NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
PARAMAGNETIC COMPLEXES

NUCLEAR MAGNETIC RESONANCE STUDIES OF PARAMAGNETIC TRANSITION METAL COMPLEXES

BY

CHUA KEE-LAM, B.SC.

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AUTHOR: Chua Kee-Lam.(Nanyang University, Singapore).
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Abstract.

Studies of the bonding and reactivity of transition metal complexes constitute a large fraction of current research in inorganic chemistry. The present thesis describes three contributions to this area. In each case ,Nuclear Magnetic Resonance studies of paramagnetic complexes are involved. An introductory chapter briefly reviews some of the pertinent background. In the second chapter the NMR theory which forms the basis for interpreting the experimental results is developed.

The major topic of the thesis is concerned with the effect of ligand substitution on the charge distribution of a transition metal complex. Interest in this topic is aroused by the many reports that the reactivity of transition metal complexes can be considerably affected by modification of the ligands. This is particularly notable in the area of

homogeneous catalysis. It seemed possible that NMR studies of paramagnetic complexes might provide a probe for these effects. With this objective in view the NMR spectra of a series of trisβ diketonato V(III) complexes have been examined. It was found that substituent changes on one ligand brought about very large (several thousand Hz) changes in the isotropic shifts of protons or fluorine atoms located on another ligand. A rather complete study has been carried out on the series of complexes formed by systematically substituting CF_3 groups for CH_3 groups on tris-acetylacetonato V(III).Ninety-nine of the possible one hundred different ^1H and ^{19}F resonances in this system have been observed and identified. This relatively large body of data enabled us to attempt an empirical analysis of the results in terms of changes in the charge distribution in the complex brought about by substitution. Arguments are presented to show that the isotropic shifts arise predominantly from contact interactions. It was found necessary to introduce two terms in the empirical equations describing the shifts. The first represents changes in the distribution of the unpaired electrons in the Vanadium(III) d orbitals brought about by modification of the crystal field potential produced by the ligands. The second represents variations in the ability of a ligand to accept electron density by metal to ligand charge transfer due to the inductive effect of the substituent. Two term empirical equations of this

type reproduce the observed shifts to within 2%. The significance of the parameters obtained from this analysis is discussed in some detail. These studies have been extended to include several other substituted β-diketone ligands. A similar analysis has proved feasible and a consistent pattern of substituent parameters is obtained.

The second topic considered is closely related to the above study. The interest in this case was in the possible importance of dipolar shifts in determining the isotropic shifts of mixed chelates. A series of six coordinated Co(II) complexes was chosen for this purpose. These compounds are known to possess considerable magnetic anisotropy and dipolar shifts are therefore to be expected. However analysis of the results reveals that the substituent shifts are very similar to those for the V(III) compounds. It appears that the mode of transmission of substituent effects proposed may be quite general for many transition metal complexes.

The third topic involved in this thesis concerns the structure of the second coordination sphere of transition metal complexes. The participation of various solvents in the second coordination sphere of tris-pyrazolylborate Co(II) has been investigated. Equilibrium constants relative to carbon tetrachloride as a second sphere ligand have been obtained. The ability of a solvent to participate in the second sphere depends predominantly on its dipole moment and it is concluded that Van der Waals

forces are responsible for outer sphere binding.

1. Introduction

The technique of Nuclear Magnetic Resonance (NMR) Spectroscopy has been applied to a very large number of fields of chemical interest. Application of the technique to paramagnetic molecules presents a number of additional experimental and theoretical problems and for this reason, in the early days of NMR, was mostly neglected. However, it was gradually realized that the very complication, viz. the additional electron-nuclear coupling could be put to advantage and NMR of paramagnetic compounds could be used as a powerful tool to probe the electronic structure of molecules. Applications to organic free radicals are relatively limited. Most work has been done on paramagnetic complexes derived from the transition metal ions and coordinating ligands. Free radicals have a relatively long electron spin relaxation time and this leads to broad NMR lines. Transition metal complexes often have shorter electron spin relaxation times and reasonbly sharp NMR lines can be observed. Several mechanisms have been postulated by which the nuclei examined in paramagnetic molecules can be influenced by the unpaired electron(s). Under favorable conditions, the NMR approach can provide direct information concerning the electronic or geometrical structures of the paramagnetic molecules which is sometimes not readily obtainable by other means. It has also proved to be very useful for studying weak interactions in solution e.g. occur in the second coordination sphere because of its high sensitivity. The development of this area of research has therefore recently attracted considerable interest among inorganic chemists.

Proton hyperfine interaction in solution NMR spectra of paramagnetic compounds was first observed in various types of free radicals, e.g. naphthalene negative ion[3], Wurster's salts[7], triphenylmethyl,dimesitylmethyl[8] and semiquinones[10]. The theory of nuclear isotropic hyperfine interaction in these π electron radicals has been developed by several investigators. Equations [10,12,15,16] for contact and dipolar shifts and the related π spin density in these paramagnetic radicals were derived. This theory is also applicable with some modification to transition metal complexes. The first observations in this area were carried out in 1957 on various paramagnetic bis(π-cyclopentadienyl) metal complexes by McConnell and co-workers [12,17]. However the potential utility of this technique was not fully appreciated until Eaton, Phillips and co-workers presented detailed analyses of ^1H and ^{19}F spectra of a variety of substituted Ni(II) aminotroponeimineates[24,27,31-35,38,44]. Valuable information regarding the molecular structures,spin density distribution and delocalization mechanisms was determined from their studies of a large number of symmetric and mixed chelates. Since then the number of publications on this topic has rapidly increased. NMR studies of paramagnetic complexes are now only restricted by the excessive linewidths of some complexes. Different sorts of information are obtained depending on the type of system chosen. A large number of systems derived from various metal ions and ligands have been investigated. A recent bibliography has been given by Eaton and Zaw [69].

The present research is concerned with two types of experiments involving NMR studies of paramagnetic complexes. The first and major part of this thesis deals with studies of mixed complexes, i. e. compounds containing two or more different ligands. The interest here is directed towards the question of how changes in one ligand affect the bonding to another ligand. This topic is pertinent to many problems dealing with chemical reactivity and catalysis and the high sensitivity of NMR isotropic shifts to small changes in structure provides an excellent approach to problems of this kind. The second topic is concerned with the solvation of complexes and the structure of the second coordination sphere. Although the number of publications on the nature of the metal-ligand bonding in transition metal complexes is very large, only a relatively small number of studies of mixed chelates have been reported. Three such series of complexes involving mixed chelates have been examined in some detail by NMR techniques. These are the

Ni(II) aminotroponeimineate complexes studied by Eaton and Phillips [24,27,31-35,38,44], the Cr(II) O-phenanthroline / bipyridine complexes studied by LaMar and Van Hecke[58,63,64,73] and to a lesser extent Ni(II) salicylaldimines by Holm and Chakravorty [43]. A theoretical paper [40] concerning the electronic structure of the mixed chelates of Ni(II) aminotroponeimineates has also been published. In the present work, mixed complexes of Vanadium(III) and Cobalt(II) have been examined.

The first series of complexes employed in this studies involves a number of substituted tris-β-diketonato V (III)chelates, The NMR isotropic shifts for this series of complexes have been shown to arise from π contact interaction. [20,45,51,74,81]. Data have been obtained for a rather complete series of complexes resulting from systematic substitution on one, two or three of the coordinated ligands. An empirical method is adopted to analyse the experimental isotropic shifts of these paramagnetic complexes. The substituent shifts (shift of a particular resonance in a complex upon substitution at another position) have been interpreted using a model involking charge redistribution in both σ and π systems of these complexes. A number of substituent parameters are derived and are discussed in terms of changes in electron density.The results are then compared with substituent effect in aromatic compounds. The important differences arise from the three dimensional nature of metal complexes which leads to interactions between the σ and π electrons of a type not found in simple aromatic compounds. The significance of the results with respect to understanding of the mechanism and variation in ligand exchange rates in catalytic or ligand exchange reaction is discussed.

The second series of complexes involves mixed chelates of a series of di-adducts of Co(II) β-diketonates. A number of investigators have studied the di-adducts of Co(II) bis (acetylacetonate) of general formula [39,41,56, 57,66,68] $L_2Co(acac)_2$, where L represents coordinating solvent , e.g. pyridine, aniline , methanol, isonitrile, dimethylsulphoxide and several others. The conclusion has been reached that in these complexes, the dipolar contribution to the isotropic shift is significant. All the mixed complex studies reported thus far have been interpreted on the basis of contact shifts. It was therefore thought desirable to undertake some detailed studies involving mixed complexes of this type to investigate the influence of dipolar effects. Our observation is that a change of substituent on one β-diketonate ligand significantly affects the shifts of proton or fluorine atoms on the other β-diketonate ligand of the same compound. An argument is presented to suggest that these substituent shifts also arise predominantly from contact rather than dipolar effect. The pattern of shifts is compared with that previously observed for V(III) β-diketonates and a similar interpretation is proposed.

Application of NMR isotropic shifts to the studies of the structure of second coordination sphere complexes have also been attempted. Earlier work in this laboratory ultilized the isotropic shifts of the ligands weakly bound in the second sphere of coordination to trispyrazolylborate Co(II) complexes[62,76,77]. The shifts are believed to arise from dipolar interaction. Ligands such as pyridine, aniline and PF_6^- were used. It was concluded that different ligands tend to occupy different positions and orientations with respect to the Co(II) complex . These investigations have been extended by studying the solvent dependence of aniline shifts in the presence of tris-pyrazolylborate Co(II). This has led to some conclusions regarding the relative magnitudes of the interactions of different solvent molecules with the metal complex.

2. Nuclear Magnetic Resonance in Paramagnetic Systems.

The technique of Nuclear Magnetic Resonance has proved to be a very powerful tool for the investigation of many problems in an increasing numbers of fields. Most applications have been concerned with diamagnetic compounds. The NMR theory pertinant to this class of compounds is very well-developed and several texts are available[71,82]. Paramagnetic compounds present some additional complexities and the relevant theory is discussed in the present chapter. Several review articles are also available [47,59,60,69].

2-1. Resonance Conditions.

Paramagnetic species may be studied by ESR method. However experiments show that not all such compounds can be detected by ESR instruments because of excessive line broadening. Fortunately, in such circumstances the NMR lines of these compounds are often sharp and NMR provides an alternative approach. It is well known that the [illegible] of ESR or NMR spectra depends on the electron spin relaxation times T_{1e}. The necessary condition for observing well-resolved ESR hyperfine structure is that T_{1e} be long such that $1/T_{1e} \ll A$, where A is a hyperfine coupling constant. For NMR, the spectral properties are determined by the nuclear spin relaxation time which in turns depends on T_{1e}, since for a paramagnetic molecule, the 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. If T_{1e} is long, NMR spectra will not appear due to short nuclear spin relaxation times caused by the fluctuating field produced at the nucleus by the transition of the electron spin. If T_{1e} is short, the very rapidly fluctuating magnetic fields produced by the electron spin are no longer effective in producing the nuclear relaxation. The fluctuations are of such a high frequency that they have negligible components of the correct frequencies to induce nuclear transition. The nucleus experiences an average field corresponding to the mean value $\langle S_z \rangle$ of the electron spin polarization which is not equal to zero due to the unequal thermal populations of the electron spin levels. Short electron spin relaxation times thus result in relatively long nuclear spin relaxation times. In these circumstances NMR spectra will be observed. In general, if either one of the following conditions[9,12] is satisfied, NMR lines can always be observed.

$$\begin{array}{ll} & T_{1e} \ll A^{-1} \\ \text{or} & T_e \ll A^{-1} \end{array} \qquad \text{..........................(2-1)}$$

T_{1e} is the electron spin relaxation time, T_e is the exchange time for the paramagnetic species, A is the hyperfine coupling constant. We shall be concerned with only the first condition. The resonances, if observed, are usually characterized by somewhat broader linewidth than for diamagnetic molecules but the separations are often larger. Thus overall the analysis is less of a problem. However, the two methods are not mutually exclusive. Electron spin lattice relaxation times are found to decrease with increasing temperature. Thus it is sometimes possible to perform NMR experiments in solution at high temperature and ESR experiments in the solid state at low temperature.

