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# MAGNETIC RESONANCE METHODS IN THE STUDY OF THE ELECTRONIC STRUCTURE OF TRANSITION METAL COMPLEXES

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## A INTRODUCTION

The description of the metal–ligand bonding in transition metal complexes presents a continuing problem for inorganic chemists Theoretical work in this area has progressed from the valence bond approach of Pauling through crystal field theory to the current molecular orbital approach Our qualitative understanding of bonding in these complexes can now be described as quite good. They are, however, complicated, many-electron systems and quantitative calculations are still far from reliable From the point of view of the chemist, much of the interest in this subject lies in just those finer details of the electronic structure which are most inaccessible to theoretical calculation Experimental approaches to the problem are therefore still of considerable value. Of the various physical techniques which provide information in this area, magnetic resonance methods are probably the most powerful. The full potentialities of the technique are only realized when the complexes are paramagnetic, in which case electron spin–nuclear spin interactions provide a very detailed probe of the electronic structure It is this area of the subject which will be described in the present review.

In principle, a paramagnetic metal complex offers a choice of magnetic resonance techniques. Transitions involving a change in electron spin quantum number may be studied by ESR and those involving a change in nuclear spin quantum number by NMR. A variety of double resonance techniques (ENDOR, the Overhauser effect) complement the straightforward experiments and related methods such as Nuclear Quadrupole Resonance and

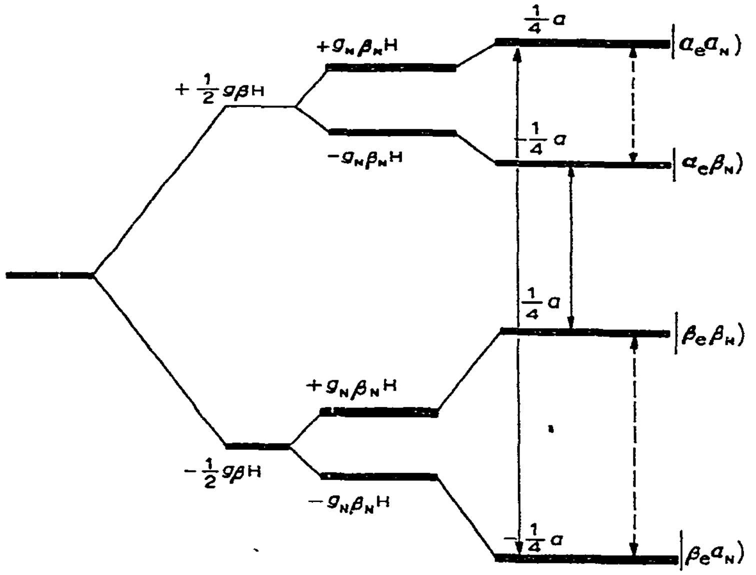


Fig 1 NMR and ESR transitions for $S = 1/2, I = 1/2$ system ←----→ NMR, ←——→ ESR

Mossbauer spectroscopy where applicable, contribute valuable supplementary data However, in the present article only simple ESR and NMR experiments will be considered

There are very few systems amenable to study by both ESR and NMR The primary reason for this can be seen by reference to Fig 1. In this figure the magnetic energy levels for a simple system comprising one electron and one nucleus of spin 1/2 are shown Two ESR transitions differing in energy by $A$, the hyperfine coupling constant, are expected There are also two NMR transitions. one at a frequency given by $h\nu = g_N\beta_N H - 1/2(A)$ and one at $g_N\beta_N H + 1/2(A)$ The appearance of the spectra, however, depend critically on the electron spin relaxation time $T_{1e}$ The necessary condition for observing well-resolved hyperfine structure in the ESR spectrum is that $1/T_e \ll A$, i e. that the relaxation time be long For the NMR spectrum the nuclear spin relaxation time determines the spectral properties For a paramagnetic complex the dominant nuclear relaxation mechanism is likely to arise from the fluctuating magnetic fields produced at the nucleus by changes in the orientation of the electron spin Thus the nuclear relaxation time is determined by the electron spin relaxation time Furthermore, the limitation on the relaxation time necessary for the observation of sharp NMR lines is much more rigorous than that for ESR Typically NMR lines are of the order of Hz broad whereas ESR line widths are measured in MHz Hence the NMR transitions indicated in Fig 1 in practice are never observed. There are, however, certain conditions under which sharp-line NMR spectra can be observed These arise in cases where the electron spin relaxation time is very short i e $1/T_e \gg A$. In these circumstances, the rapidly fluctuating magnetic fields produced by the electron spin are no longer effective in producing nuclear relaxation The fluctuations are of such a high frequency that they have negligible components of the correct frequencies to induce nuclear transitions. In these circumstances, the nucleus, instead of experiencing either the hyperfine magnetic field corresponding to interaction with an $\alpha$ electron spin or the hyperfine field corresponding to interaction with a $\beta$ spin, experiences an average local field corresponding to the mean value, $\langle S_z \rangle$, of the electron spin polarization. This mean value is not equal to zero since the population of the $\alpha$ and $\beta$ states are not equal. Hence there is a chemical shift resulting from the electron spin–nuclear spin interaction Thus it is apparent that the conditions for the ESR experiment ($1/T_e \ll A$) and for the NMR experiment ($1/T_e \gg A$) are incompatible The two types of experiments are not, however, completely exclusive. Relaxation times are temperature-dependent and in some instances it is possible to carry out ESR experiments in solids at low temperatures where $T_e$ is long and NMR experiments in solutions at high temperatures where $T_e$ is short. Examples of such cases may be found below

Not only do the two forms of magnetic resonance differ in their practical applicability, they also provide different, but complementary, information for the inorganic chemist. In ESR, attention is focussed on the metal ion and its immediate environs and the question is asked "how have the properties of the free ion been modified by interaction with the ligands?" In NMR, the focus is on the ligands and the question is "how has the electronic structure of the ligand been modified by interaction with the metal ion?". There is an obvious symmetry to the two approaches and the objective of the present review is to draw attention to some of the interlocking facets of the two fields The fundamental physics of the situation could probably be best illustrated by reviewing a number of the very elegant experiments which have been carried out on relatively simple systems such as transition metal halides. We choose, however, to adopt a more chemical criterion and to discuss instead work on transition metal chelates, the appeal of which is more chemical in nature Initially, some of the relevant theory will be briefly reviewed

## B ESR THEORY

Basically the interpretation of the ESR spectrum of an isolated transition metal ion yields values for two different kinds of parameter The spectroscopic splitting constants ($g$ values) describe the frequencies (or energies) required to bring about transitions between the different electron spin states The hyperfine coupling constants ($A$) describe the electron spin–nuclear spin interactions which give rise to the hyperfine structure observed in the spectrum Both of these parameters may be anisotropic, i e their values may depend on the orientation of the molecule with respect to the applied magnetic field In addition, ions containing more than one unpaired electron will exhibit zero-field splitting effects due to electron spin–electron spin interactions and to spin orbit coupling These interactions (which are also usually anisotropic) are described by the zero-field splitting parameters $D$ and $E$ All of these parameters are affected by the presence of ligands around the central metal atom The ligand effects can be subdivided into two kinds Initially, one may adopt the crystal field approximation of regarding the function of the ligands as one of providing an electrostatic field which will perturb the electronic structure of the metal ion This approach proves inadequate for the type of complexes we wish to discuss The breakdown occurs because chemically interesting complexes are usually covalent rather than ionic in character. In these circumstances, it is no longer satisfactory to consider only a basis set of atomic orbitals centred on the metal ion. Instead one must deal with molecular orbitals expressed as appropriate linear combinations of metal and ligand atomic orbitals Using molecular orbital theory, a set of secondary parameters (usually written $\alpha, \beta$ etc.), which are the coefficients of the various atomic orbitals in the expansions for the molecular orbitals, can be derived from the primary parameters $g$ and $A$ It is these secondary parameters which are of prime interest to the inorganic chemist since they provide detailed quantitative data on the nature of the metal–ligand bonding

The basic theory pertinent to the application of ligand field theory to ESR has been developed in a number of excellent textbooks[1] and review articles[2] The $g$ values of a complex are determined by the expectation values of the components of the vector operator $L + 2S$ (Allowing for relativistic corrections the 2 in this expression becomes 2 0023 ) In many cases the orbital angular momentum in the ground state of the molecule is completely quenched and an isotropic $g$ value of 2.0023 is obtained to zero-order approximation This will always be the case if the complex is of sufficiently low symmetry that the orbitals containing the odd electrons are non-degenerate This approximation, however, does not usually suffice for transition metal complexes Spin-orbit coupling leads to a mixing of excited state configurations with the ground state configuration and it is necessary to find the expectation values of $L + 2S$ using these corrected ground-state wave functions. Typically, therefore, perturbation theory leads to $g$ values of the form

$$g_{\parallel} = 2\left(1 - \frac{x\lambda}{\Delta}\right) \qquad g_{\perp} = 2\left(1 - \frac{y\lambda}{\Delta}\right)$$

for an orbitally non-degenerate ground state, where $\lambda$ is the spin-orbit coupling parameter, $\Delta$ is an energy difference between the ground-state configuration and an excited-state configuration and $x$ and $y$ are simple numerical factors In principle, $\lambda$ and $\Delta$ are obtainable from optical spectroscopy In practice, it is found that the $g$ values measured do not agree with those calculated unless smaller values of $\lambda$ are assumed than those obtained for the free ions Typically, a 20 or 30% reduction in the spin-orbit coupling constant is involved This effect is attributed to covalency in the metal–ligand bonding In order to calculate the $g$ values it is necessary to start with the correct molecular orbitals rather than with simple atomic $d$ orbitals. Since such a basis set will allow the electrons to spend part of their time on the ligand rather than on the metal, it is apparent that the effects of spin-orbit coupling will be reduced The equations for the $g$ values will now contain the coefficients of the atomic orbitals ($\alpha, \beta$) in the initial molecular orbitals as well as the parameters noted above. Analysis of the data, therefore, provides values for the molecular orbital coefficients. A number of individual calculations will be discussed in more detail in the sections below

