and 1730(0.43) seem too high for the N–H bending fundamental, which may not have been seen at all. The C–F stretching overtones and combinations were obvious, at 2272(0.56), 2294(0.9), 2386(0.18), and 2554(0.11). A band consisting of a sharp spike at 1294(22) and a shoulder at 1290(16) might represent the combination 473.5 + 808, intensified by coupling with a C–F stretching mode; however, a fundamental in this region may be required to explain the combination or overtone at 2554 cm.$^{-1}$. Minor peaks appeared at 392(0.24), 771(0.09), 848(0.8), 882(0.7), 1010(0.09), 1052(0.08), 1250sh(1.5), 1329(0.34), 1367 (0.12), 1899(0.3), and 2094(0.17).

For $CH_3N[P(CF_3)_2]_2$ the C–F stretching overtones and combinations were 2267(1.1), 2290(0.32), 2306 (0.34), 2325(0.10), and 2397(0.26). A strong peak at 1079(9.7) may well represent an overtone of the CF_3 deformation at 545.5, intensified by Fermi resonance with C–F stretching; and similar origins might be ascribed to weaker absorptions at 1235sh(2.0), 1270 (1.1), and 1291(0.9). Other minor peaks were 950 (0.05), 985(0.05), 1400(0.2), 1514(0.3), 1680(0.07), 1791(0.07), 1857(0.07), 1879(0.2), 1901(0.2), and 1948 (0.2). The assignment of the relatively weak 647-cm.$^{-1}$ band to P–N–P symmetric stretching seems reasonable in relation to the strong 808-cm.$^{-1}$ band for the HNP_2 case, because the CH_3N unit contributes far more to the reduced mass than the HN unit could; also, the

methyl group would partially balance the phosphorus units and hinder the motion of N, thus limiting the variation of polarity and so leading to relatively low intensity. For the NP_3 planar form, of course, the threefold symmetric N–P stretching mode would be infrared forbidden.

For $N[P(CF_3)_2]_3$ there was less observation of very weak bands because the pressure was limited to 10 mm. at the cell chamber temperature of 40°. The C–F stretching overtones and combinations appeared at 2256(1.0), 2275(0.8), 2298(0.6), 2321(0.46), 2358(0.23), and 2404(0.23). The peaks at 1095(2.3) and 1108(6.2) probably represent overtones of the in-phase and out-of-phase asymmetric CF_3 deformation (at 550.5 and 563), intensified by Fermi resonance with C–F stretching. Other satellites of the C–F stretching bands appeared at 1232sh(4.6) and 1276sh(1.4). The peaks at 900(0.4) and 939(0.4) probably belong to overtones of the P–CF_3 stretching modes at 468.5 and 486.5 cm.$^{-1}$, enhanced somewhat by the very intense asymmetric P–N–P stretching at 859 cm.$^{-1}$. Weaker and less assignable peaks were observed at 980(0.28), 1026(0.42), 1366(0.6), 1487(0.09), 1714(0.6), 1877(0.23), 1907(0.23), and 1947(0.06).

Most of the assignments in Table VII are securely based upon analogies to other compounds, but in some cases it is appropriate to indicate uncertainties by question marks or to consider alternatives.

The Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Acetylacetonates

D. R. Eaton

The n.m.r. spectra of the paramagnetic acetylacetonates of Ti(III), V(III), Cr(III), Mn(III), Fe(III), Mo(III), Ru(III), Tb(III), Eu(III), Mn(II), Fe(II), and Co(II) have been measured. Spectra were not observed for the Cu(II) and VO(II) compounds. Data on a number of diamagnetic acetylacetonates which were measured for comparison are also reported. The widths of the lines in the different compounds are discussed in relation to the relative rates of electron spin relaxation inferred from e.s.r. data. It is concluded that the isotropic shifts in line frequency in the first transition row compounds arise predominantly from contact interactions. In this series, spin can be delocalized to the ligand both by metal-to-ligand and ligand-to-metal charge-transfer processes with the latter becoming progressively more important in complexes of the later group metals. In the second transition series pseudo-contact effects become important, and in the rare earth compounds they are probably dominant. The interpretation of the contact shifts is discussed in terms of the electronic structures of the complexes and in relation to the chemistry of the metal ions.