2-2.Contact and Dipolar Shifts.

The magnetic interactions between electron and nuclear spins have been extensively reviewed by Abragam[30], Winter[37], and by Freeman and Watson[48]. The Hamiltonian for the electron-nuclear spin system in paramagnetic species is given by

$$\mathcal{H} = -g_n\beta_n I\cdot H + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_{N} + g\beta(L+2S)\cdot H + \mathcal{H}_{II} \quad \ldots\ldots(2\text{-}2)$$

The first and fifth terms represent the interactions of the nuclear and electron magnetic moments with an external magnetic field. $\mathcal{H}_{LS}$ is the spin - orbit interaction for the electronic system. $\mathcal{H}_{SS}$ is the interaction between electron spins and $\mathcal{H}_{II}$ that between nuclear spins. $\mathcal{H}_{N}$ is the hyperfine interaction term and represents the interaction between the electron spin and orbital moments and the nuclear magnetic moment. From the point of view of NMR in paramagnetic species, the most important and interesting term is $\mathcal{H}_N$, the hyperfine interaction term. The magnetic hyperfine interaction term was first derived by Fermi[1] from Dirac relativistic theory for the electron, and can be written as

$$\mathcal{H}_N = -gg_n\beta\beta_n\left\{\frac{8\pi}{3}\delta(r)(S\cdot I)+\left[\frac{(L-S)\cdot I}{r^3}+\frac{3(S\cdot r)(I\cdot r)}{r^5}\right]\right\}\ldots\ldots(2\text{-}3)$$

r is measured from the center of the nucleus. The interaction involving the delta function is the Fermi contact term. This term has a non-zero value only for the s-electrons and then the last two terms are zero. The last two terms are dipolar interaction terms and have a form analogous to that of the classical expression for the interaction of a point dipole $g_n\beta_n I$ and $g\beta S$ plus the interaction of a point dipole $g_n\beta_n I$ with a moving charge of L angular momentum. The expression for the hyperfine interaction term has also been derived on the basis of Quantum Field Theory[6].

As the result of this hyperfine interaction, the resonance of the nucleus is shifted to higher or lower field than that of a corresponding nucleus in an analogous diamagnetic compound. In solution rapid tumbling of the molecules averages some terms in this expression to zero. The remaining terms give rise to an isotropic shift. The isotropic shift is usually composed of two factors: The first of which is the so-called 'Fermi Contact Shift' which arises from the presence of unpaired electron spin density at the resonating nucleus. The second , results from through space interaction between the magnetic dipoles produced by the unpaired electron(s) and the resonating nucleus. The general expression for the proton contact shift is given by[12]

$$\Delta H_i = - A_i \frac{\gamma_e}{\gamma_N} \langle S_z \rangle \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2\text{-}4)$$

$\langle S_z \rangle$ is the average value of the electron spin in the z direction. The difficulty arises in the evaluation of $\langle S_z \rangle$. The evaluation is simple under conditions of Curie law behaviour, under such conditions, $\langle S_z \rangle = \frac{g\beta H_o S(S+1)}{3kT}$. The contact shift is then given by Bloemgergen equation[13,16]

$$\frac{\Delta v_c}{v_o} = \frac{\Delta H_c}{H_o} = - \frac{A g^2 \beta^2 S(S+1)}{g_n \beta_n \cdot 3kT} = - A \frac{\gamma_e}{\gamma_N} \frac{g\beta S(S+1)}{3kT} \quad \ldots\ldots\ldots\ldots(2\text{-}5)$$

where $A = \frac{8\pi}{3h} g g_N \beta \beta_N \left[\psi(0)\right]^2$. The Curie law contact shift equation can be expressed in terms of the susceptibility as follows:

$$\frac{\Delta v_c}{v_o} = - \frac{A}{N g_n \beta_n} \cdot \frac{N \mu^2}{3kT} = - \frac{A}{N g_n \beta_n} \chi_M = c\,\chi_M \ldots\ldots\ldots\ldots(2\text{-}6)$$

where $\mu^2 = g^2 \beta^2 S(S+1)$ for spin contribution only and χ_M is the molar magnetic susceptibility.

Most of the contribution arising from the dipolar part of the Hamiltonian is anisotropic and averages to zero for a rapidly tumbling molecule in solution but an isotropic part remains. The dipolar shift is given in general form for axial symmetry by the equation[16]:

$$\frac{\Delta\nu^{dip}}{\nu_o} = -\frac{\beta^2 S(S+1)}{27kT}(g_{\parallel}+2g_{\perp})(g_{\parallel}-g_{\perp})\frac{3\cos^2\theta-1}{r^3} \quad \ldots\ldots\ldots(2\text{-}7)$$

where θ is the angle between the principle mangetic axis and a line joining the metal atom and the magnetic nucleus under consideration; r is the distance of this nucleus from the metal atom. β is the Bohr magneton and $g_{\parallel}$ and $g_{\perp}$ are the components of the g tensor parallel and perpendicular to the magnetic field. This term goes to zero if the g-tensor is isotropic.

As can be seen from equation (2-5) and equation (2-7) the contact shift requires spin density to be delocalized into an s-orbital. The dipolar shift arises from dipole-dipole interaction. Such interactions are in general anisotropic, i.e. their magnitude depends upon the orientation of the molecule with respect to the applied magnetic field.[69] The situation may be seen from figure 2-1, assumed that the molecule is fixed in space and the direction of field H_o is changed as indicated in figure 2-1a and 2-1b. The dipole-dipole interaction as shown in figure 2-1a is obviously different from that in figure 2-1b, thus producing dipolar shifts which are different in different orientations. In the actual performance of the experiment, the direction of the field is kept constant, whereas the directions of the dipoles of electron(s) and nucleus are changing continuously because of the molecular tumbling, the shift that is observed is an average value of those shifts corresponding to different molecular orientations. This average will be non-zero only if $g_{\parallel} \neq g_{\perp}$. However, in the derivation of equations(2-5) and (2-7), several assumptions[65] were made which restrict its application to certain complexes. These are as follows:

1. r was large enough that paramagnetic metal ion may be treated as a point dipole.
2. The complex had only one thermally populated energy level in the absence of the magnetic field and the states of this ground level could be assigned a spin quantum number S.
3. For S=1, splitting of the ground level in the absence of the field (zero field splitting) could be ignored.
4. The orbital contribution to the isotropic NMR shift could be taken into account indirectly through the use of g-tensor components in equations (2-5) and (2-7) which required that there be at most only first order contribution to the magnetic moment of the complex brought about by spin-orbit mixing of the ground level with non-populated excited states.

A more general but complicated expression taking into account the above assumptions has been derived by Kurland and McGarvey[65] by the density matrix method. The derived expression for the isotropic shift of paramagnetic compound is given below:

$$\left(\frac{\Delta H}{H_o}\right)^{iso} = \frac{1}{kTq}\left[\sum^{\Gamma n,\Gamma m} e^{-\epsilon_\Gamma/KT} \langle \Gamma n|\mu\cdot H_o|\Gamma m\rangle\langle \Gamma m|A_N\cdot h_o|\Gamma n\rangle \right.$$

$$\left. -KT\sum_{\Gamma\neq\Gamma'}^{\Gamma n,\Gamma' m} Q_{\Gamma,\Gamma'}\langle \Gamma n|\mu\cdot H_o|\Gamma' m\rangle\langle \Gamma' m|A_N\cdot h_o|\Gamma n\rangle\right] \qquad \text{........(2-8)}$$

where $q = \sum_{\Gamma n} \rho_{\Gamma n,\Gamma n} = \sum_{\Gamma n} e^{-\epsilon_\Gamma/KT}$

$$Q_{\Gamma\Gamma'} = \frac{e^{-\epsilon_\Gamma/KT} - e^{-\epsilon_{\Gamma'}/KT}}{\epsilon_\Gamma - \epsilon_{\Gamma'}}$$

The eigenvalues of the Hamiltonian $\mathcal{H}^\circ$ in the absence of external magnetic field H_o are labelled as ϵ_Γ and the eigenstates for the Kramers Multiplet corresponding to ϵ_Γ as $|\Gamma n\rangle$. A_N appears in equation (2-8) consists of the operators A_F, A_D, and A_L representing respectively the Fermi contact, dipolar and the nuclear-electron orbital interactions, i.e.

$$A_N = (A_F + A_D + A_L) \qquad \text{........................ (2-9)}$$

$$A_F = \frac{8\pi}{3} g\beta \sum_i \delta(r_i) s_i$$

$$A_D = g\beta \sum_i \left[3(s_i\cdot r_i)r_i - r_i^2 s_i\right] r_i^{-5}$$

$$A_L = 2\beta \sum_i r_i^{-3}\, l_i$$

In solution, equation (2-8) should be averaged over all possible orientations to become:

$$\left(\frac{\Delta H}{H_o}\right)^{iso} = \frac{1}{3kTq}\sum_{x,y,z}^{i=}\left[\sum^{\Gamma n,\Gamma m} e^{-\epsilon_\Gamma/KT}\langle \Gamma n|\mu_i|\Gamma m\rangle\langle \Gamma m|A_{Ni}|\Gamma n\rangle\right.$$

$$\left. -KT\sum_{\Gamma\neq\Gamma'}^{\Gamma n,\Gamma' m} Q_{\Gamma,\Gamma'}\langle \Gamma n|\mu_i|\Gamma' m\rangle\langle \Gamma' m|A_{Ni}|\Gamma n\rangle\right] \qquad \text{........(2-10)}$$

Where A_{Ni} and μ_i are the components of A_N and μ respectively along a set of axes i=x, y and z which are fixed with respect to the complex. Equations (2-5) and (2-7) which are frequently used for contact and dipolar shifts arise from the first term in equations (2-8) and (2-10). The second term arises from the fact that $|\Gamma\rangle$ are not eigenfunctions of the Zeeman operator; and the interaction with the magnetic field therefore results in a second order mixing of $|\Gamma'_m\rangle$ states with ground state. When $(\epsilon_\Gamma - \epsilon_{\Gamma'})$ is of the order of kT, the contribution to the paramagnetic shift of the "Zeeman mixing" term may be large and cannot be ignored. However if isotropic shifts are to be calculated using equation (2-10), one needs to know the explicit and correct form of the wavefunctions representing the states $|\Gamma_n\rangle$ thus limiting its application. Expression for the metal ion contribution to the dipolar shift has been derived in terms of the susceptibility. The expression given by Kurland and McGarvey[65] is as follows:

$$\left(\frac{\Delta H^M}{H_o}\right)^D = \frac{1}{2R^3}\left[(1-3\cos^2\Omega)(\chi_{zz}-\bar{\chi}) + \sin^2\Omega\cos 2\psi(\chi_{yy}-\chi_{zz})\right] \quad \ldots.(2\text{-}11)$$

where $$\chi_{ii} = \frac{1}{KTq}\left[\sum^{\Gamma_n,\Gamma_m} e^{-\epsilon_\Gamma/KT}\langle\Gamma_n|\mu_i|\Gamma_m\rangle\langle\Gamma_m|\mu_i|\Gamma_n\rangle - KT\sum_{\Gamma\neq\Gamma'}^{\Gamma_n,\Gamma_m} Q_{\Gamma,\Gamma'}\langle\Gamma_n|\mu_i|\Gamma'_m\rangle\langle\Gamma'_m|\mu_i|\Gamma_n\rangle\right.$$

$$\bar{\chi} = \frac{1}{3}(\chi_{xx}+\chi_{yy}+\chi_{zz})$$

Ω is the angle between the z-axis of the complex and the unit vector along the line joining the metal ion and the ligand nucleus, and ψ is the angle between the projection of the unit vector α in the xy plane and the x axis.