The hyperfine coupling between electron spins and nuclear spins arises from two sources The first of these is a direct dipolar interaction. The magnetic moment of the electron produces a field at the nucleus, the direction of which depends on the orientation of the electron spin The situation is illustrated in Fig 2. The most notable feature of this interaction is that it is anisotropic, i e. the magnitude depends upon the orientation of the molecule with respect to the applied magnetic field Thus, referring to Fig 2, let us suppose that the electron is located at a fixed position on the $x$ axis It is apparent that application of the field parallel to the $y$ axis (Fig 2(a)) results in a dipole–dipole interaction of opposite sign to that obtained by applying the field in the $x$ direction (Fig 2(b)). In this

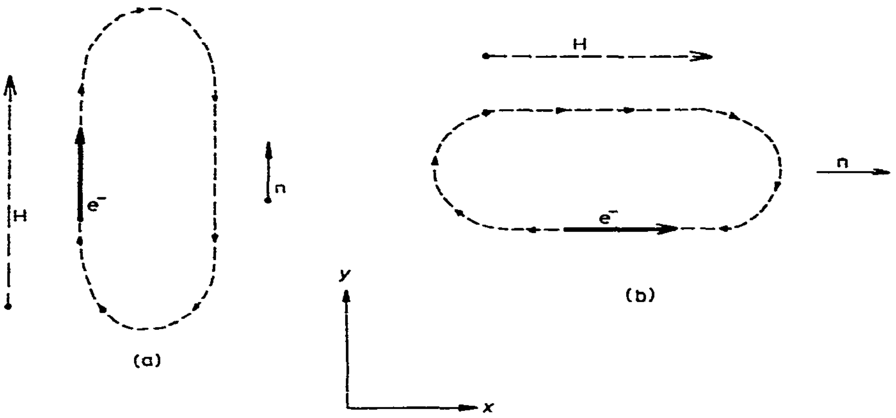


Fig 2 Dipolar interactions between an electron spin and a nuclear spin fixed in space

illustration we have kept the position of the molecule fixed with respect to the $x$ and $y$ axes and changed the direction of the field. In the actual experiment the direction of the field is kept constant and that of the molecule, fixed in a crystalline matrix, is varied The two are obviously equivalent A model in which the electrons are kept fixed in space is not a valid one for real molecules However, if the odd electron occupies an orbital with directional properties, e g an atomic $p$ or $d$ orbital, it is apparent that some directions will be preferred over others Analysis of the problem shows that the dipole–dipole coupling is proportional to the average value $\langle(3\cos^2\theta - 1)/r^3\rangle$ where $\theta$ is the angle between the direction of the magnetic field and a line joining the odd electron and the nucleus, and $r$ is the separation of the electron and metal nucleus Numerical values of this average can be readily calculated for the various $d$ orbitals In a covalent metal complex the odd electrons will be partly delocalized to the ligands. The value of $\langle 1/r^3\rangle$ for electrons located on the ligand will be much smaller than for an electron located in a metal $d$ orbital and dipolar contributions from such a source are often neglected Thus in a covalent complex, the anisotropic contribution to the hyperfine splitting will be reduced by a factor $\alpha^2$, where $\alpha$ is the coefficient of the $d$ orbital in the molecular orbital containing the unpaired electron This effect, therefore, provides a method of estimating $\alpha$ independent of that previously discussed involving the $g$ values

The second source of hyperfine coupling is the Fermi Contact Interaction This mechanism demands a finite probability of finding the odd electron at the metal nucleus, i e there must be spin density in a metal $S$ orbital Since $S$ orbitals are involved, it is an isotropic interaction An important consequence of this is that the isotropic hyperfine splitting is the same in solution, where the molecules are freely tumbling, as it is in the solid state The dipolar coupling, on the other hand, averages to zero when the molecules are freely tumbling and therefore does not contribute to the solution spectrum. A recent paper by McGarvey[3] has considered isotropic hyperfine coupling in metal complexes in some detail Unpaired electrons in $d$ orbitals do not contribute directly to this effect The major source of the interaction is thought to be spin polarization of electron pairs in filled metal orbitals notably the 3*s* orbital in the first transition series. In this respect the situation is similar to that existing in aromatic radicals for which the well-known McConnell relationship [A6]

$$a_H = Q\rho_c$$

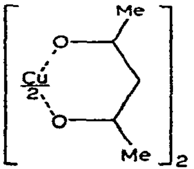
which states that the amount of spin polarization is proportional to the $p\pi$ spin density, holds There are, indeed, many complexes for which the metal hyperfine coupling provides a measure of the *d* orbital spin density [2a] In such complexes, increasing covalency results in increasing delocalization of the unpaired electrons and decreasing metal hyperfine splitting Estimates of the molecular orbital parameters obtained in this way are consistent with those obtained by the methods outlined above There are, however, some notable exceptions, especially amongst $Cu^{II}$ complexes, where the metal hyperfine coupling appears to be increasing with increasing covalency[6]. The most plausible interpretation involves interaction with higher unfilled metal *S* orbitals and a specific case will be considered in more detail below Obviously a degree of caution is necessary in this area

Finally, in some complexes, hyperfine splitting additional to that expected from the metal nucleus has been observed. This is attributed to interaction with ligand nuclei Usually, only atoms directly bonded to the metal are involved although there are occasional exceptions to this generalization In principle, both isotropic (contact) and anisotropic (dipolar) interactions are involved but since the odd electrons are predominantly on the metal so that $\langle 1/r^3 \rangle$ for ligand atoms is small the isotropic contribution usually predominates A large isotropic ligand splitting is expected in cases where the spin-containing orbital can mix directly with a ligand *S* orbital This is the case, for example, for $Cu^{II}$ complexes where the odd electron occupies a $\sigma$ antibonding orbital If it is assumed that the ligand orbitals comprise $sp^2$ hybrids, or some other suitable combination of ligand atomic orbitals, the ligand hyperfine splitting is dominated by the *S* component of the hybrid and the extent of metal–ligand orbital mixing can be calculated Usually, parameters obtained by this method agree well with those obtained from the *g* values indicating that the above assumptions are correct Line-width considerations restrict the observation of ligand hyperfine couplings of less than a gauss or so and as a result, unless there is direct delocalization of spin to the ligand *S* orbital as in the above example, ligand splitting will not be seen Thus, in $d^1$ vanadyl complexes, the odd electron is in an orbital orthogonal to the ligand $\sigma$ orbitals and no ligand hyperfine splitting has been reported

Finally, before discussing detailed results, it should be made clear that bonding parameters derived from ESR results refer only to ligand interactions with metal orbitals containing unpaired electrons Energetically, the most important interactions are, of course, with the *s*, *p* and *d* metal orbitals which hybridize to a set with appropriate geometrical properties and give rise to completely filled bonding molecular orbitals We are dealing here, therefore, with weaker additional interactions which, although they may contribute relatively little to the total bonding energy, nevertheless provide insight into the nature of metal–ligand interactions Exactly the same considerations apply to the discussions of NMR contact shifts

## C SOME ESR RESULTS

As indicated in the above paragraphs, the determination of bonding parameters from ESR data is, in principle, quite straightforward In practice the algebraic complexity of the problem tends to obscure this simplicity Initially, therefore, we will consider a $Cu^{II}$ complex without ligand hyperfine splitting. $Cu^{II}$ has only a single unpaired electron, and its relaxation properties are such that most complexes give relatively sharp lines at room temperature. As a result, a wide range of complexes have been studied. Maki and McGarvey[4] have carried out a single-crystal ESR study of $Cu^{II}$ acetylacetonate (structure I). The acetylacetonate ligand is typical of the class which chemically speaking give "covalent" compounds and the ease of formation of its complexes has led to many studies of their physical properties. Hence we will be able to compare these ESR results with NMR data on other transition metal acetylacetonates The $Cu^{II}$ compound has planar geometry and its crystal structure is isomorphous with the corresponding diamagnetic $Pd^{II}$ complex Maki and McGarvey, therefore, made their measurements on $Cu^{II}$ acetylacetonate diluted to 0 5 mole % in the $Pd^{II}$ compound. The use of such magnetically dilute crystals eliminates dipole–dipole interactions which would otherwise broaden the ESR lines The point group symmetry of the molecule is $D_{2h}$ but the rhombic distortions are sufficiently small to allow the use of the full $D_{4h}$ square planar symmetry in the theoretical treatment The relevant anti-bonding molecular orbitals can then be written