Introduction

The interactions between unpaired electrons on transition metal ions and nuclei with magnetic moments on ligands coordinated to these ions have been the subject of a number of recent n.m.r. studies.[1-5] These studies have yielded a considerable amount of useful information on the electronic structures and magnetic properties of transition metal complexes. However, a number of questions regarding the extent of the applicability of this n.m.r. technique and the interpretation of the results still remain. Thus, the condition for observing nuclear resonances in paramagnetic compounds of this type is usually stated[6] as $1/T_1 \gg a_N$,

(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(3) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 395 (1963).

(4) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **85**, 821 (1963); **86**, 379 (1964).

(5) W. D. Horrocks, Jr., and B. N. LaMar, *ibid.*, **85**, 3512 (1963).

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

where T_1 is the electron spin relaxation time and a_N the appropriate hyperfine coupling constant. A question of practical interest is which metal ions will in general have sufficiently short relaxation times to allow the observation of n.m.r. spectra and which will not. It is also usual to recognize the possibility of both contact and pseudo-contact contributions[7] to the isotropic hyperfine coupling, and it would be valuable to have at least some general empirical guidelines regarding the relative importance of these contributions in different types of complexes. The contact part of the interaction demands some delocalization of the electron spin to the ligand, and a number of mechanisms for this have been invoked at various times.[8] Either σ- or π-type molecular orbitals may be involved, and the charge transfer may be from the ligand to the metal or *vice versa*.

In the hope of providing partial answers to some of the above problems, the n.m.r. spectra of a variety of transition metal acetylacetonates of structure I have been examined.

I
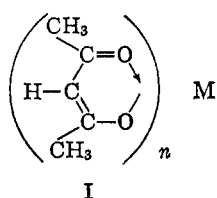
Forman, Murrell, and Orgel[9] have previously reported contact shifts for the V(III) compound. The choice of this series of compounds was determined by a number of favorable considerations. Thus, there are only two chemically distinct types of ligand protons which are present in the ratio of 6:1. The analysis of any reasonably well-resolved spectrum is therefore trivial. This is often not the case with more complex ligands, and interpretation of the shifts is open to the additional hazard of incorrect assignments. Secondly, the geometry of most of these chelates is well established with X-ray[10-12] data being available in some cases. Thirdly, there have been a number of e.p.r. studies[13-16] reported which provide data on the g-value anisotropies. These data, together with a knowledge of the geometry, allow an unambiguous calculation of the pseudo-contact contribution to the shifts. Lastly, acetylacetonates with a wide variety of transition metals are available.

Experimental

All spectra were obtained on a Varian HR-60 spectrometer. Deuteriochloroform was the solvent unless otherwise stated. Lines were measured relative to tetramethylsilane which was used as an internal calibrant to avoid susceptibility corrections. Mag-

(7) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).
(8) D. A. Levy and L. E. Orgel, *Mol. Phys.*, 3, 583 (1960).
(9) A. Forman, G. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, 31, 1129 (1959).
(10) R. B. Roof, *Acta Cryst.*, 9, 771 (1956).
(11) L. M. Shkolnikova and E. A. Shugan, *Kristallografiya*, 5, 32 (1960).
(12) B. Morosin and J. R. Brathovde, *Acta Cryst.*, 17, 705 (1964).
(13) H. S. Jarrett, *J. Chem. Phys.*, 27, 1298 (1957).
(14) H. R. Gersmann and J. D. Swalen, *ibid.*, 36, 3221 (1962).
(15) B. R. McGarvey, *ibid.*, 38, 388 (1963).
(16) B. R. McGarvey, *ibid.*, 40, 809 (1964).

netic susceptibilities of these compounds were measured by an n.m.r. method.[17] In all cases they checked well with literature values. The acetylacetonates of Ti(III) and Mo(III) are susceptible to air oxidation, and solutions of these compounds in sealed tubes were made up in an inert atmosphere. The n.m.r. spectra of a number of diamagnetic acetylacetonates were also measured, and the contact shifts taken as the difference between diamagnetic and paramagnetic frequencies. The shifts for the V(III) compound agree well with those reported by Forman, Murrell, and Orgel.[9]