For a complex with only one thermally populated multiplet of spin quantum number S, χ_{ii} is given by:

$$\chi_{ii} = \frac{\beta^2 S(S+1)}{3kT} \; g_{ii}^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2\text{-}12)$$

then the dipolar shift of the metal ion can be expressed as

$$\left(\frac{\Delta H^M}{H_o}\right)^D = \frac{\beta^2 S(S+1)}{9kTr^3}\left\{\left[g_{zz}^2 - \frac{1}{2}(g_{xx}^2 + g_{yy}^2)\right](1-3\cos^2\Omega) + \frac{3}{2}(g_{yy}^2 - g_{xx}^2)\sin^2\Omega \cos 2\psi\right\} \qquad \ldots\ldots\ldots(2\text{-}13)$$

For the case of axial symmetry, $g_{zz}=g_{\parallel}$, and $g_{xx}=g_{yy}=g_{\perp}$, equation (2-13) reduces to the corresponding equation given by McConnell and Robertson.[16]

An equation for calculating the dipolar shift in terms of of magnetic susceptibility for the bis(2,4-pentanedinoto)bis(pyridine)Co(II) which has the structure as shown in figure 2-2 has also been derived by Horrocks[70] and is given below:

$$\left(\frac{\Delta v}{v_o}\right)^D = \frac{1}{N}\left\{-\frac{1}{3}\left[\chi_z - \left(\frac{\chi_x}{2} + \frac{\chi_y}{2}\right)\right]\left(\frac{3\cos^2\theta - 1}{r^3}\right)_{ave} + \frac{1}{2}(\chi_z - \chi_y)\left(\frac{\sin^2\theta \cos 2\Omega}{r^3}\right)_{ave}\right\} \qquad \ldots\ldots(2\text{-}14)$$

Ω is the angle between the x axis and the projection of vector r on the xy plane. Thus if the dipolar shift can be calculated, then the contact shift may be obtained by substracting the dipolar part from the isotropic shift assuming that the dipolar contribution from the ligand orbital is negligible. However due to the lack of the knowledge of the parameters necessary for performing the calculation, we regard equation (2-7) under suitable condition as still a useful approach for obtaining at least qualitative information regarding the metal-ligand bond structure and related properties.

It is sometimes possible to obtain a rough estimate of the relative importance of contact or dipolar shifts without resort to complicated calculation by one of the following arguments[69]:

a.) Contact shifts should be identical in both solution and[16] solid whereas dipolar shift should differ in different phases. Comparison of solution and polycrystalline solid spectra can thus reveal the relative importance of contact to dipolar shifts. The argument has been applied to vanadocene[12,17] and the shift was concluded to be contact in origin. However because of the excessive linewidth of the poly-crystalline solids the method has not been further exploited.

b.) The presence or absence of magnetic anisotropy in a complex can generally be used to establish or disprove the dipolar contribution to the isotropic shifts. Dipolar contributions can be important if there is magnetic anisotropy. Reference to equations (2-7) and (2-13) indicate that if either one of the following conditions holds the dipolar effect will approach zero.

for equation (2-7) $\frac{\Delta H}{H_o} = 0$ if $g_{\parallel} = g_{\perp}$

for equation (2-13) $\frac{\Delta H}{H_o} = 0$ if $g_{xx} = g_{yy} = g_{zz}$

Although Jesson[53] 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 anisotropic energy, the qualitative dependence on the g value anisotropy and the molecular geometry is however maintained. Thus if ESR measurements have established that Δg is small for axial symmetry, or if theoretical arguments have shown that the ground state is orbital-ly non-degenerate and well separated from the excited states which can be mixed in by spin-orbit coupling or Zeeman interaction, it is reasonably to assume that the observed shifts are predominantly contact in origin.

c.) Other lines of argument for estimating the extent of dipolar contribution without any knowledge of magnetic properties have also been developed:

1. Estimation of the ratios of dipolar shifts from their geometrical dependence: Provided the geometry of the molecule is known and the principal axis of the symmetry can be identified, values of the geometrical factors $(3\cos^2\theta-1/r^3)$ for axially symmetric molecule may be calculated for each proton. Dipolar shifts if present in significant amount must be proportional to these values. If the experimental ratios of the shifts diverge widely from that of the geometrical factors and particularly if the signs are wrong this may indicate that dipolar effects do not predominate. However,

relatively small contact contribution may markedly affect the ratios of the shifts.

ii. If the mechanisms of electron delocalization are the same for complexes formed from two metal ions M_1^{+n} and M_2^{+n} with the same type of ligands of similar structure and if the contact shift is known to be predominant in one of the complexes, e.g. in M_1^{+n} complex, and if the ratio of the shifts $\gamma_{ij} = \frac{\Delta v_i}{\Delta v_j}$ for any two different nuclei in the same ligand is the same to that of the other complexes, e.g. M_2^{+n} complex then the contact shift should predominate in the second complex[66].

iii. If the mode of the spin delocalization can be identified and the shifts show good proportionality to calculated spin density, a contact mechanism may be inferred. The argument is most persuasive for the π delocalization mechanism. It should be noted that the use of these arguments has led to some controversy[39,41,61,72].

We have thus far discussed the various ways to estimate the relative importance of contact and dipolar contribution to the isotropic shift. In system where the π delocalization mechanism is the predominant process, it is particularly useful to study the contact shifts of such system since the spin density in π organic radicals have been studied in a number of cases. A short description of the spin density and hyperfine interaction in π system is thus necessary and will be given in the following section.

2-3. Spin Density

A. Spin density and hyperfine interaction in π system.

Of particular interest in the studies of transition metal complexes is the spin density distribution on the coordinated ligand and the mechanisms responsible for spin delocalization since they can shed light on the nature of metal-ligand bonding and the orbitals concerned. In order to obtain such information one may then make use of equation (2-5) (in spite of its approximate nature) and the theory of hyperfine interaction in π type organic free radicals proposed by H.M.McConnell.[15] The theory states that for such an organic free radical, the hyperfine coupling constant A_x for a fragment X attached to the sp^2-carbon atom resulting from contact interaction is proportional to the spin density ρ_{c-x} on the p_π orbital of the sp^2-carbon atom as given by the equation[10,15]:

$$A_x = Q_x \frac{\rho^{\pi}_{c-x}}{2S} \qquad \ldots\ldots\ldots\ldots\ldots(2\text{-}15)$$

where Q_x is a proportionality constant, the value of which depends on the group X attached to the sp^2-carbon atom. Experiments show that $Q_H = -22.5$ G[14] whereas Q_{CH_3} varies considerably in magnitude (from $+5$ to $+30$ G)[18,32,34,36]. The signs of Q_H and Q_{CH_3} are different indicating that spin density reaches the corresponding proton through different mechanisms. It is believed that for a $>$C-H fragment, an indirect $\pi - \sigma$ spin polarization is operating such that α spin on the p_π orbital of a sp^2-carbon induces β spin density on the proton attached to it, thus giving rise to a negative sign for Q_H. For a Methyl group Q_{CH_3} is positive because an unpaired electron on the sp^2-carbon atom can be delocalized directly into the 1s orbital of the hydrogen atom[18,19], an effect which is commonly known as "hyperconjugation".

Applying this theory to paramagnetic complexes when the coordinating ligands contain extended π electron system, the contact shift is related to the π spin density through the coupling constant A given by equation (2-5) and equation (2-15). Conventionally contact interaction constants A are derived from ESR spectroscopy. However, in ESR, signs of A are undetermined. When applicable the NMR approach has the advantage over ESR that signs of contact interaction constants are given by the directions of the shifts. (Higher or lower field shifts with respect to the corresponding nucleus in the analogous diamagnetic complexes). Thus contact shift measurements can yield information about spin density distribution in the π system of the ligand coordinated to the paramagnetic metal ion.

B. Possible mechanisms of spin delocalization.

Several modes by which spin density can reach a particular nucleus in paramagnetic complexes are outlined below; both σ and π delocalization may occur depending on the symmetry of the molecule. For σ contributions the effect usually falls off rapidly with increasing the number of bonds separating the magnetic nucleus from the metal ion. The isotropic shifts arising from this source are expected to decrease in a similar manner.

For π contribution, it is perhaps most profitable to illustrate this point by reference to a specific example. Vanadium(III), a d^2 system is chosen for such purpose[69]. In an octahedral crystalline field, the five 3d orbitals split into e_g and t_{2g} sets. The e_g set of orbitals can participate in σ-bonding with coordinating ligands whereas the t_{2g} set can π bond with the ligand π orbitals. Thus in an octahedral field, the two unpaired electrons of V(III) complex will occupy the t_{2g} orbitals which are of lower energy. Spin density may then delocalize through one of the following mechanisms:

1. The spin-containing orbitals can mixed directly with empty ligand π^* orbitals of similar energy thus giving rise to positive spin density on the ligand π^* orbitals. This π spin density can be related to the hyperfine coupling constant of a hydrogen atom or methyl protons by the McConnell relationship, i.e. equation (2-15).

2. The second mechanism responsible for spin delocalization is the ligand to metal charge transfer. The metal d_π orbitals can interact with filled ligand π orbitals and if the metal orbitals are less than half-filled as in the present example, either positive or negative spin electron(s) could be donated. In the former case there will

be excess negative spin on the ligand system whereas excess positive spin density will be present in the latter case.

3. Changing the symmetry of the molecule can also effect the spin delocalization mechanism, for example if the symmetry of the molecule is lower than O_h e.g. D_3 symmetry, in this case the d_{xy}, d_{xz} and d_{yz} orbitals are no longer the eigenstates of the system. There will be a mixing of d orbitals and new functions which are eigenstates in the D_3 symmetry must be constructed from linear combinations of the 3d orbitals. Symmetry arguments independent of any model of the interaction between metal atom and ligands show that the t_{2g} orbitals split to give an e orbital and an a_1 orbital.i.e.

O_h point group	$\longrightarrow$	D_3 point group
e_g	$\longrightarrow$	e
t_{2g}	$\longrightarrow$	$a_1 + e$

However , symmetry argument itself does not indicate the relative energy of the orbitals. The forms[26] of the correct linear combinations of the 3d orbitals belonging to the respective representations for O_h and D_3 symmetry have been worked out and are tabulated in Table 2-1. Two states that belong to the same representation of the group can mix if the energy difference between them is not too large. The forms of orbitals indicated in Table 2-1 may be regarded as approximate correct(depends on the energy difference between the states) due to the possible mixing of two sets of orbitals that belong to the same representation. The set of e (σ) orbitals may mix with the e(π) set of orbitals and each set of the orbitals may gain some of the properties of the other. Small amounts of σ orbital properties may then be introduced into the e (π) orbitals which can also mix with the ligand σ^* orbitals thus leading to direct delocalization of α spin to the coordinated ligands.