(I)

$$B_{1g} \quad \alpha d_{x^2-y^2} - \frac{\alpha'}{2}(-\sigma_x^a + \sigma_y^b + \sigma_x^c - \sigma_y^d)$$

$$B_{2g} \quad \beta_1 d_{xy} - \frac{(1-\beta_1{}^2)^{1/2}}{2}(P_y^a + P_x^b - P_y^c - P_x^d)$$

$$A_{1g} \quad \alpha_1 d_{3z^2-r^2} - \frac{\alpha_1'}{2}(\sigma_x^a + \sigma_y^b - \sigma_x^c - \sigma_y^d)$$

$$E_g \quad \begin{cases} \beta d_{xz} - \dfrac{(1-\beta^2)^{1/2}}{2^{1/2}}(P_z^a - P_z^c) \\ \beta d_{yz} - \dfrac{(1-\beta^2)^{1/2}}{2^{1/2}}(P_z^b - P_z^d) \end{cases}$$

The superscripts $a, b, c$ and $d$ label the four ligand oxygens and the ligand $\sigma$ orbitals are hybrids of the oxygen $s$ and $p$ atomic orbitals of the form

$$\sigma_k^m = nP_k^m + (1-n^2)^{1/2}S^m$$

The coefficients $\alpha$ and $\alpha_1$ give a measure of the ligand contribution to the $\sigma$ orbitals and $\beta$ and $\beta_1$ of the out-of-plane and in-plane $\pi$ mixing respectively The objective is to determine these coefficients Overlap has been neglected for the $\pi$ orbitals The odd electron is in the $B_{1g}$ orbital These orbitals are eigenfunctions if spin-orbit coupling is neglected They can, however, be mixed by the spin-orbit coupling L S It is, therefore, necessary to determine first a new basis set treating $\mathcal{H}_{LS}$ as a perturbation This basis set can then be operated on by the appropriate magnetic perturbation terms and the results expressed in the form of the spin Hamiltonian.

$$\mathcal{H} = \beta_0 [g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + A S_z I_z + B(S_x I_x + S_y I_y) +$$
$$+ Q[I_z^2 - \tfrac{1}{3} I(I+1)] - \gamma \beta_N H\ I$$

In this Hamiltonian, the first term represents the electron Zeeman effect, the second and third arise from hyperfine interactions, the fourth from nuclear quadrupole interactions and the final term from the nuclear Zeeman effect Spin-orbit coupling mixes the $B_{2g}$ and $E_g$ orbitals with the spin-containing $B_{1g}$ orbital but not the $A_{1g}$ orbital The expressions for the spin Hamiltonian parameters therefore contain $\alpha$, $\beta$ and $\beta_1$ but not $\alpha_1$ Solution of the problem gives

$$g_{\parallel} = 2\ 0023 - 8\rho [\alpha\beta_1 - \tfrac{1}{2}\alpha'(1-\beta_1{}^2)^{1/2}\, T(n)]$$
$$g_{\perp} = 2\ 0023 - 2\mu [\alpha\beta - \frac{1}{\sqrt{2}}\alpha'(1-\beta^2)^{1/2}\, T(n)]$$
$$A = P[-\tfrac{4}{7}\alpha^2 - \kappa + (g_{\parallel}-2) + \tfrac{3}{7}(g_{\perp}-2) - 4\rho\alpha'(1-\beta_1{}^2)^{1/2}\, T(n) - \frac{3\sqrt{2}}{7}\mu\alpha'(1-\beta^2)^{1/2}\, T(n)$$
$$B = P[\tfrac{2}{7}\alpha^2 - \kappa + \tfrac{11}{14}(g_{\perp}-2) - \frac{11\sqrt{2}}{14}\mu\alpha'(1-\beta^2)^{1/2}\, T(n)$$
$$Q' = \frac{-e^2 q \alpha^2 \langle r^{-3} \rangle_0}{7}$$

where

$$\rho = \frac{\lambda_0 \alpha \beta_1}{E_{xy} - E_0} \qquad \text{and} \qquad \mu = \frac{\lambda_0 \alpha \beta}{E_{xz,yz} - E_0}$$

$T(n)$ is a function of the ligand atomic orbitals which can be calculated if $n$ is known It is assumed that $n = (2/3)^{1/3}$ corresponding to $sp^2$ hybridization $\lambda_0$ is the spin-orbit coupling constant for the free $Cu^{2+}$ ion and the quantity $P$ given by

$$P = 2\gamma \beta_0 \beta_N \langle r^{-3} \rangle_0$$

also refers to the free $Cu^{2+}$ ion. In the expressions for the hyperfine coupling constants, the first term is the dipolar contribution, the second the Fermi contact contribution and the remaining terms are second-order corrections resulting from mixing in of the excited states A relationship between $\alpha$ and $\alpha'$ is also required and this is given as

$$\alpha' \approx (1-\alpha^2)^{1/2} + \alpha S$$

where $S$, the overlap between $d_{x^2-y^2}$ and the ligand $\sigma$ orbitals is calculated to be 0.094.

$\langle r^{-3}\rangle_0$ refers to the orbitals of the free divalent ion and is calculated to be 7 25 au. The measured experimental quantities are

$g_{\parallel} = 2.266_1$ $\qquad g_{\perp} = 2\ 053_5$

$A = -1\ 60 \times 10^{-2}\ \mathrm{cm}^{-1}$ $\qquad B = -0\ 19_5 \times 10^{-2}\ \mathrm{cm}^{-1}$

$Q' = 7 \times 10^{-4}\ \mathrm{cm}^{-1}$

From optical spectroscopy, the further information obtained is

$E_{xy} - E_0 = 15{,}000\ \mathrm{cm}^{-1}$ $\qquad E_{xz,yz} - E_0 = 25{,}000\ \mathrm{cm}^{-1}$ $\qquad \lambda_0 = -828\ \mathrm{cm}^{-1}$

Sufficient information is now available to calculate the bonding parameters The results obtained are

$\alpha^2 = 0\ 81$ $\qquad \beta^2 = 0\ 99$ $\qquad \beta_1{}^2 = 0.85$ $\qquad \kappa = 0\ 33$

This value of $\kappa$ agrees well with that obtained from the isotropic hyperfine splitting of $Cu^{2+}$ in ionic salts and confirms the assumption implicit in the above treatment that, in this case, the isotropic splitting is not sensitive to the degree of covalency. The qualitative deduction from the bonding parameters is that the $B_{1g}$ and $B_{2g}$ orbitals have significant ligand character but the $Eg$ orbital is largely metallic We will compare these conclusions with those obtained for acetylacetonates of the earlier transition metals below

It is interesting to ask how these interactions are modified by substitution on the acetylacetonate ligand This question could be answered by carrying out single-crystal studies on subsituted $Cu^{II}$ acetylacetonates analogous to the study described above. Experimentally, this would be a rather formidable task and as yet it has not been undertaken. Measurements on solutions or on polycrystalline solids are much less tedious but still yield a limited amount of information on the bonding The work of Kuska and Rogers[5] on substituted $Cu^{II}$ acetylacetonates serves to illustrate the possibilities

Analysis of solution ESR spectra yield two parameters, namely the average $g$ value ($g = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$) and the isotropic hyperfine coupling constant, $A$ It is apparent from the expressions given previously for $g_{\parallel}$ and $g_{\perp}$ that bonding parameters cannot be obtained directly from the average $g$ If a McConnell-type relationship exists for the isotropic hyperfine coupling it should give a measure of the spin density in the Cu atom and hence determine the covalency of the spin-containing orbital Kuska and Rogers[5] have investigated this possibility and have obtained the results shown in Table 1 Initially, they assumed that $A$ would be given by an equation

$$A = P[-\alpha^2\kappa_0 + (g - 2\ 0023) + \text{second-order terms}]$$

where $\kappa_0$ is the isotropic coupling constant for the free $Cu^{2+}$ ion and $\alpha$ has been defined above. The values of $\alpha^2$ obtained using this equation are listed in the table as "apparent $\alpha^2$". These values imply that substitution with electron-withdrawing groups such as $CF_3$ leads to an increase in the amount of spin on the ligand, i e make the bond less ionic This is contrary to what would be expected on chemical grounds and is not supported by polarographic data on the same compounds It was concluded that the initial assumption that the hyperfine coupling gives a measure of the metal spin density was in error McGarvey[3] has carried out a perturbation treatment to investigate the effects of coval-

TABLE 1

ESR hyperfine splitting constants and other data for copper acetylacetonates

| Substituents | | | ESR $A$ value ($cm^{-1} \times 10^4$) | $g$ Value | Apparent $\alpha^2$ | Anisotropy $\alpha^2$ |
|---|---|---|---|---|---|---|
| R′ | R″ | R‴ | | | | |
| $CH_3$ | $CH_3$ | $CH_3$ | 78 5 | 2 121 | 0 784 | 0 821 |
| $CH_3$ | H | $CH_3$ | 77 2 | 2 123 | 0 779 | 0 753 |
| $CH_3$ | Cl | $CH_3$ | 76 | | | |
| Phenyl | H | $CH_3$ | 76 4 | 2 124 | 0 777 | 0 795 |
| Phenyl | H | Phenyl | 75 3 | 2 124 | 0 770 | |
| $CF_3$ | H | $CF_3$ | 54 7 | 2 150 | 0 698 | 0 828 |

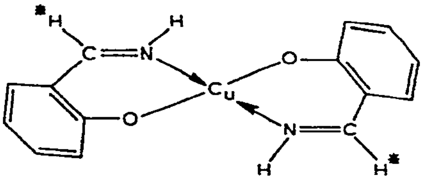
ency on the hyperfine coupling and has confirmed this conclusion. The essence of the problem is that the participation of the 4*s* orbital as well as that of the 3*d* orbitals must be considered Thus $\kappa_0$ will not be a constant but is made up of two terms, one representing spin density in the 3*d* orbital and one spin density in the 4*s* orbital Kuska and Rogers suggest that the signs of these contributions are opposite and since both will depend on the covalency it follows that the isotropic coupling does not provide a direct measure of $\alpha^2$.