Results

(*i*) *Line Widths*. Proton resonances attributable to the ligands of the paramagnetic acetylacetonates of Ti(III), V(III), Cr(III), Mn(III), Fe(III), Mo(III), Ru(III), Mn(II), Fe(II), Co(II), Ni(II), Eu(III), and Tb(III) were observed. No resonances attributable to a paramagnetic species could be found in vanadyl acetylacetonate or in cupric acetylacetonate. The widths of the observed resonances varied considerably, and some approximate line widths together with some relevant e.p.r. data[13-16] are given in Table I. In general the conditions necessary for the observation of sharp line n.m.r. spectra and those necessary for the observation of sharp line e.p.r. spectra are opposed; *i.e.*, n.m.r. requires a short electron spin relaxation time and e.p.r. a long one. The present results are consistent with this theoretical prediction. Thus, in cases where the e.p.r. spectrum has been observed at room temperature the n.m.r. is either not observed or is very broad. Where the e.p.r. has only been observed at liquid nitrogen temperature, the n.m.r. lines are moderately broad, and where the e.p.r. was not observed, the n.m.r. lines are relatively sharp. However, it is also apparent from these results that the e.p.r. and n.m.r. spectra are not mutually exclusive. In suitable intermediate cases, it is perfectly possible to observe both types of resonance.

(*ii*) *Line Shifts*. The observed resonance frequencies for the paramagnetic acetylacetonates are given in Table II and those for a number of diamagnetic compounds in Table III. In the cases of Ti(III) and Cr(III), where the resonances are very broad, it was not possible to locate the single proton with any certainty. The acetylacetonates of Co(II) and of Ni(II) are known to be polymerized in solution and in agreement with this gave rise to complex spectra which could not be analyzed. In the hope of circumventing this difficulty, these compounds were examined in deuterated pyridine where the predominant species is probably octahedral $M(AA)_2(py)_2$. The cobalt compound gave the expected two-line spectrum, and these frequencies are recorded in the table. The nickel results were less straightforward, but it appears that the shifts are small and to high field. There were no other ambiguities in the assignments.

Discussion

The observed n.m.r. shifts in these compounds can arise either from contact interactions or from pseudo-contact interactions, or from a combination of both. The contact interaction contribution is given by eq. 1

(17) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

Table I. N.m.r. Line Widths

	Ti	V	VO	Cr	Mn	Fe	Mo	Ru	Cu
N.m.r. line width, c.p.s.	2000	25	?	1000	100	800	200	100	?
E.p.r.[a]	R.T.	No	R.T.	R.T.	No	R.T.	80°K.	80°K.	R.T.

[a] R.T., spectrum observed at room temperature; 80°K., spectrum observed only at liquid N_2 temperature; No, spectrum not observed: ref. 13–16.

Table II. N.m.r. of Paramagnetic Acetylacetonates[a]

	Ti(III)[b]	V(III)	Cr(III)	Mn(III)	Fe(III)
CH_3	~ −3500	−2744	−2320	−1505	−1243
H	?	−2404	?	−1085	+1644

			Mo(III)[b]		Ru(III)
CH_3			−7448		+ 324
H			−2300		+1772

	Eu(III)[c]	Tb(III)[d]	Mn(II)	Fe(II)[b]	Co(II)[e]
CH_3	−421	−2829	~0	−1053	−1577
H	−360	−8647	−1502	−50	−1404

[a] In $CDCl_3$ except where noted; 60 Mc.p.s.; shifts in c.p.s. from TMS. [b] In C_6D_6. [c] In $(CD_3)_2SO$. [d] In CD_3OH. [e] In C_5D_5N.