4. Other more subtle mechanisms e.g. unpaired electron in essentially non-bonding π orbitals may polarize the spin of paired electron(s) in neighbouring σ bonding orbitals leading to excess β spin in the ligand σ orbitals . The effect may be pronounced only for atoms attached to the metal, which can again polarize the spin in the filled ligand π orbitals. Thus it is clear that incorrect identification of the delocalization mechanism can lead to false conclusions.

C. Utility of contact shift: Illustrative examples.

Perhaps it is best to illustrate the potential usefulness of contact interaction in terms of the types of information that may be obtained by refering to some of the published results. The following discussions serve for this purpose.

a). Contact shifts in symmetric chelates.

The contact shifts equation for a system involving equilibrium between square planar and tetrahedral forms such as in tetrahedral Ni(II) aminotroponeimineate[44,47] is given as follow:[46]

$$\left(\frac{\Delta v_i}{v_o}\right) = \frac{-A_i}{2S}\frac{\gamma_e}{\gamma_N}\frac{g\beta S(S+1)}{3kT}\left[\exp(\Delta E - T\Delta S)/RT + 1\right]^{-1} \quad \ldots(2\text{-}16)$$

where A_i is the hyperfine coupling constant for nucleus i and is related to π spin density by the McConnell relationship. Spin density can then be obtained by using the experimental isotropic shifts and equations (2-15) and (2-16) assuming that the shifts arise from contact interaction.Spin density calculations using the valence bond approximation have been attempted. The significance of this method is that spin correlation effect has been automatically taken into account. Good agreement between the experimental and calculated spin density was obtained assumed that an electron of β spin has been partially transferred from the ligand to the metal ion. That π contact interaction will in general make larger contribution to the isotropic shift can also be illustrated by the work of LaMar and Van Hecke who have carried out extensive studies on the complexes[58,63,64] of chromiun(II) with o-phenanthrolines (o-phen) and α,α-bipyridines (bipy). In the following section emphasis will be placed on discussions of the information obtainable from NMR contact shifts of the mixed chelates of tetrahedral Ni(II) and octahedral Cr(II).

b). Contact shifts in mixed chelates.

Interesting results have been obtained in the NMR studies of mixed chelates. Studies with Ni(II) aminotroponeimineates have shown that the extent of spin delocalization and hence of metal-ligand π bonding is insensitive to ligand substitution for symmetric chelates. However, in the mixed chelates the spin delocalized to one ligand is found to be enhanced at the expense of the other ligand. The reduction in total spin density on one ligand is very nearly equal to the additional spin density acquired by the other ligand. The observation that electron withdrawing substituents reduced the spin density on the coordinated ligand and electron donating substituents have the converse effect is in accordance with the proposed delocalization mechanism involving ligand to metal charge transfer. Spin densities calculated for the corresponding positions of two symmetric and their mixed chelates are given in figure 2-3.

Before proceeding, it is necessary to discuss first the symmetry of the orbitals concerned in different crystal field field environments. Thus in a tetrahedral field the five d orbitals are split into t_2 and e sets.Only the t_2 set will be of interest since for a d^8 system, the e set of orbitals in a tetrahedral (or lower) field are filled. The symmetric chelate of Ni(II) aminotroponeimineate belongs to D_{2d} point group, thus the t_2 set of orbitals which are of interest is split into b_2 and e sets.The e set can participate in π bonding with the ligand π orbitals but b_2 cannot. In the mixed chelate, the e set of D_{2d} point group is further split into b_1 and b_2 orbitals in this C_{2v} symmetry:

$$\begin{array}{l} \underline{T_d \longrightarrow D_{2d}} \\ t_2 \longrightarrow e+b \end{array} \qquad \begin{array}{l} \underline{D_{2d} \longrightarrow C_{2v}} \\ e \longrightarrow b_1 + b_2 \\ b \longrightarrow a_1 \end{array}$$

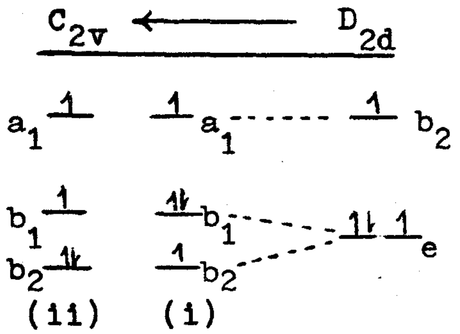
A b_1 d-orbital on the nickel atom has the correct symmetry to bond with the π orbital of one ligand and b_2 d-orbital can π bond with that of the other ligand. However, no unambiguous theoretical argument can be used to determine whether the e or the b orbital is of lower energy. The answer to this question is provided by the temperature dependence of the contact shifts of the symmetrical and mixed chelates. There are two factors which could contribute to the splitting of b_2 and e levels in D_{2d} symmetry point group:

(i). π -bonding effect: A splitting will arise because in the D_{2d} symmetry, the e orbital can participate in π bonding but b_2 cannot. Since good agreement between experimental and calculated spin density distribution was obtained based on the supposition that an unpaired electron of β spin has partially donated from the top filled ligand π orbital to metal d_{π} orbital indicating that e orbital has participated in bonding with the filled π ligand orbital. This result is to place the e orbital at a higher energy than b_2 orbital.

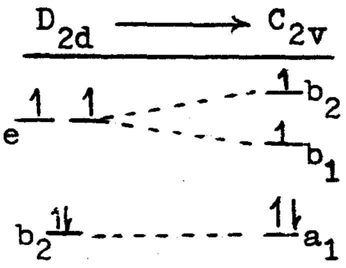
(ii). Crystal field effect: The deviation of the crystal field from that of a regular tetrahedron causes an unsymmetrical distribution of charge hence a splitting of orbitals concerned due to the lowering of symmetry, e.g. from

T_d to D_{2d} point group. There is no way to predict the relative energy of e and b_2 orbitals due to this effect. Two possible relative energy schemes of orbitals in Ni(II) aminotroponeimineate proposed by Lin and Orgel[40] and by Eaton and Phillips[44] are given below:

Case (A):



Case (B):



In an attempt to explain the unsymmetrical distribution of spin density in the mixed chelates, Lin and Orgel[40] have suggested the possibility as shown in case (A). They argued that configuration (i) would lead exclusively to spin delocalization to one ligand and configuration (ii) to the other so that a Boltzmann-type distribution results in the preferential delocalization of spin to one ligand. However, two experimental results on the mixed chelates have been shown to disagree with this possibility.

a). The temperature dependence of the relative shifts in the mixed complexes. Since the redistribution in total spin density of one ligand is very nearly equal to the additional spin density acquired by the other ligand. It is useful to introduce a parameter ξ_i which is a measure of the competitive effectiveness of a given ligand e.g. N,N'-di-p-Cl-phenyl aminotroponeimine relative to the N,N'-diethylaminotropone-imine ligand in the mixed complexes as defined below:

$$\xi_i = \frac{\Delta \nu^i_{Et} - \Delta \nu^i_{p\text{-}Cl\text{-}Ph}}{\frac{1}{2}\left(\Delta \nu^i_{Et} + \Delta \nu^i_{p\text{-}Cl\text{-}Ph}\right)} = \frac{\rho^i_{Et} - \rho^i_{p\text{-}Cl\text{-}Ph}}{\rho^i_{mean}}$$

where Δv^i_{Et} and $\Delta v^i_{p\text{-}Cl\text{-}Ph}$ refer to the contact shifts of the ith proton of the N,N'-diethyl or N,N'-di-p-Cl-phenyl aminotroponeimine ligand in the mixed chelate. (refer to figure 2-3). Results on the mixed chelates showed that the spin density on the N,N'-diethyl-aminotroponeimine ligand has increased while that of N,N'-di-pCl-phenyl substituted one decreased. According to Lin and Orgel's argument, the ξ_i defined above should increase with decreasing temperature as a result of Boltzmann distribution law that the lower level should become more highly populated. However experiments over a range of 120°C showed that the ratios of the spin densities ξ_i on different ligands of the mixed chelates actually decrease somewhat with decreasing temperature, a result which is in contrary to their interpretation.

b). If the crystal field effect did offset the ordering of orbitals due to π bonding effect, it would depend on the structures in the immediate neighbourhood of the nickel atom. Experimental results of mixed chelates with all the groups surrounding the nickel atom are identical but with different substituents at the far away γ-position where a direct electrostatic interaction seem unlikely also indicated substantial change in the relative amount of spin delocalized to the two ligands. Thus the crystal field effect is seen to be of lesser importance than the π bonding effect.

Thus for the aminotroponeimineates the relative ordering of the d-levels is believed to be predominantly determined by the π bonding interaction and to correspond to the configuration in case (B). The experimental results can then be explained by the fact that in tetrahedral complexes, the d-orbitals participating the π bonding are not orthogonal to the σ-bonding orbitals so that a d-orbital of the metal atom oriented for maximum overlap with the π orbital of one ligand will not be so for the other ligand hence two unlike groups will enter into competition with the result that 'stronger d_{π}-bonding group will approach maximum bonding at the expense of the weaker bonding group' thus cause a corresponding change in spin density.

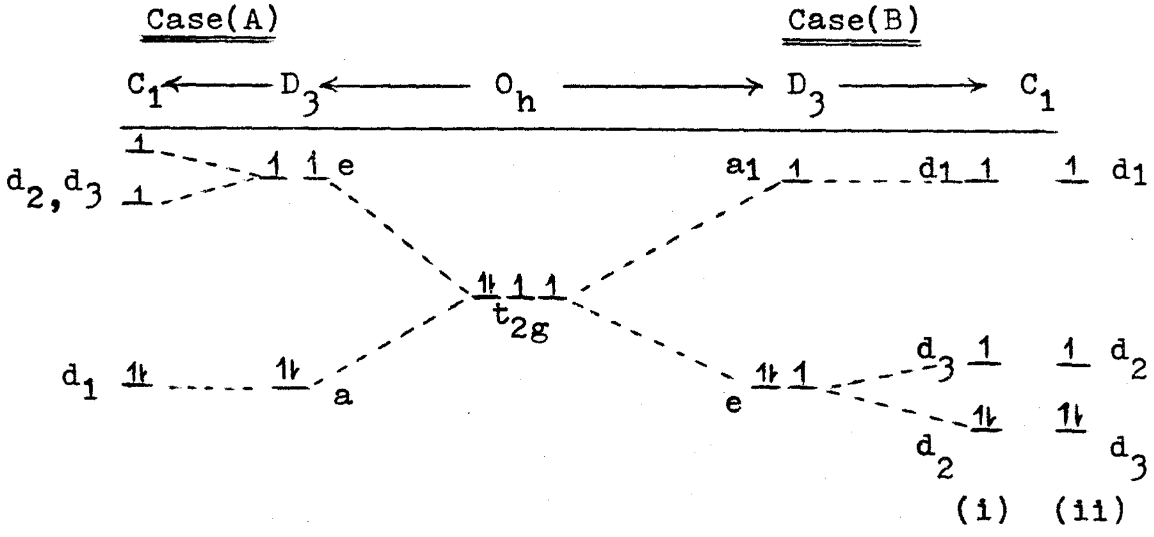
Similar arguments have been applied to octahedral Cr (II) mixed complexes. Experimentally it has been observed that[58,63,64,73]:

a. The isotropic shifts of the complexes $(phen)_3Cr(II)\cdot Cl_2$ and $(4,7\text{-}CH_3\text{-}phen)_3Cr(II)\cdot Cl_2$ which have the D_3 symmetry as shown in figure 2-4, followed the Curie law approximately. The shifts are attributed primarily to contact effect with π type spin density dominant at all positions except at 2,9-positions where some dipolar and σ contributions may be possible.

b. Complexes with unsymmetrical methyl substituted ligands e.g. (4-CH_3-phen)$_3$Cr(II).Cl_2 displayed four equally intense peaks for some ligand protons(e.g. the four nonequivalent CH_3 groups) indicating that the cis and trans isomers are present in statistical amounts.Dipolar contribution is seen to be unimportant since the four 4-CH_3 peaks show the largest spread while the geometrical factors for this position is the smallest in these complexes.

c. Temperature dependent studies indicated that the unsymmetrical chelates did not all follow the Curie law, for example, for the (4-CH_3-phen)$_3$Cr(II).Cl_2 complex, of the four widely separated 7-H peaks, one followed the Curie law approximately, two contact shifts decreased much faster and one decreased much slower with increasing temperature. Similar results were observed for the four 4-CH_3 peaks.