In a later paper, Kuska et al [6] have obtained values for the anisotropic hyperfine coupling constants of these substituted $Cu^{II}$ acetylacetonates by examining the spectra obtained in frozen chloroform solutions. Combination of this data with the isotropic splitting constants obtained in solution gives the dipolar contribution to the hyperfine splitting This quantity should be proportional to $\alpha^2$ and rearrangement of previous equations gives

$$\alpha^2 = \frac{7}{4}\left[\frac{A_\parallel}{P} - \frac{|A|}{P} + \frac{2}{3}g_\parallel - \frac{5}{21}g_\perp - \frac{6}{7}\right]$$

Thus $\alpha^2$ can be obtained in a manner which does not depend on the mechanism of the contact interaction Some values of $\alpha^2$ obtained from the dipolar interactions are also shown in Table 1 It is apparent that the trend is the opposite of that obtained from the isotropic $A$'s and is thus consistent with the polarographic and other data mentioned above. It is interesting to note that the spectrum of the diphenyl acetylacetonate (compound 4 of Table 1) is found to be complicated by additional hyperfine splitting from the phenyl protons No detailed analysis of this additional splitting was achieved

An example of the successful analysis of hyperfine splitting from ligand nuclei is provided by the work of Maki and McGarvey [7] on $Cu^{II}$ bis salicylaldehyde imine. This compound has the structure



It was examined as a single crystal magnetically dilute in the corresponding nickel compound. To simplify the spectrum, isotopically pure $^{63}$Cu was used. It is to be anticipated that the four lines due to the copper hyperfine splitting will be further split by the two nitrogen atoms directly attached to the metal. A five-line pattern is predicted. In fact a more complicated eleven-line pattern is observed. The additional splitting can be attributed to a pair of nuclei with spin 1/2 which in the present case can only be protons. The most likely origin of the splitting might be thought to be the N–H protons since these are closest to the metal atom but deuteration disproved this possibility. However, methylation of the adjacent carbon did eliminate the additional splitting which must therefore be attributed to the proton marked H*. Analysis of the spectrum yielded the parameters

$g_x = 2.040_2$ $\quad g_y = 2.050_0$ $\quad g_z = 2.200_4$

$A = -1.85 \times 10^{-2}$ cm$^{-1}$ $\quad B = -0.21 \times 10^{-2}$ cm$^{-1}$

$A$ $^{14}$N = 11.1 gauss $\quad A$ *H = 5.5 gauss

The similarity of $g_x$ and $g_y$ shows that the Cu–N and Cu–O bonds are similar in character. These values yield the bonding parameters

$\alpha^2 = 0.83$ $\quad \beta^2 \geqslant 0.91$ $\quad \beta_1{}^2 = 0.74$ $\quad \kappa = 0.34$

Comparison with the values previously given for Cu$^{II}$ acetylacetonate shows that the only significant difference is a rather higher ligand contribution to the in-plane $\pi$ orbitals. It appears that the contact contribution is most important for the nitrogen hyperfine splitting–dipolar interactions are estimated to contribute only ~ 1.5% of the total splitting. The contact part is given by

$$W = \left(\frac{\alpha'^2}{4}\right)(2\gamma\beta_0\beta_N)\frac{-8\pi}{9}\delta(r)$$

where $\alpha'$ is the coefficient of the nitrogen orbital in the spin-containing molecular orbital. A value of $\alpha'^2 = 0.25$ (consistent with $\alpha^2 = 0.83$ given above when allowance is made for overlap) gives a calculated coupling of $10.8 \times 10^{-4}$ cm$^{-1}$ compared with an experimental value of $10.4 \times 10^{-4}$ cm$^{-1}$. The spin-containing orbital has symmetry $B_{1g}$ (predominantly $d_{x^2-y^2}$). It should be noted that the N–H proton lies near a node of this orbital but that the C–H proton, which shows hyperfine coupling, lies close to a direction of maximum electron density.

The $d^9$ configuration found in the above copper complexes is particularly favourable for ESR studies of metal–ligand bonding. The $d^1$ configuration found in vanadyl complexes is also favourable. The reasons are similar. It is an $S = 1/2$ ion and in the relatively low-symmetry vanadyl complexes with orbitally non-degenerate ground states the spectra are easy to observe. Kivelson and Lee[8] have carried out a study of vanadyl acetylacetonate. They use a set of molecular orbitals similar to those used by Ballhausen and Gray[9] in their calculations on this molecule. These orbitals have the form

$$\psi_{b_2} = \beta_2 d_{xy} + \tfrac{1}{2}\beta_2'(P_{y_1} + P_{x_2} - P_{y_3} - P_{x_4})$$

$$\psi_{b_1} = \beta_1 d_{x^2-y^2} + \tfrac{1}{2}\beta_1(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

$$\psi_{e_{\pi x}} = \epsilon_\pi d_{xz} + \epsilon'_\pi P_{x_5} + \frac{1}{\sqrt{2}}\epsilon''_\pi (P_{z^1} - P_{z^2})$$

$$\psi_{a_\perp} = \alpha_\perp(d_{z^2} + S_0) + \alpha'_\perp \sigma_5$$

$$\psi_{a_\parallel} = \alpha_\parallel(d_{z^2} - S_0) - \tfrac{1}{2}\alpha'_\parallel(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

The symmetry of the complex is strictly $C_{2v}$ but the assumption of $C_{4v}$ symmetry implicit in the above orbitals is justified by the rather small rhombic distortion The subscripts 1-4 refer to the oxygens of the acetylacetonate ligands and 5 to the vanadyl oxygen As written above, these are all bonding orbitals, $a_\perp a_\parallel$ and $b_1$ being $\sigma$ bonding, $b_2$ in-plane $\pi$ bonding and $e$ out-of-plane $\pi$ bonding The coefficients in the corresponding antibonding orbitals are denoted by stars All these anti-bonding orbitals are unoccupied except for $b_2^*$ which is singly occupied Expressions can be derived for $g_\parallel, g_\perp, A_\parallel$ and $A_\perp$ involving these molecular orbital coefficients which are quite similar in form to those given above for the $d^9$ case Experimentally, $g_\parallel = 2\ 054, g_\perp = 2\ 023, A_\parallel = 166\ 5 \times 10^{-4}$ cm$^{-1}$, $A_\perp = 63\ 5 \times 10^{-4}$ cm$^{-1}$ It is assumed that $\beta_2^* = 1$ $\beta_2{}^{1*} = 0$, i e , there is no in-plane $\pi$ interaction This seems to be generally a valid assumption for vanadyl complexes which is supported by the failure to observe ligand hyperfine structure with nitrogen ligands This may be contrasted with the behaviour of Cu$^{\mathrm{II}}$ complexes The other derived parameters are

$$\beta_1^{*2} = 0\ 84 \qquad \beta_1'^{*2} = 0\ 44 \qquad \epsilon_\pi^{*2} = 0\ 95$$

Thus it is deduced that the $\sigma$ orbitals are considerably delocalized — it may be noted that the overlap is substantial The out-of-plane $\pi$ orbitals are only slightly delocalized and it is stated that this probably involves predominantly the vanadyl oxygen

The analysis of the ESR spectra of metal complexes with more than one unpaired electron is more complicated than those of $S = \frac{1}{2}$ systems It is necessary to take account of electron–electron dipolar interactions An illustrative example is provided by the work on Cr$^{\mathrm{III}}$ acetylacetonate This molecule was examined by Singer[10] and more recently by McGarvey[11] The latter used a sample magnetically dilute in the Co$^{\mathrm{III}}$ compound The spectrum can be fitted to the spin Hamiltonian

$$\mathcal{H} = g\beta H\,S + D(S_z^2 - \tfrac{5}{4}) + E(S_x^2 - S_y^2)$$

The $g$ values are the main source of information on the electronic structure $D$ and $E$ which describe the dipolar interactions are very sensitive to distortions of the molecule from octahedral symmetry but are not sensitive to the detailed nature of the molecular orbitals McGarvey found the following parameters

$g = 1\ 9802 \pm 0\ 0005$
$|D| = 0\ 600 \pm 0\ 001$ cm$^{-1}$
$|E| = 0\ 0085 \pm 0\ 0005$ cm$^{-1}$

In addition, he was able to observe hyperfine coupling from the $^{53}$Cr isotope ($I = 3/2$ abundance 9 54%) which gave the additional parameters

$A = 16\ 2 \pm 0.1 \times 10^{-4}\ \mathrm{cm}^{-1}$
$B = 16.9 \pm 0.1 \times 10^{-4}\ \mathrm{cm}^{-1}$