Table III. N.m.r. of Diamagnetic Acetylacetonates[a]

	Co(III)	Rh(III)	Mg(II)[b]	Zn(II)	Zr(IV)	Th(IV)
CH_3	−133	−128	−122 −109	−120	−117	−115
H	−331	−328	−319	−328	−327	−327

[a] In $CDCl_3$; shifts in c.p.s. at 60 Mc.p.s. Data on diamagnetic acetylacetonates have been reported by R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958); J. A. S. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962). [b] It appears from this result that the Mg compound is not a symmetric chelate.

$$\frac{\Delta H_i}{H} = \frac{\Delta \nu_i}{\nu} = -a_i \frac{\gamma_e}{\gamma_n} \frac{g\beta S(S+1)}{6S'kT} \quad (1)$$

and the pseudo-contact contribution by eq. 2. In

$$\frac{\Delta H_i}{H} = \frac{\Delta \nu_i}{\nu} = -\frac{1}{r^3} \frac{\beta^2 S(S+1)}{27kT}(3\cos^2\theta - 1) \times$$

$$(g_\| + 2g_\perp)(g_\| - g_\perp) \quad (2)$$

these equations ΔH_i and $\Delta \nu_i$ are the differences in resonance field or frequency of the nucleus i at applied field H or frequency ν, respectively; a_i is the hyperfine coupling constant; γ_e and γ_n are the magnetogyric ratios of the electron and nucleus; S is the total electron spin and S' is the total spin of those unpaired electrons involved in delocalization; r is the distance from the metal atom to the nucleus n; and θ is the angle between a line joining these points and the principal magnetic axis of the molecule. The other symbols have their usual significance. The pseudo-contact contribution can be calculated from a knowledge of the g values and the geometry of the molecule.[18] Some pseudo-

(18) Equation 2 was derived[7] on the assumption that the electron spin relaxation time T_1 is greater than the rotation correlation time τ of the molecule. McConnell and Robertson[7] have derived a slightly different formula for the case that $\tau > T_1$, and it is possible that this is the applicable case for some of these chelates. The paper of McConnell and Robertson contains a misprint in the formula for this second case in that the term containing the g values written as $(3g_\|^2 - g_\|g_\perp + 4g_\perp^2)$ should read $(3g_\|^2 + g_\|g_\perp - 4g_\perp^2)$ which correctly reduces to zero when $g_\| = g_\perp$. The net effect is that shifts calculated on the second assumption will be larger by a factor of $3(3g_\| + 4g_\perp)/5(g_\| + 2g_\perp)$. Use of this

contact shifts for octahedral acetylacetonates using g values taken from the literature and the bond distances and bond angles reported in an X-ray diffraction study of the ferric compound[10] are given in Table IV. More

Table IV. Pseudo-Contact Acetylacetonates[a]

	CH_3	H
Ti	+4	+18
Mo[b]	−291	−862
Ru	+89	+355
Cr	0	0

[a] Shifts in c.p.s. at 60 Mc.p.s. [b] Mo(III) has a large zero field splitting so that only the $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$ transition is observed in the e.p.r. spectrum which is described by a spin Hamiltonian with $S = \frac{1}{2}$. The above shifts have been calculated with $S = \frac{1}{2}$ and the assumption that the zero field splitting $> kT$ so that only $\pm\frac{1}{2}$ states are populated. For small zero field splittings the g values will be more nearly isotropic.

recent X-ray studies on the Cr(III)[11] and Mn(III)[12] compounds have indicated that all in this series have very similar geometries.

Consider first the series of octahedral (D_3) acetylacetonates formed by Ti(III), V(III), Cr(III), Mn(III), and Fe(III). Direct calculation shows that the pseudo-contact effect is negligible for Ti and Cr. There is indirect evidence that the same may be true for V. Thus, Forman, Murrell, and Orgel[9] examined the spectra of both V(III) acetylacetonate and the compound in which the CH is replaced by C–CH_3. They found that the proton resonance of the CH_3 group in the latter compound was shifted to high field, i.e., in the opposite direction to the CH resonance of the former compound. This result is to be anticipated if the shifts arise from contact interactions resulting from spin delocalized in the π-system of the ligand since Q_H is negative and Q_{CH_3} positive when Q is defined by the equation

