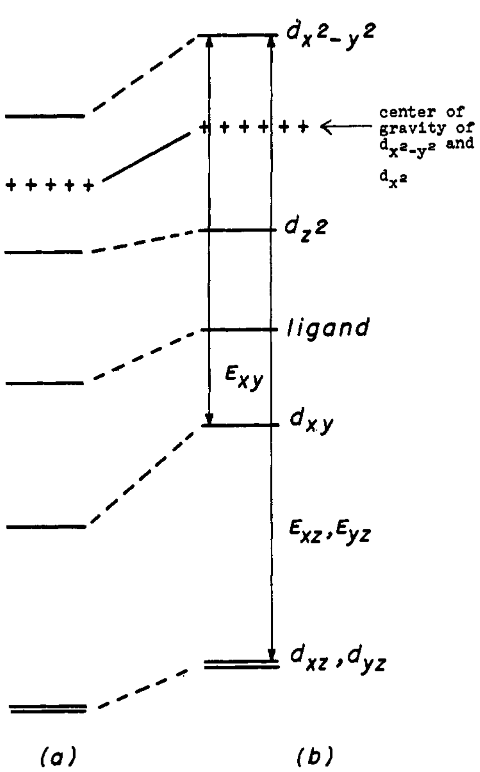

Figure 2. The effect of varying the electron-withdrawing power of substituents on substituted acetylacetonates on the d orbital energies of square-planar copper(II) complexes. The electron-withdrawing power decreases from left to right, *i.e.*, the $-CF_3$ substituent is indicated in (a) and CH_3 in (b).

tron density to the metal and electrostatic crystal field effects contribute to the raising of the metal $d_{x^2-y^2}$ orbital. The ligand σ orbitals also raise in energy because of the induction properties of the substituent, but of the two effects raising the $d_{x^2-y^2}$ orbital energy apparently outweighs the raising the ligand σ orbital energy. A net increase in separation results with a corresponding smaller amount of mixing. The $g_{\parallel}$ value decreases as the substituent becomes less electron withdrawing corresponding to an increase in the energy of d_{xy}.

We have extended our previous model used to explain isotropic shifts to two different cases: solvent effects and variation of the electron-withdrawing ability of a ligand on the esr parameters. The former was a straightforward extension of the model; the latter required an additional assumption. Evidence supporting our application of the same model to the two cases is provided by a plot of g_{ave} *vs.* A. For both solvent and substituent effect cases, all of the experimental points fall on the same straight line.[4] This observation suggests that similar processes are affecting the copper ground electronic state in both cases and that it is valid to apply the same model to the two. We cannot eliminate the possibility of 4s mixing in B_{1g}. Further experimental evidence is needed to support or refute these arguments. We hoped to be able to use ligand hyperfine structure as a test of our model and in this regard examined the results of esr studies of pyridine and substituted pyridine copper(II) complexes. Nitrogen hyperfine structure was observed, but no direct correlation was found between A and the A_n arising from the ligand nuclei.[12,13] This result is not too surprising since substituents on the pyridine could produce a larger change in the nitrogen coefficient in the total MO than they produce in the ligand σ coefficient in the metal–ligand B_{1g} MO. These effects destroy the relationship between A and A_n predicted by eq 6, 16, and 17. The recent observation of nitrogen hyperfine coupling in the esr spectra of several $Cu(hfacac)_2$ adducts[14] and a crystallographic studying proving that bases are not always added in the axial positions[15] in the solid state further emphasizes our thesis that one cannot deduce information about the overall bonding by probing what is happening in nonbonding or antibonding molecular orbitals. Our model predicts that the effect of a geometry change from D_{4h} to C_{2v} or C_{4v} to C_1 site symmetry would cause a decrease in A. The effect of such a change on Figures 1 and 2 would be to decrease the splitting of the $d_{x^2-y^2}$ and d_{z^2} orbitals, thus lowering the $d_{x^2-y^2}$ orbital's energy and increasing the mixing with ligand orbitals. This decrease in A is observed[14] for the pyridine complex, but, in practice, it is difficult to use this as a criterion for geometry. A C_{4v}–C_{2v} geometry change will also be manifested by the appearance of ligand hyperfine coupling. In such cases, esr parameters should be interpreted by a combination of the model of Figures 1 and 2 and by the general increase caused by the lowered symmetry. The solvent effect could be used as a test if delocalization onto $Cu(acac)_2$ protons could be observed by nmr studies of the complex in various solvents. The long electron spin relaxation time prevents nmr contact shift studies since the ligand protons are relaxed so efficiently. However, use of a free-radical spin relaxer[16,17] might allow such studies to be made. We would expect that as the solvent becomes more basic, the contact shift would increase.

Acknowledgment. We gratefully acknowledge the generous support of this research by the National Science Foundation through Grant GP 25554.

---

(12) W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, **48**, 1529 (1965).

(13) K. Wuthrich, *ibid.*, **49**, 1400 (1966).

(14) B. B. Wayland and M. D. Wisniewski, *Chem. Commun.*, 1025 (1971).

(15) G. W. Bushnell, *Can. J. Chem.*, **49**, 555 (1971).

(16) R. W. Kreilick, *Mol. Phys.*, 14, 495 (1968).

(17) R. W. Kreilick, *J. Amer. Chem. Soc.*, **90**, 2711 (1968).