Attempts to explain this anomalous behaviour led to the conclusion that the electronic ground state of these tris Cr(II) complexes is ^3E. In order to understand this, it is necessary to consider first the symmetry properties of the metal d_π orbitals and the ligand π molecular orbitals of the symmetrical ligands and then similar arguments may be applied to the unsymmetrical ligands. The metal d_π orbitals which are designated as t_{2g} in an octahedral field split into e and a_1 orbitals in the trigonal field (D_3). The M.O.'s for a symmetric bidentate ligand will be designated as ψ or χ depending whether they remain unchanged or changed sign under the symmetry operation with respect to reflection in the symmetry plane perpendicular to the plane of the ligand molecule. ψ orbitals can interact with metal e orbitals while χ orbitals may interact with e and a_1 d-orbitals. Based on the coordinate system as shown in figure 2-5, the proper linear combinations of the d_π orbitals and the ψ and/or χ ligand π orbitals which may interact for D_3 symmetry are tabulated in Table 2-2. An unpaired spin in in the a_1 orbital will interact equally with each of the three ligands whereas for the e orbitals, this is not the case. The important question here is to determine in the D_3 symmetry the relative energy of a_1 and e orbitals. Two possible configurations due to a more important trigonal (D_3) distortion followed by a small splitting due to rhombic distortion is shown below



In case (A), the configuration leads to an ^3A ground state in the D_3 point group. For the trans-isomer of the unsymmetrical tris chelates, the symmetry of the molecule is lower than D_3. There will be a small splitting of the e orbitals. In the designated d_2 and d_3 orbitals each contains an unpair -ed electron and simple Curie behaviour for the contact shifts of all the signals e.g. all four 4-CH_3 or 7-H signals of Cr(II)(4-CH_3-phen)$_3$ would be predicted. This is in contrary to the experimental results. In case (B), the configuration leads to the ^3E ground state in the symmetrical tris chelates. The split orbitals at lower symmetry e.g. in the trans isomers of the unsymmetrical tris chelates are also shown. The d_1 orbital will always has one unpaired electron while two split components of e: d_2 and d_3 contain three electrons between them. Two states will then be possible as indicated by (i) and (ii). Since d_2 and d_3 interact differently with the three ligands in the trans isomers, the temperature dependence of the shifts will not follow a simple Curie law since the populations of d_2 and d_3 orbitals vary with temperature.

Assume that:

1. The unpaired electron resides in the ligand highest π bonding (HBO) M.O.: Thus if d_2 is lower than d_3 in energy, then in the limit T→0, only d_3 will contain unpaired electron. Inspection of Table 2-2 shows that ligands B and C

will receive an equal amountsof spin density.On the other hand if $T \rightarrow \infty$, the unpaired spin population of d_2 and d_3 will be equal and ligand A, B and C will receive equal amounts of spin density. The energy scheme therefore predicts that as the temperature is increased from the lower limit,two contact shifts (from ligand B and ligand C) will decrease faster and one slower (from ligand A) than predicted by Curie law. The three trans 4-CH_3 and 7-H shifts should converge with increasing temperature due to equalizing the d_2 and d_3 spin population which is in agreement with observation. For the case that d_2 lies higher than d_3, two contact shifts should decrease slower and one faster with increasing temperature than Curie behaviour which is in contrary to the observations. The fourth 4-CH_3 or 7-H peak arising from the cis isomer is predicted to exhibit simple Curie behaviour in all cases since the e orbital is still degenerate in this isomer.

2. If the unpaired spin resides in the lowest π anti-M.O.: In this case only if d_2 is higher than d_3 can the observation agree with prediction. Since the spin-containing M.O. cannot be specified, it is not possible to determine the relative energy of d_2 and d_3 in the trans isomer of the unsymmetrical tris chelates. However it is shown that only case(B) is capable of accounting for the anomalous temperature dependence of contact shifts no matter whether the spin is in π bonding or π anti-bonding orbitals. Thus the ground state for the

$Cr(II)(o\text{-}phen)_3 \cdot Cl_2$ is determined to be ^3E.

Table 2-1

Linear combinations of d orbitals in O_h and D_3 point groups.

O_h group	orbital symmetry	D_3 group	orbital symmetry
$d_{x^2-y^2}$ d_{z^2}	e_g	$d_{x^2-y^2}$ d_{z^2}	e
d_{xy}	t_{2g}	$1/\sqrt{3}\ (d_{xy} + d_{xz} + d_{yz})$	a_1
d_{xz}		$1/\sqrt{2}\ (d_{xz} + d_{yz})$	e
d_{yz}		$1/\sqrt{6}\ (2d_{xy} - d_{xz} - d_{yz})$	

Table 2-2.

Symmetry orbitals for D_3 point group.

Orbital symmetry	metal $d\pi$ orbitals	ligand π orbitals
e	d_2: $1/\sqrt{2}(d_{xz}-d_{yz})$	$1/\sqrt{6}(2\psi_A+\psi_B+\psi_C)$
	d_3: $1/\sqrt{6}(2d_{xy}-d_{xz}-d_{yz})$	$1/\sqrt{2}(\psi_B-\psi_C)$
a	d_1: $1/\sqrt{3}(d_{xy}+d_{xz}+d_{yz})$	$1/\sqrt{3}(\chi_A+\chi_B+\chi_C)$
e	d_2: $1/\sqrt{2}(d_{xz}-d_{yz})$	$1/\sqrt{2}(\chi_B-\chi_C)$
	d_3: $1/\sqrt{6}(2d_{xy}-d_{xz}-d_{yz})$	$1/\sqrt{6}(2\chi_A-\chi_B-\chi_C)$

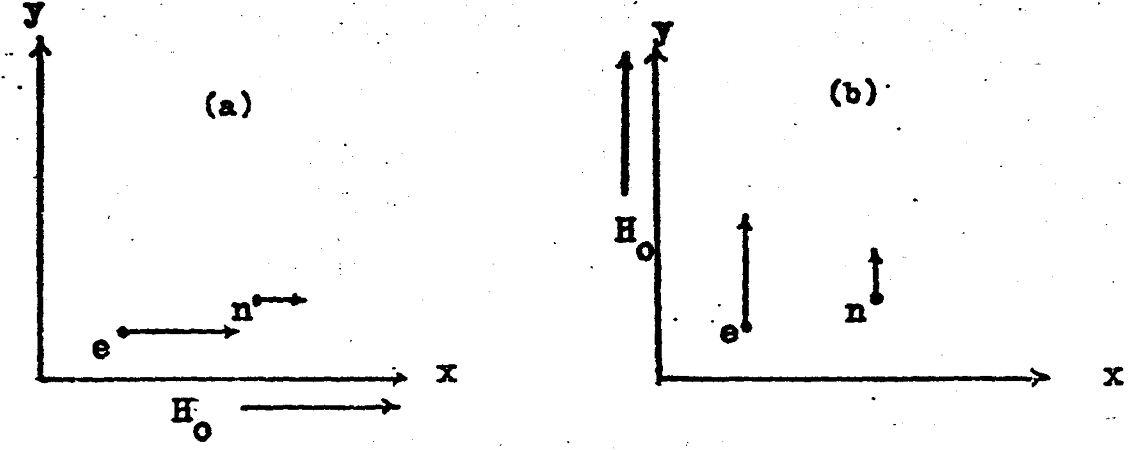


Figure 2-1. Dipolar interactions between an electron spin and a nuclear spin fixed in space.

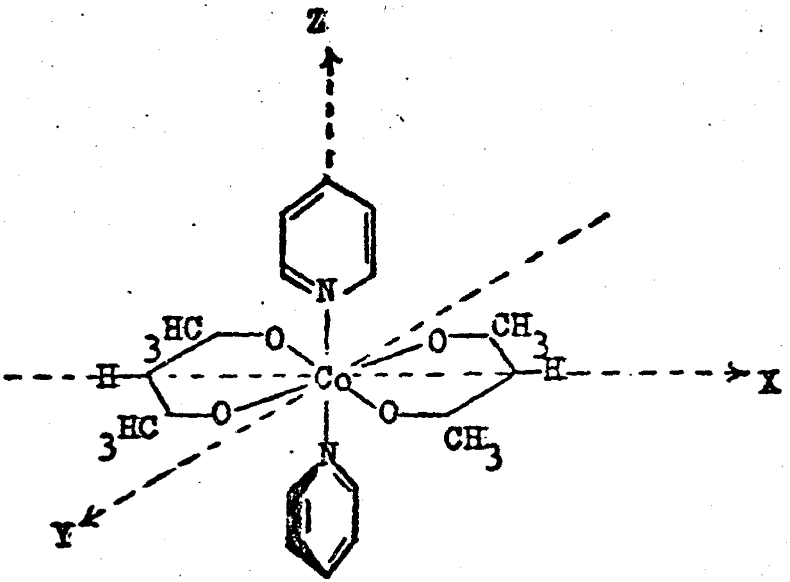
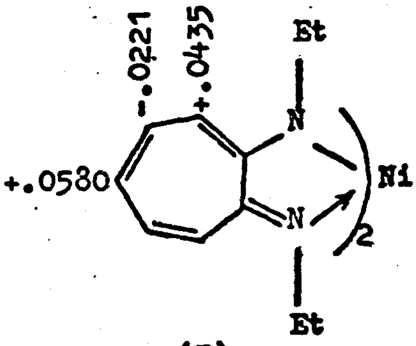
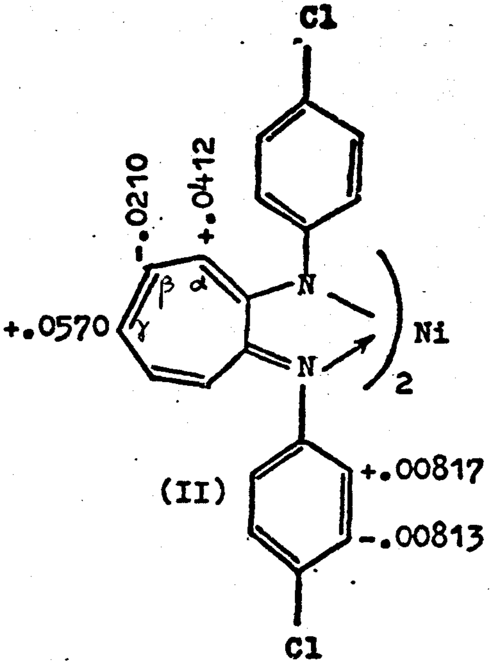