$$a_H = Q\rho_C \quad (3)$$

where ρ_C is the carbon spin density. The geometry of the chelate is, however, such that no change in sign is predicted for the pseudo-contact interaction. The contact interaction must, therefore, be predominant, and the pseudo-contact contribution may well be negligible again. X-Ray results have shown that $Fe(AA)_3$ has a symmetric octahedral structure so that it seems probable that the g value for this d^5 ion will be isotropic. This leaves the d^4 Mn(III) case for which there is no argument one way or the other. However, the smooth change in the n.m.r. shifts from Ti(III) to Fe(III) suggests strongly that there is no abrupt change in mechanism along the series, and it would seem to be a fair assumption that the shifts in the Mn(III) compound are also

alternate formula will not affect any of the qualitative conclusions presented in the present paper. The author is indebted to Dr. J. P. Jesson for an illuminating discussion of this topic.

predominantly contact in nature. Pseudo-contact effects will therefore be neglected in the ensuing discussion of this series.

The contact mechanism implies that the electron spin has been partly delocalized from the metal atom to the ligand. This can occur either through the ligand π-orbitals or through the σ-orbitals. The result of Forman, Murrell, and Orgel suggests that the spin is in the ligand π-system, and this is perhaps the more likely situation since all the σ-orbitals will be either strongly bonding or strongly antibonding and therefore distant in energy from the basically nonbonding metal d-orbitals. The positions of the relevant orbitals are shown diagramatically in Figure 1. These are two possible types of interaction, namely between the metal d-orbitals and the bottom antibonding ligand π-orbital and between the metal d-orbitals and the top bonding ligand π-orbitals. The former will correspond to charge transfer from the metal to the ligand and the latter to charge transfer from the ligand to the metal. It may be noted that in this point group (D_3), both types of interaction with either set of d-orbitals are allowed by symmetry.[19] The metal-to-ligand charge transfer must result in the delocalization of positive spin. The ligand-to-metal charge transfer must result in the delocalization of positive spin if the d-shell is half-filled or more since only β-electrons can then be accepted leaving an excess of α-electrons on the ligand, but will probably result in negative spin delocalization for a less then half-filled d-shell since the maximum spin multiplicity will be preserved by the transfer of an α-electron. A simple Hückel calculation of the spin densities in the different orbitals allows a qualitative distinction to be made between the different cases. The results of such a calculation are given in Table V.

Table V. Molecular Orbital Calculations

	Acetylacetonate	
Energy top bonding		$+0.9417\beta$
Energy bottom antibonding		-0.6103β

	Spin densities			
	Top bonding		Bottom antibonding	
	Hückel	McLachlan	Hückel	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)	$+0.5683$	$+0.7291$	$+0.0000$	-0.1658

	Aminotroponeimineate	
Energy top bonding		$+0.3808\beta$
Energy bottom antibonding		-0.6662β

The Hückel method of calculation does not take into account the electronic correlations which can give rise to negative spin densities in nonalternant systems (such as the acetylacetone radical). The simplest method of estimating such effects is that of McLachlan[20] in which the α- and β-spins are allowed to occupy separate Hückel-type orbitals. The results of such a calculation for both the metal-to-ligand and the ligand-to-metal charge-transfer cases are included in Table V. Taken in conjunction with the knowledge that the Q in eq. 3 will be negative for a single proton but positive for a

(19) L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).
(20) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

CH$_3$ group, these results lead to the following predictions for the contact shifts.

(a) For metal-to-ligand charge transfer a large positive spin density is expected at the carbon bearing the CH$_3$ group leading to a large low-field shift. For the carbon bearing the single proton the moderately large negative spin density will also lead to a low-field shift. If anything this type of calculation will tend to underestimate this shift.

(b) Ligand-to-metal α-spin transfer will leave a β-spin on the ligand. This has its largest density at the C–H position and will give rise to a large low-field shift of this proton. The calculation gives a small positive spin density at the C–CH$_3$ position (less than 10% of the neighboring C–H spin density), but in view of the approximations involved this could equally well be a small negative spin density. A small shift is therefore predicted for the CH$_3$ group which could be to high field or low field.

(c) Ligand-to-metal β-spin transfer will have just the opposite effect to b above, *i.e.*, a large high-field shift for the C–H proton and a small shift of indeterminate sign for the CH$_3$ protons.