The lack of anisotropy in the $g$ value and the small anisotropy of the hyperfine coupling is expected in view of the orbitally non-degenerate ground state ($^4A_{2g}$) The $g$ value differs from that of the free electron since spin-orbit coupling leads to mixing of the ground state with the $^4T_{2g}$ excited state. Crystal field theory leads to the expression

$$g = 2\ 0023 - \frac{8\lambda}{\Delta E(^4T_{2g})}$$

The observed $g$ value may be compared with those of the hexa-aquo Cr$^{\mathrm{III}}$ complex ($g$ = 1 976) and the hexacyano complex ($g$ = 1 992) The intermediate value for Cr$^{\mathrm{III}}$ acetylacetonate implies that the complex is more covalent than the aquo compound but less covalent than the cyanide There is a similar trend in the metal hyperfine coupling constants, $A$ $\mathrm{Cr(H_2O)_6}^{3+} = 17\ 0 \times 10^{-4}$, $A$ $\mathrm{Cr(CN)_6}^{3-} = 14\ 7 \times 10^{-4}\ \mathrm{cm}^{-1}$ which supports this conclusion McGarvey has examined a number of Cr$^{\mathrm{III}}$ complexes and carried out a more quantitative analysis The $^4T_{2g}$ excited state arises from a configuration in which an electron has been promoted from the half-filled $t_{2g}$ orbitals to the $e_g$ orbitals These latter are anti-bonding $\sigma^*$ orbitals and as such are mixtures of metal $d_{z^2}$, $d_{x^2-y^2}$, $s$ and $p$ orbitals and appropriate ligand $\sigma$ combinations The expression for the $g$ value becomes

$$g = 2\ 0023 - \frac{8\lambda P_d}{\Delta E(^4T_{2g})}$$

where $P_d$ is a function of the $e_g$ orbital coefficients The value of $P_d$ of 0 68 is considered to indicate considerable $\sigma$ mixing In this treatment $\pi$ interactions are neglected This is justified to some extent by the value of the metal hyperfine coupling constant which is relatively little changed from that of the aquo complex This latter inference rests on the assumption that the hyperfine coupling constant, being a ground-state property, depends only on the coefficients of the half-filled $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals which in turn can be mixed only with ligand $\pi$ orbitals

As a final ESR example, we will consider the work on Co$^{\mathrm{II}}$ trispyrazolyl borate carried out by Jesson[12] Co$^{\mathrm{II}}$ has a $d^7$ configuration and the electron spin relaxation is such that its complexes are usually suitable for NMR studies in solution at room temperature This is the case for the present complex. It appears that the shifts are predominantly dipolar in character and it is therefore important to establish the ESR parameters to aid the interpretation of the NMR★. At liquid-helium temperature the relaxation time is sufficiently long to allow observation of the ESR spectrum. However, at this temperature only the lowest of the Kramers doublets resulting from the combined effect of the trigonal distortion and spin-orbit coupling on the $^4T_{1g}$ ground state is populated The spectrum can therefore be analysed using the Spin Hamiltonian

$$\mathcal{H} = \beta[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + A S_z I_z + B(S_x I_x + S_y I_y)$$

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★ An alternative which is now considered preferable is to measure the single-crystal magnetic susceptibilities (W D Horrocks and E S Greenberg, W D Horrocks and D W Hall, preprints)

The $g$ value and the hyperfine coupling are both highly anisotropic ($g_{\parallel} = 8.46 \pm 0.01$, $g_{\perp} = 0.97 \pm 0.01$, $A = 0.0362 \pm 0.0003$ cm$^{-1}$, $B < 0.0001$ cm$^{-1}$). The anisotropic $g$ value, of course, favours dipolar NMR shifts. Combination of this ESR data with optical spectroscopy allowed calculation of the $g$ values for other Kramers doublets in the ground-state manifold and hence provides basic data for interpretation of the NMR. Since the ESR parameters are determined predominantly by the geometry and spin-orbit coupling of the complex, they do not provide a great deal of direct evidence on the nature of the bonding. This is generally true for orbitally degenerate ground states. In his calculation of the $g$ values, Jesson used an orbital reduction factor of 0.9 for the matrix elements of the orbital angular momentum and reduced the free ion spin orbit coupling by 20%. Both of these factors are indicative of covalency. Similarly, the analysis of the hyperfine coupling suggested about 15% charge transfer to the ligand. However, the information on metal—ligand interactions obtained by ESR on this type of compound is, at best, qualitative.

## D. NMR THEORY

In principle, the theory applicable to the NMR of paramagnetic complexes is more straightforward than the corresponding ESR theory. In practice, the difficulties of interpretation are such that it may be fairly stated that all results reported thus far should be regarded as having qualitative rather than quantitative significance. Basically, there are two problems. The first is to separate the dipolar effects from the contact effects. Only the contact contribution provides direct information regarding the bonding. The contact shifts, when obtained, give directly the spin densities in the $S$ orbitals of the magnetic nuclei. Usually there is no direct overlap of these orbitals with the spin-containing metal orbitals and they have acquired unpaired electron density indirectly from other ligand orbitals. It is the disentangling of these indirect pathways which provides the information on metal—ligand bonding and which constitutes the second problem.

The separation of dipolar and contact effects has been attempted in a number of ways. McConnell[A5] first pointed out that contact shifts should be identical in both solution and solid whereas dipolar shifts should differ in the different phases. Comparison of solution and polycrystalline solid spectra should therefore establish the presence of dipolar effects. McConnell and Holm[K1] applied this principle to vanadocene and concluded the shift was contact in origin but the method has not been further exploited. The experimental problem lies in the excessive line widths of NMR lines of polycrystalline solids. It has been suggested[A21,R1] that the different dependences of nuclear $T_1$'s and $T_2$'s on hyperfine coupling constants could form the basis of a method for identifying contact interactions. This suggestion does not appear to have been followed up, probably because of the experimental difficulties of measuring short $T_1$'s.

The most generally used arguments to establish or disprove dipolar contributions to isotropic shifts have been based on experimental data or theoretical inferences on the presence or absence of magnetic isotropy in a complex. Dipolar (sometimes called pseudocontact) effects can only be present if there is magnetic anisotropy. Thus McConnell and Robertson[A5] derived the expression

$$\Delta H = -\frac{\beta^2 H_0 S(S+1)}{27kT}\,(g_{\parallel} + 2g_{\perp})(g_{\parallel} - g_{\perp})\,\frac{(3\cos^2\theta - 1)}{r^3}$$

for the dipolar contribution in solution In this expression, $\theta$ is the angle between the principle magnetic axis and a line joining the metal atom and the magnetic nucleus under consideration and $r$ is the distance of this nucleus from the metal atom This equation demands at least a three-fold axis The other symbols have their usual significance It is apparent that the dipolar shifts will be equal to zero if $g_{\parallel} = g_{\perp}$ Later work by Jesson[A14] has shown that the exact form of the dipolar expression depends on the relative values of the electron spin relaxation time, the correlation time for molecular tumbling and the Zeeman anisotropy energy The qualitative dependence on the $g$ value anisotropy and the molecular geometry is, however, maintained Still more recently Horrocks[A16] has pointed out that previous treatments have neglected the contribution of the second-order Zeeman effect, which may be substantial in some cases, and has suggested that it would be preferable to evaluate the dipolar contribution to isotropic shifts from measurements of the anisotropy of the magnetic susceptibility rather than of the $g$ values Thus, although it appears that the theory of dipolar shifts is working towards a definitive form, it must be concluded that most of the quantitative calculations published thus far are unreliable It is probable, though, that many of the qualitative conclusions which have been made in the past will not be substantially altered by refinements in the theory Thus it has often been postulated that in octahedral or near-octahedral $Ni^{II}$ complexes, dipolar effects can be neglected since magnetic anisotropy is not expected from the orbitally non-degenerate $^3A_2$ ground state. Shifts of such complexes have therefore been treated as purely contact in origin and it seems unlikely that this assumption can be seriously in error Similarly, for other complexes such as $Cr^{III}$ acetylacetonate and $Ti^{III}$ acetylacetonate where the $g$ values are known to be either isotropic or only slightly anisotropic, it is improbable that a more refined theory will alter the conclusion that the shifts are predominantly contact in origin Thus if ESR measurements have established that the $g$ value anisotropy is small or if theoretical arguments show that the ground state is orbitally non-degenerate and well-separated from excited states which can be mixed in by spin-orbit coupling, it seems fairly safe to assume that isotropic shifts observed will be predominantly contact in origin

Three other lines of argument have been developed to estimate the extent of the dipolar contribution to NMR shifts in paramagnetic molecules. They may be grouped together in that none of them requre any prior knowlege of the magnetic properties of the molecule The first such method depends on estimating the ratios of the pseudo-contact shifts from their geometrical dependence Providing the geometry of the molecule is known and there is sufficient symmetry to identify a principal axis without ambiguity, values of $(3\cos^2\theta - 1)/r^3$ can be calculated for each proton and the dipolar shifts must be proportional to these values If the experimental shifts diverge widely from these ratios, and particularly if the signs are wrong, it can be deduced that dipolar effects do not predominate This argument has been applied to $Cr^{II}$ complexes[C1] It is open to the objection that relatively small contact contributions can affect the ratios Secondly, if the mode of spin delocalization can be identified and the shifts show good proportionality to calculated spin densities, this has been taken as good evidence for a contact mechanism. The argument is most persuasive for $\pi$ delocalization in a non-alternant system for which the alternation of positive and negative spin densities, and hence of high and low field shifts, provides a rather characteristic pattern. An extension of this argument rests on the observation that a methyl group shifts in the opposite direction to a proton substituted at the corresponding position Such an observation is readily interpretable by a $\pi$ delocalization mechanism (see below) but would require very specific geometry for a dipolar mechanism* Single inferences along these lines are inconclusive but if a large number of data can be fitted to a single $\pi$ delocalization mechanism, it must be regarded as rather good evidence for the preference of a contact to a dipolar mechanism If the spin density calculations are reliable, the residual dipolar contribution can be found by subtraction A third method depends on the comparison of the ratios of shifts for complexes with the same ligand but different metal atoms This has been applied most extensively to octahedral $Ni^{II}$ and $Co^{II}$ complexes It is argued that the $Ni^{II}$ complexes show only contact shifts, that the mechanism of delocalization will be the same for both $Ni^{II}$ and $Co^{II}$, hence that the ratios of the contact shifts will be the same for both complexes and that discrepancies in the observed ratios must therefore be attributed to dipolar effects in the $Co^{II}$ complex[A16] The crucial assumption is that delocalization mechanisms are the same for $Ni^{II}$ and $Co^{II}$ and this has led to some controversy[G56] Obviously none of these methods is completely unambiguous