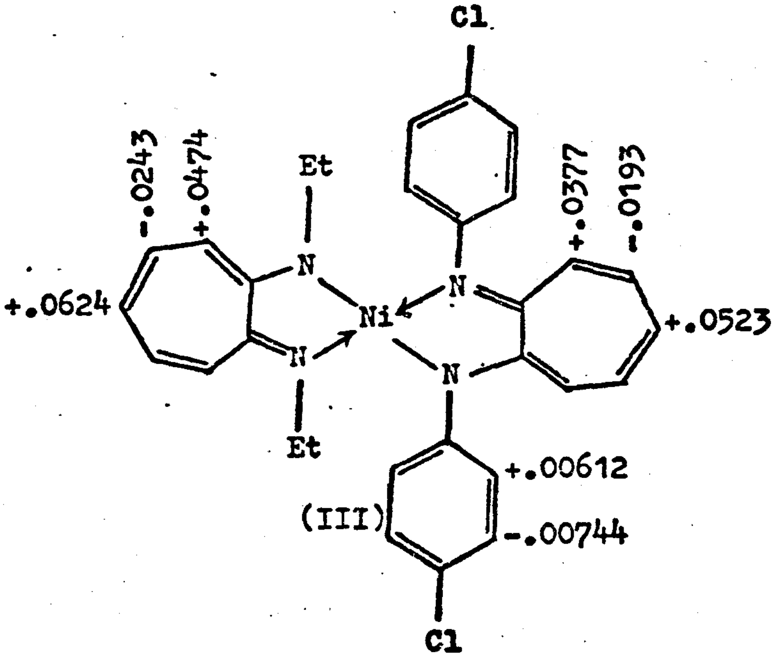
Figure 2-2. Structure of $Co(acac)_2 \cdot 2py$.



(I)



(II)



(III)

Figure 2-3. Spin density distribution in two symmetric (I and II) and their mixed Ni(II)aminotroponeimineates.

(A)

(B)

Figure 2-4. Structures of $(phen)_3Cr(II)$ (A) and $(4,7\text{-}CH_3\text{-}phen)_3Cr(II)$ (B).

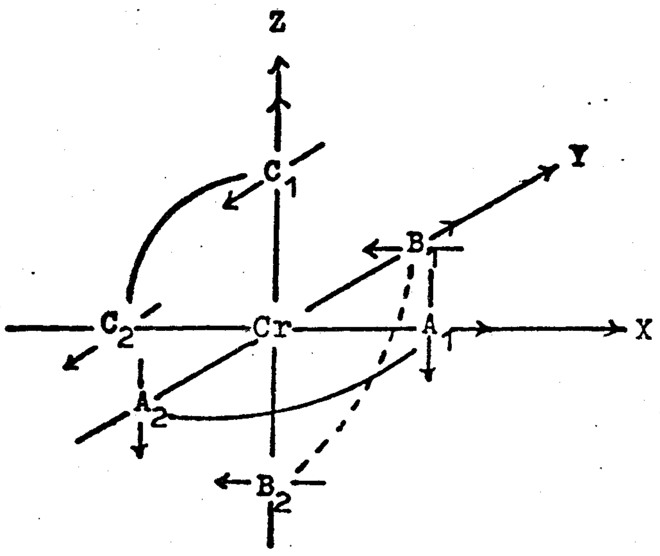
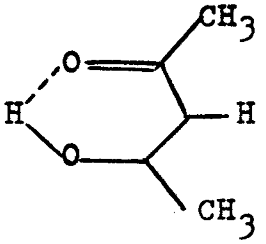


Figure 2-5. Coordinate system of $Cr(II)(phen)_3$.

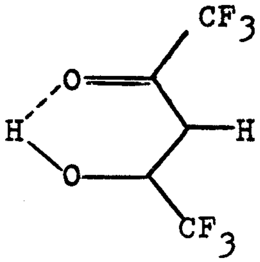
3. Experimental

3-1. Sources and preparation of compounds.

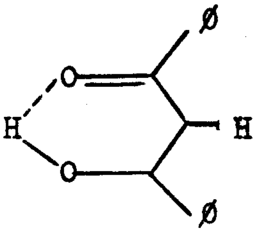
The following compouhds were employed for studies. The structures of some β-diketones and abbreviations are given below:



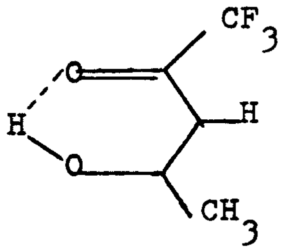
I. Hacac



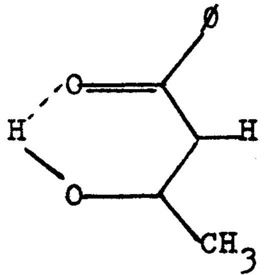
II. Hhfac



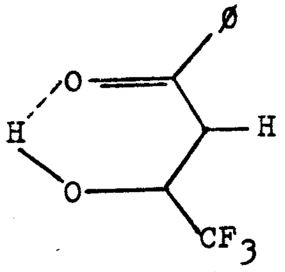
III. Hϕ-ϕ



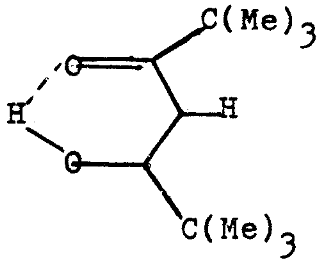
IV. Htfac



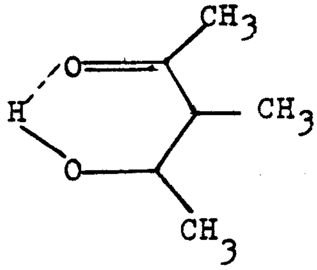
V. Hϕ-ac



VI. Htf-ϕ



VII. $HMe_3C\text{-}CMe_3$



VIII. H-γMe-acac

The following abbreviations for vanadium(III) and cobalt(II) complexes will be used throughout.

$V(acac)_3$: Tris-acetylacetonato vanadium(III)

$V(hfac)_3$: Tris-hexafluoroacetylacetonato vanadium(III)

$V(\phi\text{-}\phi)_3$:	Tris-1,3-diphenyl-1,3-propanedionato vanadium (III).
$V(tfac)_3$:	Tris-1,1,1-trifluoroacetylacetonato vanadium (III).
$V(\phi\text{-}ac)_3$:	Tris-benzoylacetonato vanadium (III).
$V(tf\text{-}\phi)_3$:	Tris-4,4,4-trifluoro-1-phenyl-1,3-propanedionato vanadium (III).
$V(\gamma\text{-}me\text{-}acac)_3$:	Tris-3-methyl-2,4-pentanedionato vanadium (III).
$Co(acac)_2L_2$:	Di-adduct of bis-acetylacetonato cobalt(II).
$Co(\phi\text{-}\phi)_2L_2$:	Di-adduct of bis-1,3-diphenyl-1,3-propanedionato cobalt(II).
$Co(Me_3C\text{-}CMe_3)_2L_2$:	Di-adduct of bis-2,2,6,6-tetramethyl-3,5-heptanedionato cobalt(II).

A). Sources: The ligands i.e. acetylacetone (I), hexafluoroacetylacetone (II), 1,3-diphenyl-1,3-propanedione (III) . 1,1,1-trifluoroacetylacetone (IV), benzoylacetone (V), 4,4,4-trifluoro-1-phenyl-1,3-propanedione (VI) and 2,2,6,6-tetramethyl-3,5-heptanedione (VII) were obtained from Eastman Kodak Co. and 3-methyl-2,4-pentanedione (VIII) from Koch Light Laboratory. The inorganic compounds vanadium (III) trichloride, cobalt(II) chloride and organometallic compounds $V(acac)_3$ and cobalt(II) acetylacetonate were obtained from the Research Organic/Inorganic Chemical Co., Deuterated compounds such as dimethylsulphoxide-d_6 , pyridine-d_5 and acetonitrile-d_3 were obtained from Merck Sharp & Dohme.

B). Preparation of compounds:

Deuterated acetylacetone: Deuterated acetylacetone was prepared by adding acetylacetone to an excess of D_2O followed by a small amount of sodium carbonate. The mixture was refluxed for 24 hours, cooled and extracted with anhydrous ether. This process was repeated four times and the mixture then distilled. The fraction distilling over at 129°C was collected. Purity was established by the absence of proton NMR spectra. It was further characterized by the isotropic shifts of mixed chelates with tris-hexafluoroacetylacetonato vanadium(III) and tris-1,3-diphenyl-1,3-propanedionato vanadium(III).

Tris-β-diketonato vanadium(III): All the tris vanadium(III) complexes were prepared by a method analogous to that described by Morris et al[54].

CCl_4 was heated with the passage of N_2 gas through a side-tube for about 5 min. to get rid of the dissolved oxygen. The respective ligand and vanadium trichloride were added quickly in a N_2 atmosphere and the mixture refluxed for about 2 1/2 hours with stirring. N_2 gas was passed slowly and continuously to prevant air oxidation of the compound. The resulting solution was filtered in a nitrogen atmosphere while hot and the filtrate allowed to cool after which the solvent was removed by vacuum distillation. The resulting brown solid was purified by either recrystallization from CCl_4 or by vacuum sublimation. The former method was employed if the ligand in its pure form is a liquid whereas the alternative is used if it is a solid. The purity was checked by the NMR proton and fluorine spectra. The complexes so prepared were observed to have the following relative stability to air oxidation.

$V(hfac)_3$
$V(tfac)_3 > V(acac)_3 > V(\phi\text{-ac})_3 > V(\phi\text{-}\phi)_3 > V(\gamma\text{-Me-acac})_3$
$V(tf\text{-}\phi)_3$

Cobalt(II)β-diketonates: The Co(II) complexes of hexafluoroacetylacetone, 1,3-diphenyl-1,3-propanedione and 2,2,6,6-tetramethyl-3,5-heptanedione were prepared in the following way.

0.02 moles of appropriate β-diketone ligand were dissolved in a small amount of methanol, added with about 30 ml of distilled water with stirring. The mixture was heated gently and 6N ammonia solution added until the solution showed slightly basic to litmus paper. Another solution was prepared by dissolving 0.1 mole $CoCl_2 \cdot 6H_2O$ in about 30 ml of distilled water. The second solution was added to the first with stirring. If no precipitate formed, more ammonia solution was added dropwise until a precipitate did appear, then 5 drops in excess added. The precipitate was collected and washed with water and then with CCl_4 & dried under vacuum.

Tris-pyrazolylborate cobalt(II): The compound was prepared by Dr. S. Trofimenko in a manner described previously[62,76].

3-2. Measurement of NMR isotropic shifts in solution.