Since there are no symmetry limitations, whether the d-orbitals interact predominantly with the bonding or the antibonding ligand orbitals will depend on the relative energy separations. It is apparent from the above considerations that the shift of the CH$_3$ resonance will depend predominantly on the metal-to-ligand charge transfer.[21] The observed shifts indicate that the extent of this charge transfer decreases smoothly in the series from Ti(III) to Fe(III). Because of the dependence of the contact shifts on the spin quantum number S (eq. 1), the decrease in the charge transfer along the series is actually greater than is indicated by the actual contact shifts. If we wish to compare the absolute amounts of charge delocalized by this mechanism, the spin densities must be normalized so that $S = S'$ and the hyperfine coupling constants for a given position and hence the amount of charge delocalized are proportional to $\Delta\nu/(S + 1)$. If, on the other hand, the fraction of the total d-electron charge delocalized is required since the number of d-electrons increases from one to five, the correct quantity to compare is $\Delta\nu/S(S + 1)$. These figures are given in Table VI, together with the actual values of the spin

Table VI. Contact Shifts[a] and Spin Densities

	$\Delta\nu_{CH_3}$	$\dfrac{\Delta\nu}{S+1}$	$\dfrac{\Delta\nu/S \times}{(S+1)}$	$\rho^b \times 10^3$	$F^c \times 10^3$
Ti	-3367	2245	4489	$+28.9$	68.8
V	-2611	1306	1306	$+16.6$	39.5
Cr	-2187	875	583	$+11.1$	26.4
Mn	-1372	457	229	$+5.7$	13.6
Fe	-1110	317	127	$+4.0$	9.5

[a] In c.p.s. relative to the CH$_3$ resonance of cobalt(III) acetylacetonate. [b] Calculated from $a_H = Q\rho_C$ with $Q = +27$ gauss. [c] $F =$ the fraction of unpaired electron delocalized.

densities and the total fractional amount of spin delocalized which is calculated on the assumption that the Hückel spin density distribution is correct. This

(21) It has been deduced from the optical spectrum of Cr(III) acetylacetonate that the low lying π-levels interact strongly with the 3d orbitals: T. S. Piper and R. C. Carlin, *J. Chem. Phys.*, 36, 3330 (1962).

latter assumption is only approximately true so that the fraction of spin delocalized is only reliable to within a factor of two or three. These latter figures show that between $^1/_{10}$ and $^1/_{100}$ of an electron is delocalized by this mechanism.

In contrast to the CH_3 shift the shift of the single proton depends markedly on both the metal-to-ligand and the ligand-to-metal charge-transfer processes. The latter contribution will be as follows. For Ti(III) and V(III) the preferred process will be to donate an α-electron into the lower lying d-orbitals leaving a β-electron on the ligand and reinforcing the low-field shift arising from the metal-to-ligand charge transfer. For Cr(III) and Mn(III) there will be a choice of either donating a β-electron to the lower half-filled d-orbitals or an α-electron to the upper empty d-orbitals. The preferred possibility will depend on the relative magnitudes of the exchange interaction and the ligand-field splitting. It might perhaps be anticipated that the exchange effect will predominate and that an α-spin will enter the d-orbitals reinforcing the low-field shift, since all of this series of complexes are spin-free, indicating that exchange effects dominate the ligand-field splittings. However, the separation between the top π-ligand orbital and the relevant d-orbital will be greater in Mn and Cr than in Ti and V by the ligand-field splitting so that this factor will tend to reduce the mixing of the two orbitals. With Fe(III), the only possibility is the donation of a β-electron, leaving α-spin on the ligand and giving rise to a high-field proton shift. Insofar as data are available, the observed shifts are in good agreement with these considerations. In particular, the abrupt change from a low-field shift to a high-field shift on passing from Mn to Fe strongly supports this interpretation. It may also be noteworthy that the Mn CH shift is a smaller fraction of the CH_3 shift than in the case of V. This may reflect the additional ligand-field energy which has to be overcome to effect the charge transfer, which leads to a smaller contribution from the ligand-to-metal charge-transfer process.