The overall conclusions reached thus far on the question of dipolar versus contact shifts can be summarized as follows In the first transition series there seems to be little doubt that the shifts of octahedral $Cr^{III}$ and $Ni^{II}$ complexes arise from the contact effect It is widely agreed that octahedral $Co^{II}$ complexes show large, and in many cases predominant, dipolar effects Octahedral $V^{III}$ and $Cr^{II}$ and tetrahedral $Ni^{II}$ have been widely studied and all the interpretations advanced have been based on contact effects in spite of the fact that theory indicates dipolar effects should be present It appears to the present author that by and large the attribution of the shifts in these complexes is probably correct for the reason that all the complexes studied are distorted from octahedral or tetrahedral geometry sufficiently to give orbitally non-degenerate ground states well separated (several thousand $cm^{-1}$) from excited states Detailed measurements of the magnetic and spectroscopic properties of these complexes would do much to clarify the situation. Tetrahedral $Co^{II}$ appears to show dipolar shifts[F8] in spite of its orbitally non-degenerate ground state, presumably because of mixing of low-lying excited states. Data on the remaining first-row ions are rather scarce but the experimental evidence, such as it is, favours predominantly contact interactions Data on second- and third-row transition metal complexes and on rare earth complexes are even more sparse but it is to be anticipated that dipolar interactions will be relatively more important if only because of the larger spin-orbit coupling constants.

We may now turn to the origin of the contact shifts McConnell and Robertson[A5] related the contact shift to the hyperfine coupling constant $A$ by the expression

$$\frac{\Delta H}{H_0} = -A \frac{\gamma_e}{\gamma_H} g \frac{\beta S(S+1)}{3kT}$$

In this expression, $\Delta H$ is the shift at applied field $H_0$ $A$, in turn, is related to the spin density ($[\psi(0)]^2$) at the nucleus in question by

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* Recent INDO calculations suggest that $\sigma$ delocalization can also lead to a reversal of $CH_3$ shifts (W D. Horrocks and D.L. Johnson, preprint)

$$A = \frac{8\pi}{3h} g_e g_N \beta_e \beta_N [\psi(0)]^2$$

Thus, measurement of the contact shift immediately gives the spin density at the nucleus Since only $S$ orbitals have a finite density at the nucleus, in the simplest case a proton contact shift immediately gives the contribution of the $H$ $1s$ orbital to the partly filled molecular orbital However, this simplification is inadmissible since it neglects spin correlation This problem was first encountered by ESR spectroscopists in the case of aromatic ion radicals For these radicals the unpaired electron clearly occupies a $\pi$ molecular orbital which has a node at the hydrogen atoms Nevertheless, there is finite hyperfine coupling due to hydrogens and $\pi$-$\sigma$ spin polarization must be invoked. The information which one would like to obtain from contact shift measurements relates to the amount of mixing of specific ligand orbitals with specific metal orbitals and hence a description of the covalency of the various types of metal–ligand bonding In principle, this requires comparison of the observed shifts with $S$ orbital spin densities obtained by complete, many-electron calculations with full allowance for spin correlation In practice, such calculations are not feasible for molecules including transition metals

In spite of the above limitations, contact shift measurements can yield valid information on metal–ligand interactions in certain cases. The main requirements is that is should be possible to identify a single dominant delocalization mechanism If more than one such mechanism is present, the bonding information is likely to be, at best, very qualitative It is probably most profitable to illustrate the type of information that can be obtained in this way by reference to some specific examples as will be done in the next section but we summarize, at this point, some of the possible modes of spin delocalization

It is assumed, initially, that the unpaired electrons occupy predominantly metal $d$ orbitals in a manner determined by simple crystal field theory. Thus a $V^{III}$ complex (approximately octahedral) will have two unpaired electrons in the $t_{2g}(d_{xy}, d_{xz}, d_{yz})$ orbitals. The Boltzman distribution will determine that the $\alpha$ spin states of these unpaired electrons are favoured in a magnetic field. The spin-containing orbitals can mix directly with an empty ligand $\pi^*$ orbital of similar energy giving rise to $\alpha$ spin density in ligand $p\pi$ atomic orbitals. The $\pi$ spin densities can be related directly to hydrogen atom or methyl group hyperfine coupling constants using the theory developed for the ESR of aromatic radicals This corresponds to $\pi$ "back-bonding" with metal-to-ligand charge transfer and the ligand hyperfine coupling constants would be a measure of the extent of this process There is also the possibility that the metal orbitals could interact with a filled ligand $\pi$ orbital This corresponds to $\pi$ bonding with ligand-to-metal charge transfer Since the $d$ orbitals are less than half-filled, either an $\alpha$ electron or a $\beta$ electron could be donated In the former case there will be excess $\beta$ spin density remaining on the ligand and in the latter case excess $\alpha$ spin density Since the wave functions and hence the spin density distributions are usually different for the $\pi$ and $\pi^*$ orbitals and since the signs of the contact shifts are different for $\alpha$ and $\beta$ spin densities, we can, in principle, distinguish these possibilities. However, if the symmetry is less than octahedral, the $d_{xy}, d_{xz}$ and $d_{yz}$ orbitals can also mix with ligand $\sigma^*$ orbitals. This can lead to direct delocalization of $\alpha$ spin to hydrogen atoms on the ligand In general, the spin density in $\sigma$ orbitals will fall off rather rapidly with an increasing number of bonds separating the magnetic nucleus from the metal atom and this argument is often used to identify or refute $\sigma$ delocalization. It has obvious hazards. Still more subtle delocalization mechanisms may be encountered. Thus unpaired electrons in essentially non-bonding $\pi$ orbitals may polarize the spins of paired electrons in neighbouring $\sigma$ bonding orbitals leading to excess $\beta$ spins in the ligand $\sigma$ orbital Again the main delocalization may be to the $\sigma$ orbitals of the atom attached directly to the metal but this can polarize filled ligand $\pi$ orbitals. Since incorrect identification of the delocalization mechanism will lead to incorrect inferences with regard to the bonding, it is apparent that results in this area must be assessed with some care

Finally, we might say a word about the calculation of ligand spin densities The most desirable approach would obviously be a complete calculation involving all metal and ligand orbitals with full allowance for electron correlation. Needless to say such calculations have not been carried out In a number of cases (notably metallocene complexes), extended Huckel calculations on the complete molecule have been used to obtain spin densities[K7]. These lack allowance for correlation effects but the reasonable agreement with experiment suggests they may be fair approximations This does not imply, however, that the method will necessarily work equally well in other cases especially where both positive and negative spin densities occur. A more common procedure has been to carry out a calculation on a radical derived from the ligand, to compare the relative spin densities at different positions, and hence to deduce the fraction of an electron delocalized which gives a measure of the metal-ligand interaction. The majority of applications have been to $\pi$ radicals of the non-alternant type showing large negative spin densities In such cases it is essential to include electron correlation and single electron Huckel calculations are inadmissible. Earlier workers resorted to valence bond calculations (which automatically include correlation) and these were surprisingly successful in a number of cases[G5] Later, MacLachlan developed a rather simple molecular orbital technique for dealing with this situation and this has been widely used[B3]. Calculations on $\sigma$ radicals are more limited and have been confined to the extended Huckel[A15] and linear combination of bond orbital methods[G26] neither of which include correlation In general, the success of these calculations is such that the conclusions reached with regard to the type of orbital containing the unpaired electrons and qualitative estimates of the amount of delocalization can be regarded as reliable in favourable circumstances In the present state of the art, this is perhaps the maximum amount of information which can be derived from contact shift studies.

## E SOME NMR RESULTS

The study of the isotropic NMR shifts of paramagnetic metal complexes has been an active area of research for almost ten years. During this period a rather substantial number of papers has been published and an attempt has been made to provide a bibliography. In the present section, only a small number of selected papers will be reviewed These have been chosen, somewhat arbitrarily, to try and illustrate the utility of this type of experiment in studies of metal-ligand bonding The contributions of the papers listed to other areas of interest, ranging from isomerism in metal complexes to hyperconjugation in the organic ligands, have been substantial so that the following examples by no means represent a balanced selection.