Tris β-diketonato vanadium(III) system: A sample of the complex was dissolved in $CDCl_3$ to give a solution of about 0.1 M and proton and ^{19}F NMR isotropic shifts of each of the pure chelates were measured. The shifts are independent of concentration. Shifts of the mixed chelates were measured by adding the alternative ligands to the original complexes. The resonances arising from the original chelates gradually disappeared and new lines appeared . the intensities increasing with added ligand concentration. This result must be attributed to ligand exchange. In the system as V(III)/acac/tfac/hfac, shifts of all the possible different mixed chelates can be obtained in this way.i.e.

$$\underset{(1)}{V(acac)_3} \xrightleftharpoons[Hacac]{Htfac} \underset{(1)}{V(acac)_2tfac} \xrightleftharpoons[Hacac]{Htfac} \underset{(3)}{V(tfac)_2acac} \xrightleftharpoons[Hacac]{Htfac} \underset{(2)}{V(tfac)_3}$$

$$V(acac)_3 \xrightleftharpoons[Hacac]{Hhfac} \underset{(1)}{V(acac)_3hfac} \xrightleftharpoons[Hacac]{Hhfac} \underset{(1)}{V(hfac)_2acac} \xrightleftharpoons[Hacac]{Hhfac} \underset{(1)}{V(hfac)_3}$$

$$V(hfac)_3 \xrightleftharpoons[Hhfac]{Htfac} \underset{(1)}{V(hfac)_2tfac} \xrightleftharpoons[Hhfac]{Htfac} \underset{(3)}{V(tfac)_2hfac} \xrightleftharpoons[Hhfac]{Htfac} V(tfac)_3$$

$$\mathrm{V(acac)_3} \underset{\mathrm{Hacac}}{\overset{\mathrm{Hhfac}}{\rightleftharpoons}} \mathrm{V(acac)_2hfac} \underset{\mathrm{Hacac}}{\overset{\mathrm{Htfac}}{\rightleftharpoons}} \underset{(2)}{\mathrm{V(acac)(hfac)(tfac)}}$$

The number in the bracket indicates the number of isomers. A total of sixteen isomers are possible with 32 CH_3 , 32 CF_3 and 36 CH resonances. For all these exchange reactions, equilibrium appeared to have been attained in the time between mixing the solutions and examining in the NMR spectrometer. There is no significant additional broadening of the NMR lines such as would be anticipated if exchange rates were comparable to the reciprocal of the chemical shift difference. Shifts of the pure and mixed chelates of other systems were obtained in a similar manner.

^1H spectra were obtained on a HA-100 instrument at 37°C using TMS as internal reference. ^{19}F spectra were obtained similarly with $CFCl_3$ internal reference. ^{19}F spectra were obtained at 94.1 Mc/s and the shifts converted to 100 Mc/s for comparison with the proton shifts. The temperature dependence of the shifts were measured using a DP-60 spectrometer. All NMR samples were carefully prepared in a dry nitrogen atmosphere.

Di-adducts of bis β-diketonato Co(II) system: A solution of the di-adducts of Co(II) β-diketonate was prepared by adding the coordinating solvent such as pyridine-d_5, dimethylsulphoxide-d_6 and acetonitrile-d_3 to the corresponding complex in the mole ratio of 320 to 1. The coordinating solvent was present in excess to ensure that the complex was present in monomeric form with two coordinating solvent molecules occupied the trans positions of a distorted octahedron [39,61,70]. CCl_4 was added to give a final concentration of 0.005 M of the di-adducts complex.

The isotropic shifts of the pure and mixed chelates were obtained in the similar manner to that described for V(III) complexes. ^1H spectra were obtained on a HA-100 instrument at 37°C with TMS as internal reference. ^{19}F spectra were obtained on a DP-60 spectrometer operated at 56.4 Mc/s. $CFCl_3$ was used as internal reference. The shifts were converted to 60 Mc/s.

Second sphere coordination: N. M.R. samples for this study were made up by preparing 7 ml of 0.3 M tris-pyrazolylborate Co(II) in CCl_4, then 0.3 ml of aniline was added, mixed thoroughly. Each N.M.R. tube was filled with 0.73 ml of the solution followed by the appropriate solvent in increasing amounts. Shifts of the aniline protons were measured in all cases. Proton NMR spectra of this system were measured on a HA-1000 instrument. Shifts were obtained at 37°C with TMS as internal reference.

3-3. Analysis and assignment of the spectra.

Assignment of the resonances arising from the symmetric vanadium chelates presents no difficulty. All complexes lines were shifted substantially from those of the free ligands and were significantly broadened . As an example, consider the V(III)/acac/tfac/hfac system, assignment of lines arising from the symmetric chelates are unambiguous. The CH_3 resonance is six times as intense as the CH resonance. In the unsymmetric chelates e.g. $V(tfac)_3$ which may exist in cis and trans forms, it was possible to assign which signals arise from cis and which from trans isomers from the relative intensity of the resonances. The cis-isomer has all the CH_3 ,CH, or CF_3 groups equivalent and only one resonance for each of the distinct nuclei. In the trans-isomer, all the CH_3 groups , for example are nonequivalent. The resonances therefore occur in groups of three lines of equal intensity. Assignment of individual peak is based on a model which was employed for the analyses of the experimental data and will be described in the followibg chapter. Assignment of signals to the different mixed chelates were achieved in the following way: Thus in a typical experiment in which Hhfac was added incrementally to $V(acac)_3$, the two new CH_3 resonances which appeared initially are assigned to $V(acac)_2(hfac)$ and the third which appeared later to $V(acac)(hfac)_2$. The assignments are then checked by adding Hacac to $V(hfac)_3$. CH_3 and CH assignments for compounds involving tfac were obtained by using deuterated acetylacetone. These experiments enabled the resonances of the tfac ligands to be distinguished from those of the acac ligands. All the compounds except V(acac)(tfac)(hfac) can be identified by experiments involving appropriate pairs of the binary mixtures. Lines from V(acac)(tfac)(hfac) were identified by obtaining a variety of spectra from ternary mixtures and eliminating lines previously assigned to other mixed chelates. The ^1H spectra obtained by adding increasing amounts of hexafluoroacetylacetone to $V(acac)_3$ is shown in figure 3-1. Figure 3-2 shows a spectrum and assignments of $V(III)(acac)_3$ and 1,3-diphenyl-1,3-propanedione mixture. In figure 3-3, more complicated ^1H spectra are shown to illustrate the assignments of the resonances arising from the mixed chelates. Figure 3-3a shows the numbers of lines obtained by adding one small drop of 1,1,1-trifluoroacetylacetone to $V(acac)_3$ the lines are correctly assigned to arise from $V(acac)_3$ and $V(acac)_2(tfac)$. Figure 3-3b is a spectrum obtained by adding more 1,1,1-trifluoroacetylacetone to $V(acac)_3$. Additional lines indicated as a, b, c, ... m,n and o are then assigned to arise from the three isomers of $V(acac)(tfac)_2$. (compounds IV , V and VI of figure 4-1 with $X=CH_3$, $Y=CF_3$). The signals designated as e, i, and j not obvious in this spectrum are clearly shown up in the spectrum obtained by adding a small drop of acetylacetone to $V(tfac)_3$ as shown in figure 3-4. In figure 3-5 the ^{19}F NMR spectra of lines arise from the non-equivalent CF_3 groups for mixture of $V(tf\text{-}\emptyset)_3$ and 1,3-diphenyl-1,3-propanedione and mixture of $V(\emptyset\text{-}\emptyset)_3$

and 1,1,1-trifluoroacetylacetone are shown. Assignments of signals to the mixed chelates of Co(II) system were similarly obtained. A ^1H spectrum with correct assignments of the mixture of Co(acac)$_2$.2py and 1,3-diphenyl-1,3-propanedione thus obtained is shown in figure 3-6. Figure 3-7 is the ^1H spectrum of a mixture of tris-pyrazolylborate Co(II) and aniline in CCl_4. Only the resonance arise from the phenyl ring protons are shown in this figure.

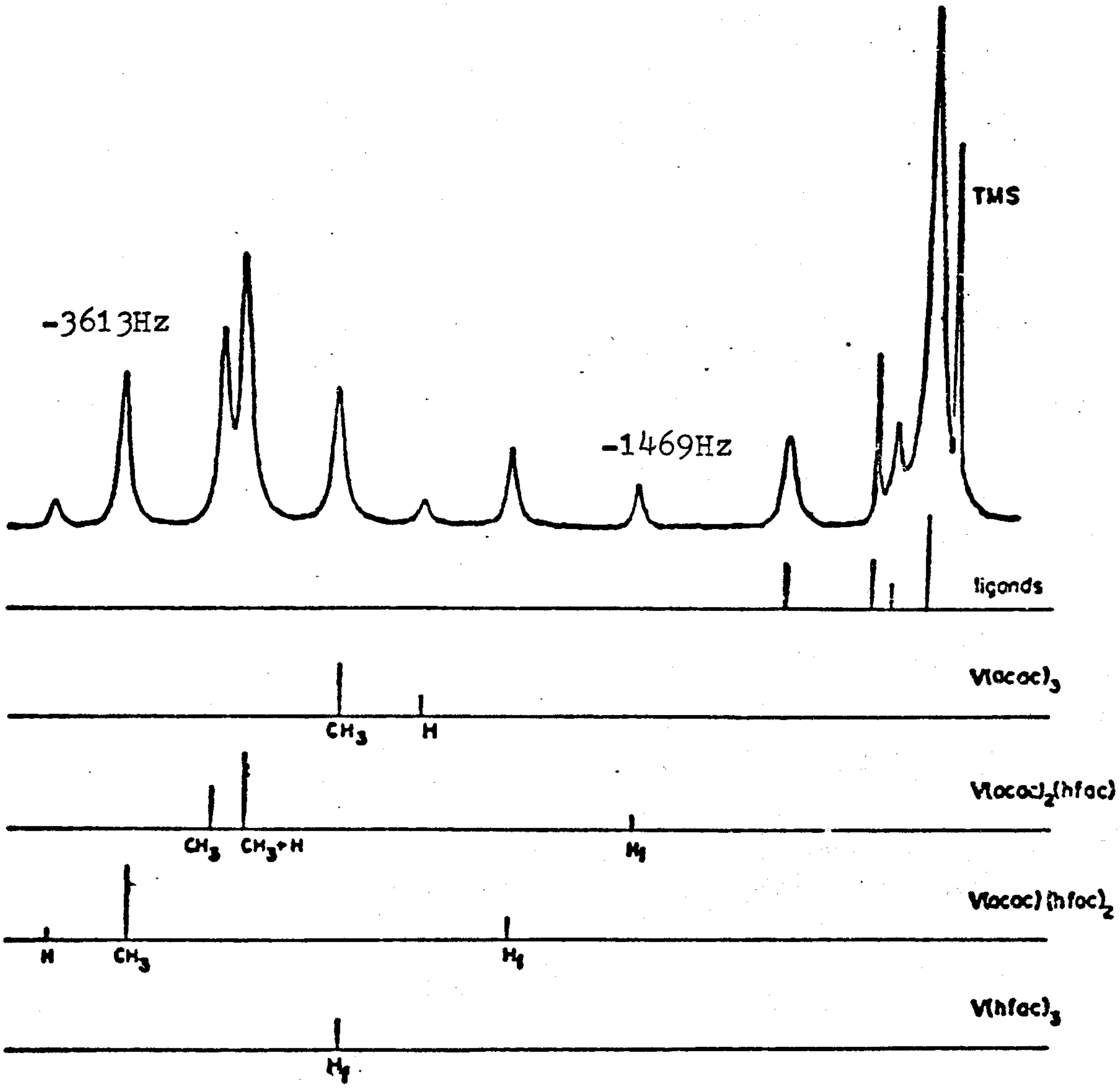


Figure 3-1. ^{1}H spectrum and assignments of a mixture of $V(acac)_3$ and hexafluoroacetylacetone.