The ordering of the energy levels in these compounds is that given in Figure 1. It is suggested that the changes on passing along the series from Ti to Fe are brought about by differences in the position of the d-orbitals relative to the ligand bonding and antibonding orbitals. For Ti(III) the d-orbitals are relatively close in energy to the lowest antibonding π-orbital and interact strongly with it resulting in metal-to-ligand charge transfer. As the nuclear charge increases, the energy of the d-orbitals relative to the ligand orbitals decreases. This is a well-recognized effect and is reflected in atomic ionization potentials, for example. The result is a progressive diminution in the interaction with the antibonding orbitals and an increasing importance to interaction with the bonding orbitals leading to ligand-to-metal charge transfer. It may be noted that both types of charge-transfer bands have been recognized in the electronic spectra of these transition metal acetylacetonates although there is still some disagreement about the exact assignments.[22-24]
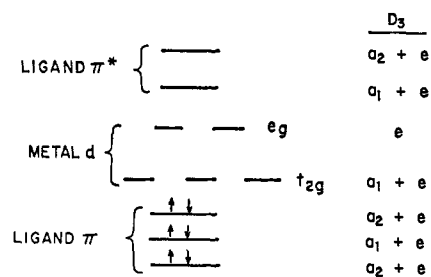
Figure 1. Molecular orbital diagram for octahedral (D_3) metal acetylacetonates.

On passing to the second row transition metal ions Mo(III) and Ru(III), it is apparent that the pseudo-contact effects are no longer negligible. They do not, however, appear to account for all of the observed shift. The apparent large g-value anisotropy for the d^3 Mo(III) is associated with the large zero field splitting in this ion which is probably $\sim kT$. Lacking a knowledge of the magnitude of this zero field splitting or of the g values of the states with spin other than $\pm^1/_2$, it is not possible to calculate the pseudo-contact contribution exactly. From the results of Table IV, though, it seems that the pseudo-contact effect can only account for a portion of the n.m.r. shifts and that the metal-to-ligand charge transfer is even more pronounced than in the corresponding Cr compound. The Ru(III) compound differs from the Fe(III) compound in being spin paired. Both the CH_3 and CH shifts are to high field and it would seem that only the ligand-to-metal charge-transfer process is effective. This is consistent with the absence of electrons in the higher pair of d-orbitals which would be expected to interact most strongly with the ligand antibonding orbitals.

Of the remaining compounds, there is no definite information on the geometry or g values of Mn(II) or Fe(II) so that interpretation of the shifts would be unduly speculative. The rare earth chelates of Eu(III) and Tb(III) have the stoichiometries $M(AA)_3 \cdot 3H_2O$ and are therefore not octahedral. The g values are not known, but the shifts are most probably predominantly pseudo-contact. The very much larger shift for Tb is in line with the much higher magnetic susceptibility of this compound. Finally, there is the case of Co(II) acetylacetonate. In pyridine solution a simple, two-line spectrum is obtained, and the predominant species is probably $Co(AA)_2(py)_2$. The results of Happe and Ward[25] have shown that in cobalt acetylacetonate–pyridine complexes there is a significant pseudo-contact effect but that it is not predominant. However, there may well have been more complex polymeric species present under their conditions of relatively low pyridine concentrations so that use of their results to estimate the pseudo-contact contribution to the shifts observed in the present work is probably not justifiable. It is, however, interesting to note that the shifts for the Co(II) compound, if assumed to be contact in origin, are not inconsistent with the pattern of the remaining first long period acetylacetonates. Thus, as argued above, the CH_3 shifts indicate that with increasing nuclear charge the d-orbitals contract

(22) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).
(23) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961).

(24) J. P. Fackler, T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, **4**, 130 (1965).
(25) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

and interact less strongly with the ligand antibonding orbitals. However, on passing from Fe(III) to Co(II), the addition of a positive nuclear charge is accompanied by the addition of two electrons. It is not implausible that the additional shielding of two electrons will more than compensate for one unit of nuclear charge so that the shift for Co(II) is rather greater than that for Fe(III) and is, in fact, quite close to that for Mn(III).