The first series of complexes to be extensively studied were the $Ni^{II}$ aminotroponeimine-

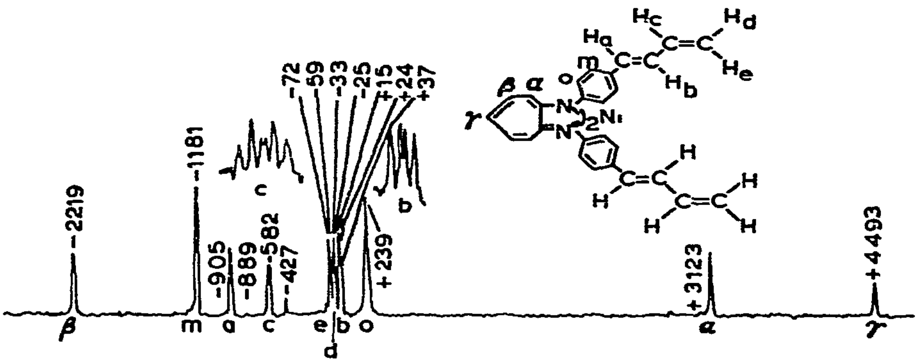
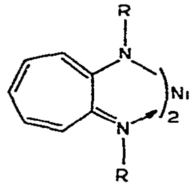


Fig 3 $^1$H spectrum of Ni$^{II}$ *N,N'*-bis(*p*-1,3-butadienylphenyl)aminotroponeimineate CDCl$_3$ solvent, TMS reference

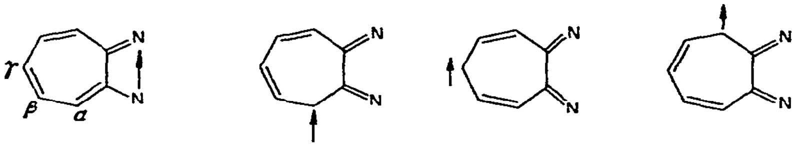
ates of structure (II)[G6] In the light of subsequent work, this was an extremely fortuitous series of compounds with which to start. In contrast to other compounds, the results can be interpreted in a relatively simple manner, the ligands allow wide synthetic flexibility and the NMR relaxation properties are particularly favourable. There is only one complication, namely that there is an exchange process, fast on the NMR time scale, between a planar diamagnetic isomer and a tetrahedral paramagnetic isomer. As a result, the observed shifts are the average of the paramagnetic and diamagnetic forms For our present purpose we will neglect this aspect of the studies It was originally considered that the fast isomer exchange determined the fast electron spin relaxation but this does not appear to be correct. However, for whatever the cause, the NMR lines are sharp enough to resolve spin-spin splitting in many cases and shifts of up to 15,000 Hz at 60 MHz are observed A typical spectrum is shown in Fig 3 The most notable qualitative feature about this spectrum is the existence of both high and low field shifts Closer examination of this and related molecules shows that the fundamental pattern is very simple — protons attached to successive carbons shift in opposite directions. This pattern is maintained indefinitely as the ligand $\pi$ system is extended. This pattern can be interpreted very simply with a model involving contact shifts due to spin delocalization in the $\pi$ system. The proton hyperfine coupling constants can be used to obtain $\pi$ spin densities from the relationship



II

$$A_H = Q\rho_C$$

where $Q$ is a constant of numerical value approximately $-22.5$ gauss The theory pertinent to the use of this equation was developed to interpret the ESR of aromatic radicals High field shifts correspond to positive $\pi$ spin densities and low field shifts to negative $\pi$ spin densities A simple valence bond formulation suffices to determine which positions will experience positive spin densities and which negative spin densities. Thus, if a radical is formed by transferring an electron from the aminotroponeimineate ion to the metal, the principal contributing structures will be



Reasonable structures placing positive spin at the $\alpha$ and $\gamma$ positions can be written, but there is no such possibility at the $\beta$ position Experience with similar radicals, such as the allyl radical, suggests that this position will acquire negative spin density by spin polarization of the filled $\pi$ orbitals Similar valence bond structures can easily be written for the more complex ligands obtained by substituting aromatic moieties on the nitrogen or at the $\gamma$ position Spin densities on these radicals can be calculated by the valence bond method and compared with the experimental results Since we are not dealing with "free" radicals but only with ligands with some radical character, the fit of the model must be judged from the relative spin densities at the different positions If a common scaling factor gives satisfactory agreement at all positions, this scaling faction is a measure of the fraction of an electron delocalized and hence of the amount of $\pi$ interaction Table 2 gives some comparisons of calculated and experimental spin densities The implication is that about 1/10 of an electron is delocalized to the aminotroponeimineate framework and about 1/30 to aromatic fragments attached to the nitrogen The overall agreement is better than might have been expected from the rather unsophisticated method of calculation

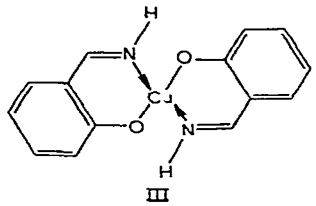
Thus the immediate conclusion is that $\pi$ interaction is sufficiently important to give rise to about a 10% contribution from structures involving delocalization of the unpaired electrons to the ligand. It should be noted that tetrahedral $Ni^{II}$ has unpaired electrons in the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals which are capable of direct overlap with the ligand $\pi$ system so there is no necessity to postulate any indirect mode of delocalization. Furthermore,

TABLE 2

Spin densities in nickel$^{II}$ $N,N'$-bis($p$-1,3-butadienylphenyl) aminotroponeimineate

| Proton | $\rho_{obs}$ | $\rho_{calc}$ | Proton | $\rho_{obs}$ | $\rho_{calc}$ |
|---|---|---|---|---|---|
| $\alpha$ | +0.0410 | | a | −0.00586 | −0.00465 |
| $\beta$ | −0.0210 | | b | +0.00422 | +0.00643 |
| $\gamma$ | +0.0568 | | c | −0.00281 | −0.00219 |
| *ortho* | +0.00792 | +0.01099 | d | +0.00342 | +0.00288 |
| *meta* | −0.00869 | −0.00629 | e | +0.00305 | |

the interaction must involve ligand-to-metal charge transfer since molecular orbital calculations [E8] show that the spin density distribution in the $\pi^*$ orbital is incompatible with the experimental results Considering the consistency of the results over the substantial number of compounds studied, it seems certain that the shifts arise predominantly from this mechanism Smaller contributions from other sources are, however, by no means excluded Thus the observation of shifts in *N*-alkyl substituents and discrepancies in some of the proton shifts of aromatic substituents at positions relatively close to the metal are certainly indicative of some $\sigma$ contribution Recently, $^{13}$C shifts have been observed for one of these compounds and it is considered that they are also indicative of some $\sigma$ delocalization [G55]. Similarly, although the arguments against a substantial dipolar effect are strong, a small contribution from this source cannot be excluded Thus, even in this well-studied system, one must be content with qualitative conclusions about the bonding Even with more reliable calculations on the spin density distribution, it is unlikely that one will be able to be more explicit than to estimate 10% for the $\pi$ delocalization



III

The Ni$^{II}$ salicylaldimines of structure (III) are a similar series of compounds which have also been rather extensively studied [G17] Again, the suggested interpretation involves delocalization into the ligand $\pi$ system by $d\pi$–$p\pi$ interaction In this case, the delocalization is smaller, amounting only to about 1/30th of an electron Probably the interacting $\pi$ orbital is energetically less favourably situated for interaction with the $d$ orbitals than in the aminotroponeimineates. The reservations expressed in the last paragraph apply equally well here but the predominant mechanism seems to be well established

In both of the above cases the rather large number of chemically distinct ligand protons allows extensive comparison of observed and calculated spin densities which is a valuable aid in establishing the delocalization mechanism However, in cases with less favourable relaxation conditions, the lines are broad and a complex ligand is likely to give rise to difficulties in the assignment of lines For comparisons between different metal ions it is therefore better to choose a simple ligand. A series of first-row transition metal acetylacetones has been examined with this consideration in mind [B2] The observed isotropic shifts are given in Table 3 There are only two chemically distinct types of proton, present in the ratio of six to one, so for any reasonable resolved spectrum there is no assignment problem In spite of this the lines were too broad in the cases of Ti$^{III}$ and Cr$^{III}$ to locate the single C–H proton It was argued that, in the early transition metals at least (up to Fe$^{III}$), dipolar effects are not important This argument is by no means watertight for all the complexes but in the authors' opinion is probably substantially correct because there is a smooth progression of the shifts (as seen from the figures of Table 3) in a series which includes both complexes where dipolar effects can be certainly eliminated and those where it is less certain The suggested interpretation was based on spin delocalization

TABLE 3

NMR of paramagnetic acetylacetonates

| | $\mathrm{Ti^{III}}$ | $\mathrm{V^{III}}$ | $\mathrm{Cr^{III}}$ | $\mathrm{Mn^{III}}$ | $\mathrm{Fe^{III}}$ |
|---|---|---|---|---|---|
| $CH_3$ | ~ −3500 | −2744 | −2320 | −1505 | −1243 |
| H | | −2404 | | −1085 | +1644 |

Shifts in Hz at 60 MHz from TMS

TABLE 4

Molecular orbital calculations

| | Acetylacetonate |
|---|---|
| Energy top bonding | +0 9417 $\beta$ |
| Energy bottom anti-bonding | −0 6103 $\beta$ |

| | Spin densities | | | |
|---|---|---|---|---|
| | Top bonding | | Bottom anti-bonding | |
| | Huckel | McLachlan | Huckel | McLachlan |
| O | +0 0890 | +0 0710 | +0 0799 | +0 0852 |
| $C_1$ (C−$CH_3$) | +0 1260 | +0 0640 | +0 4201 | +0 4979 |
| $C_2$ (C−H) | +0 5683 | +0 7291 | +0 000 | −0 1658 |

to the $\pi$ system Table 4 contains calculated $\pi$ spin densities for both the bottom anti-bonding $\pi$ orbital and the top bonding $\pi$ orbital Both the $CH_3$ and the single H shifts can be related to these spin densities but in the first case the $Q$ value should be taken as positive (~ +27 gauss) and in the second case negative. These calculations lead to the following predictions for the contact shifts

(*a*) For metal-to-ligand charge transfer to the lowest unoccupied $\pi$ orbital, the $CH_3$ will have a large low field shift and the single hydrogen will also move to low field shift though somewhat less

(*b*) Ligand-to-metal charge transfer will leave unpaired spin density in the highest occupied $\pi$ orbital For a less than half-filled *d* shell, an $\alpha$ electron will be transferred This gives rise to a large low field shift of the single hydrogen and a small shift of indeterminate sign for the $CH_3$ For a half-filled or more shell, the signs are reversed, i e. a large high field shift is predicted for the single hydrogen. The experimental results can be fitted rather nicely to these predictions At the beginning of the series ($\mathrm{Ti^{III}}$) it is postulated that the *d* orbitals are relatively close in energy to the $\pi^*$ orbital and metal-to-ligand transfer predominates. On passing along the series, the increasing nuclear charge lowers the energy of the *d* orbitals and ligand-to-metal charge transfer must also be considered Delocalization in the $\pi^*$ orbital decreases from about 7% to 1% of an electron from $\mathrm{Ti^{III}}$ to $\mathrm{Fe^{III}}$. The change in sign of the C—H shift at $\mathrm{Fe^{III}}$ is predicted from the ligand-to-metal charge transfer mechanism. Perhaps even more significantly the interpretation is consistent with the chemistry of these ions The complexes showing the largest tendency to metal-to-ligand charge transfer involve those ions most easily oxidized and where ligand-to-metal charge transfer is involved the ions are reducible to a lower oxidation state It should be emphasized, though, that results of this kind do not have more than qualitative significance. It is plausible from the expectation that the $d$ orbitals will be closer in energy to the $\pi$ orbitals of the ligand than to the $\sigma$ orbitals that $\pi$ delocalization will be more important than $\sigma$ delocalization There is also some experimental evidence to this effect from the early observation of Forman et al [B1] that substitution of $CH_3$ for the single hydrogen of the $V^{III}$ complex reversed the sign of shift as expected for a $\pi$ radical There could, however, easily be enough $\sigma$ delocalization to spoil quantitative interpretations in addition to the uncertainties introduced by possible dipole interactions and inaccurate spin density calculations Chemically, however, results of this kind are of importance in demonstrating trends in the bonding and in giving a qualitative idea of the extent of $\pi$ interaction.

It is appropriate to discuss next a case where several delocalization mechanisms have been shown to occur simultaneously In a recent paper, Cramer and Drago [G46] have discussed contact shifts in complexes of the type $NiL_6^{2+}$ where L is a pyridine or substituted pyridine. There had been previous reports of shifts for nickel pyridine complexes with distorted octahedral or distorted tetrahedral geometry. The use of regular octahedral complexes enabled the authors to dismiss the possibility of dipolar effects with some certainty and also to eliminate direct delocalization into the $\pi$ system The unpaired electrons reside in an $e_g$ orbital which can interact with ligand $\sigma$ orbitals but which is orthogonal to the $\pi$ orbitals At room temperature there is fast ligand exchange so that only averaged shifts are observed but the contact shifted resonances can be obtained at –40°C. The observed shifts are shown in Table 5. For the pyridine complex itself, the general pattern is

TABLE 5

$NiL_6^{2+}$ contact shifts

| Ligand L | | $\Delta\nu$ (c/sec) |
|---|---|---|
| Pyridine | O | –3820 |
| | M | –1420 |
| | P | – 445 |
| 4-Methylpyridine | O | –4570 |
| | M | –1500 |
| | P–$CH_3$ | + 422 |
| 3-Methylpyridine | O | –4320 |
| | M | –1575 |
| | P | – 450 |
| | M–$CH_3$ | – 313 |
| 4-Vinylpyridine | O | –2631 |
| | M | –1236 |
| | $H_3$ | – 195 |
| | $H_2$ | + 53 |
| | $H_1$ | – 218 |

Shifts in Hz at 60 MHz relative to TMS

that expected for $\sigma$ delocalization The shifts are to low field, indicating the protons can sense directly the $\alpha$ spin on the metal, and diminish rather rapidly with distance from the nickel. The results on some of the substituted pyridines indicate that this mechanism is not completely satisfactory In particular, the high field shifts of the $CH_3$ of 4-methylpyridine and of H2 of 4-vinylpyridine cannot be explained in this manner The suggestion is made that polarization leads to spin density in the $\pi$ system Extended Huckel calculations suggested about $4 \times 10^{-2}$ spin density in the $\sigma$ orbitals $\beta$ spin density in the $\pi$ orbitals is about an order of magnitude less than this and it was not possible to identify the specific orbital These results seem quite plausible [*]. It might be noted, though, that the observation of both high and low field shifts does not necessarily implicate $\pi$ orbitals. Such effects have been observed in some substituted $Ni^{II}$ aminotroponeimineates in which the substituent has no $\pi$ system. The only firm conclusion is that one-electron calculations for such systems are not sufficient

The above papers are indicative of the kind of attempts which have been made to obtain information on metal–ligand bonding directly from contact shift measurements There are a large number of variations on the themes already introduced In this final section we would like to indicate some of the more indirect uses of NMR in this area The work of Jesson et al [F23] on cobalt$^{II}$ pyrazolylborates has already been mentioned The predominant shift mechanism is dipolar and so does not provide direct information on the bonding. There is, however, a significant contact contribution so that bonding parameters are likely to be obtained as a by-product from detailed studies of this kind A very recent paper by McGarvey [A18] has re-examined the theory of these $d^7$ systems and introduced some quantitative changes in the interpretation. We refer the reader to the original paper for details Work of this kind involving continuing refinement of the theory emphasizes the limitation of most of what has been published so far to qualitative significance At the other end of the scale a recent paper by Rakshys [G53] illustrates very nicely the usefulness of the NMR technique in an empirical way The molecules studied were complexes of the type $Ni(acac)_2L_2$ (acac = acetylacetone, L= substituted anilines) in which the contact shifts were correlated with stability constants Both electronic and steric effects appear to be important and the NMR measurements provide a sensitive probe for disentangling these effects Finally we might mention the rather limited number of studies on complexes with mixed ligands [G13,G19] The interest here lies in the approach which contact shifts offer to the question of how substituent changes in one ligand affect bonding to other ligands This is an important problem in studies of substitution mechanisms of complexes and in homogeneous catalysis It has been demonstrated that rather large effects are observed in the NMR spectra of mixed complexes The suggested interpretations have been based on differences in the occupation of the spin-containing metal orbitals as the various ligands are changed This would appear to be a very promising area which awaits more systematic experimental exploitation

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[*] Recent INDO calculations suggest that it may be possible to interpret these results purely on the basis of $\sigma$ delocalization (W D Horrocks and D L Johnson, preprint)

## F. CONCLUSION

For the reasons outlined in the Introduction, it is not possible to make explicit comparisons between ESR and NMR results on metal–ligand bonding It is, however, feasible to make some comments on the consistency of the general pictures which emerge from the two types of studies The results described above have been very largely confined to chelate complexes of the first-row transition metal ions Both techniques demonstrate that covalency is a factor of major importance in this class of compounds In both cases interactions allowed by symmetry considerations are most important Thus. ligand hyperfine splitting is observed in $Cu^{II}$ complexes but not in $V^{IV}$ complexes $\pi$ delocalization appears to be dominant from contact shift studies of tetrahedral $Ni^{II}$ complexes but is subsidiary to $\sigma$ effects in octahedral $Ni^{II}$ complexes where spin can reach the $\pi$ system only indirectly ESR results indicate up to 20% contribution of ligand $\sigma$ orbitals to formally $d$ orbitals but in general less than 10% ligand contribution to $\pi$ orbitals NMR results agree with this limitation on $\pi$ bonding Perhaps one of the more direct comparisons is that of 5% ligand $\pi$ contribution in vanadyl acetylacetonate from ESR and about the same percentage in $V^{III}$ acetylacetonate from NMR The NMR technique is more sensitive but less specific Thus, a detailed single-crystal ESR study can separate out the different modes of spin delocalization without ambiguity It will probably not, however, detect 2 or 3% contribution of a given type of ligand orbital Such a contribution will be sufficient to impart substantial contact shifts to the NMR spectrum but there is no simple experimental criterion for disentangling the mechanisms This sensitivity of the NMR method means that relatively exotic indirect modes of spin delocalization which can be safely neglected in ESR must be considered in interpreting the NMR spectra The theory for ESR is rather well developed and allows quantitative interpretations to be put forward with some confidence. That for NMR is more complex and cannot be applied with certainty without sophisticated many-electron calculations on complete complexes The overall result is that ESR gives us a reliable quantitative description of a few classes of complexes NMR has given a large amount of essentially qualitative data on a much wider range of compounds Both techniques are capable of much wider exploitation and jointly are likely to continue to make a substantial contribution to our understanding of the electronic structure of transition metal complexes

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