There are some clear parallels between the interactions discussed above and the chemistry of the transition metal ions. Thus, the ease of electron transfer from metal to ligand is clearly related to the ease of oxidation of the ion to the next highest valence state and that of transfer from ligand to metal to the ease of reduction to the next lowest valency. In the series Ti(III), V(III), and Cr(III), there is a sharp decline in the ease of oxidation in accord with the decreased spin delocalization in the antibonding orbital indicated by the contact shifts. In the group VI elements, Mo(III) is much more easily oxidized than Cr(III) and this again is reflected in the larger shifts observed. On passing to the series Cr(III), Mn(III), Fe(III), reduction to the lower valency becomes an important consideration and this is accompanied by significant contact shifts arising from ligand-to-metal charge transfer. If the Co(II) shifts are indeed predominantly contact, the process must be one of metal-to-ligand transfer as might have been anticipated from the existence of very stable Co(III) complexes. The Ni(II) compound on the other hand does not show this behavior and this can be correlated with the relative instability of Ni(III).

In conclusion, there is now perhaps sufficient data available from this work and previous studies on the n.m.r. of paramagnetic transition metal complexes to allow some tentative generalizations to be made regarding the interpretations of the observed shifts.

1. In the first transition series, providing the complexes are of fairly high symmetry, pseudo-contact effects do not seem to be very important. In the second transition series they become more significant, and in rare earth complexes they probably dominate.

2. For a given ligand and different metal ions, interactions with both bonding and antibonding ligand π-orbitals can occur. A qualitative prediction of which will be the more important can probably be made in many cases by consideration of the ease of reduction to the lower valency or of oxidation to a higher valency.

3. For a given metal ion and different ligands the crucial factor is the energy separation between the metal d-orbitals and the various ligand molecular orbitals. This is illustrated by data given in Table V comparing calculated energy levels for the aminotropone-imine and acetylacetonate ions. In the former case there is a bonding orbital of rather high energy and in accordance with this, ligand-to-metal spin transfer seems to dominate most of the aminotroponeimineates so far examined.[26] In the latter case both the top bonding and the bottom antibonding orbital are lower in energy and as discussed above metal-to-ligand charge transfer must also be considered. The possibility also remains that a σ-orbital may be the most favorably situated and this is perhaps the case for ligands such as pyridine[25] and amino acids.[27] A simple MO calculation, using Hoffman's[28] extended Hückel treatment if σ-orbitals are also to be considered, would be sufficient to make a qualitative prediction about the behavior of a given ligand. The extent of the applicability of these generalizations can only be determined when more detailed and extensive experimental results become available.

(26) Reference 1 and D. R. Eaton, W. R. McClellan, and J. F. Weiher, unpublished results.
(27) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).
(28) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

Structure Mimicry in Solid Solutions of 3d Metal Complexes with N-Methylsalicylaldimine (Msal-Me)

L. Sacconi, M. Ciampolini, and G. P. Speroni

Contribution from the Istituto di Chimica Generale e Inorganica, Universita' di Firenze, Florence, Italy. Received February 11, 1965

The complex bis(N-methylsalicylaldiminato)zinc(II) (Znsal-Me) is a pentacoordinate dimer. The complexes Cosal-Me and Mnsal-Me are isostructural with the Znsal-Me complex. Each of the former forms a binary solid solution with the latter when recrystallized at room temperature from common organic solvents. The diamagnetic complex Nisal-Me (forms α and β), although planar, also forms binary solid solutions with Znsal-Me. In a solid solution rich in the latter compound, Nisal-Me assumes the molecular and crystalline structure of the zinc complex and becomes pentacoordinate and paramagnetic. Addition of Znsal-Me to a Nisal-Me-rich organic solution, followed by crystallization, results in the formation of a solid solution which has the structure of the γ form of Nisal-Me. This form is paramagnetic and probably polymeric. It is normally obtained by heating crystalline diamagnetic Nisal-Me above 180°. In this solid solution, Znsal-Me transforms to the molecular and crystalline structure of γ-Nisal-Me which may be considered as the host lattice in this case. Analogous structural mimicry is demonstrated also by Cusal-Me with Znsal-Me. Cosal-Me in benzene or chloroform transforms partially to the monomeric tetrahedral form.