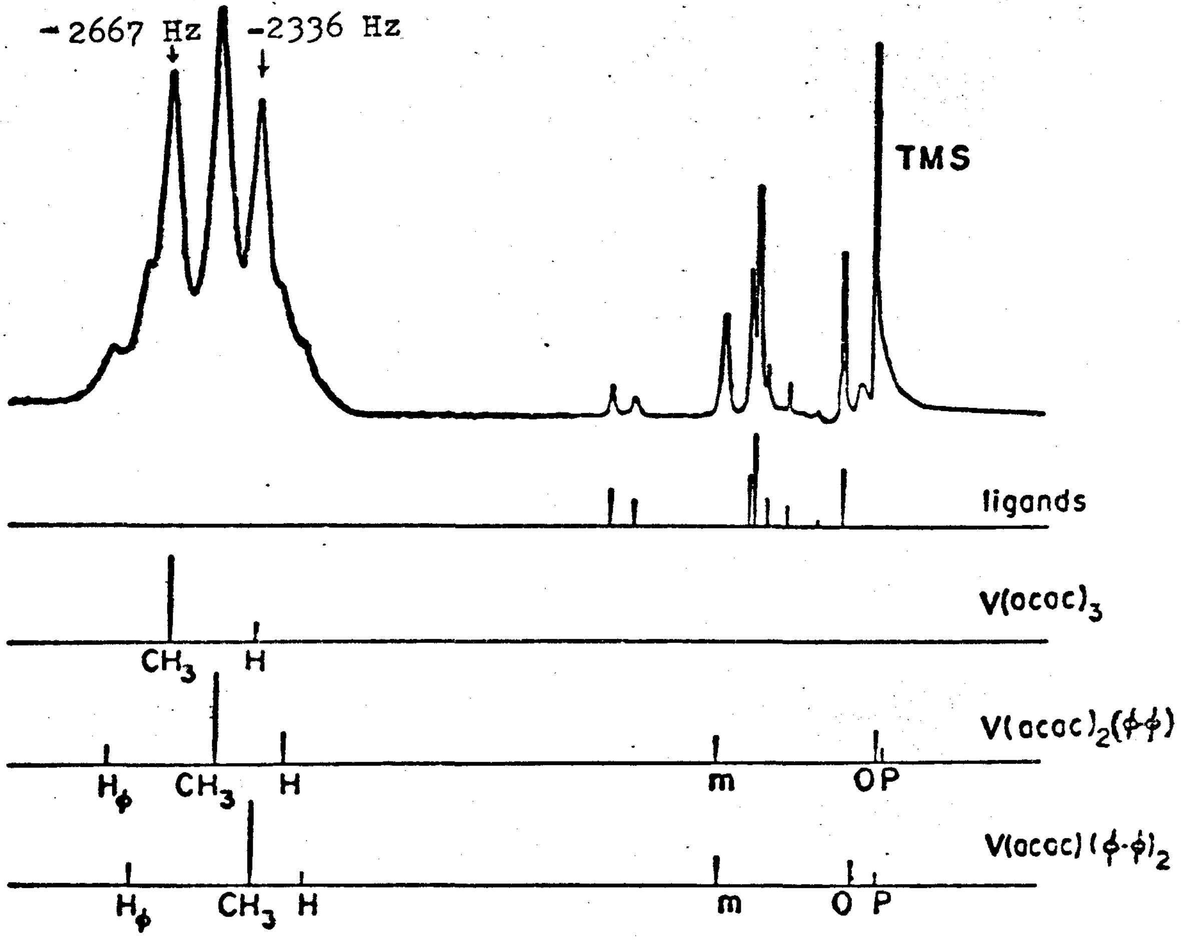


Figure 3-2.

^{1}H spectrum and assignments of a mixture of V(acac)$_3$ and 1,3-diphenyl-1,3-propanedione.

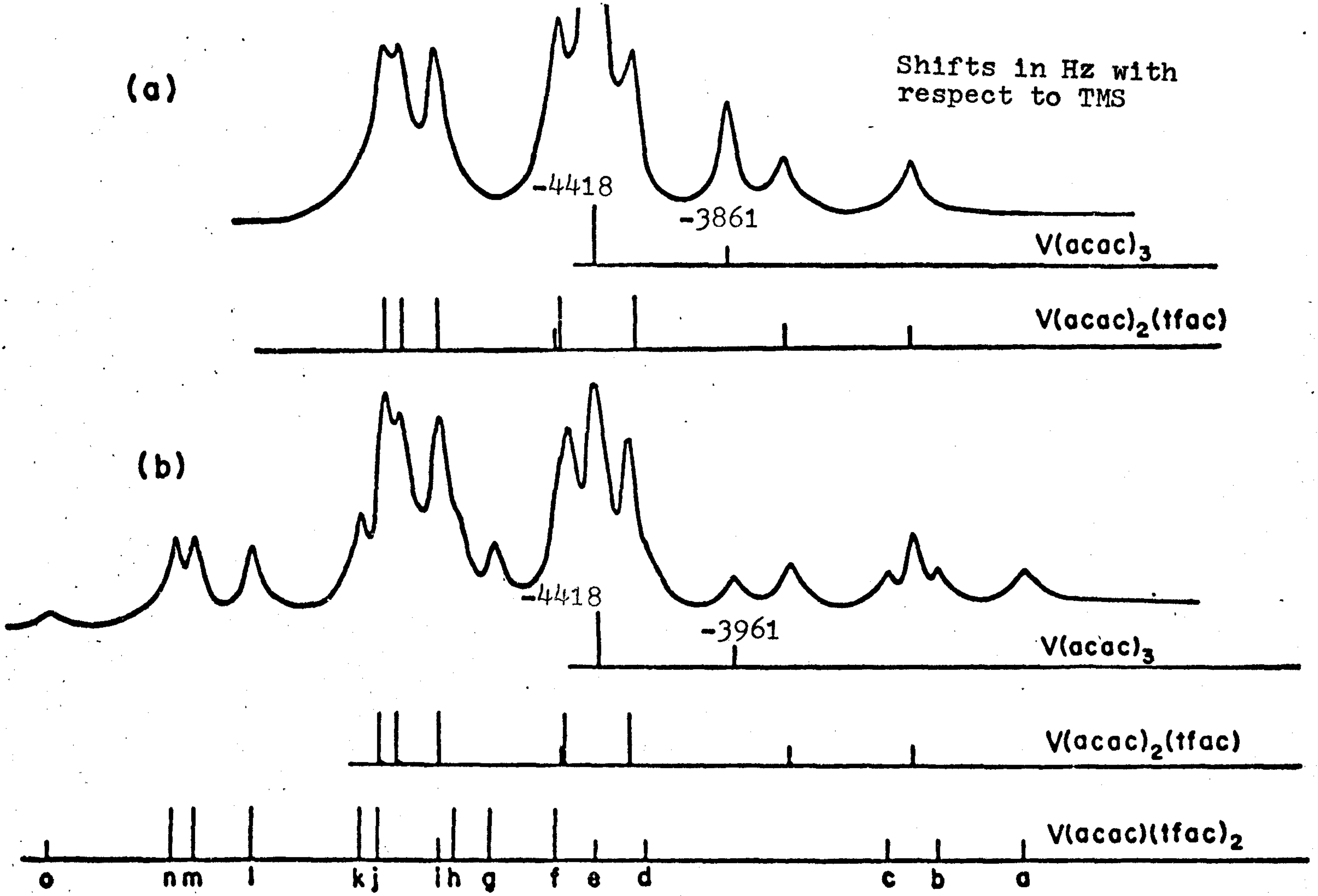


Figure 3-3. ^{1}H spectra of mixtures of V(acac)$_3$ and H-tfac.

(a), V(acac)$_3$ and 1 drop of H-tfac; (b), V(acac)$_3$ and more H-tfac.

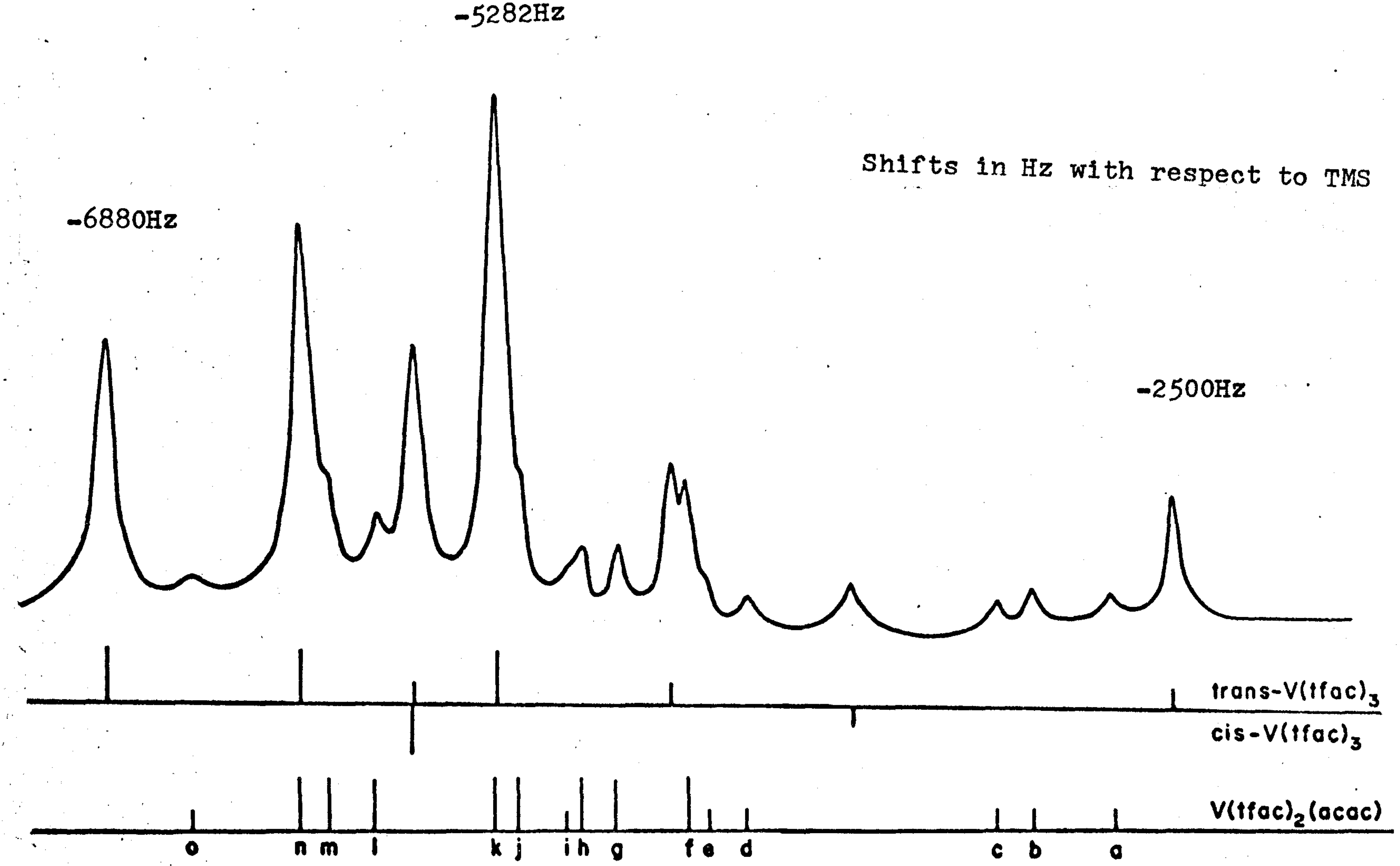


Figure 3-4. ^{1}H spectrum of a mixture of V(tfac)$_3$ and acetylacetone.

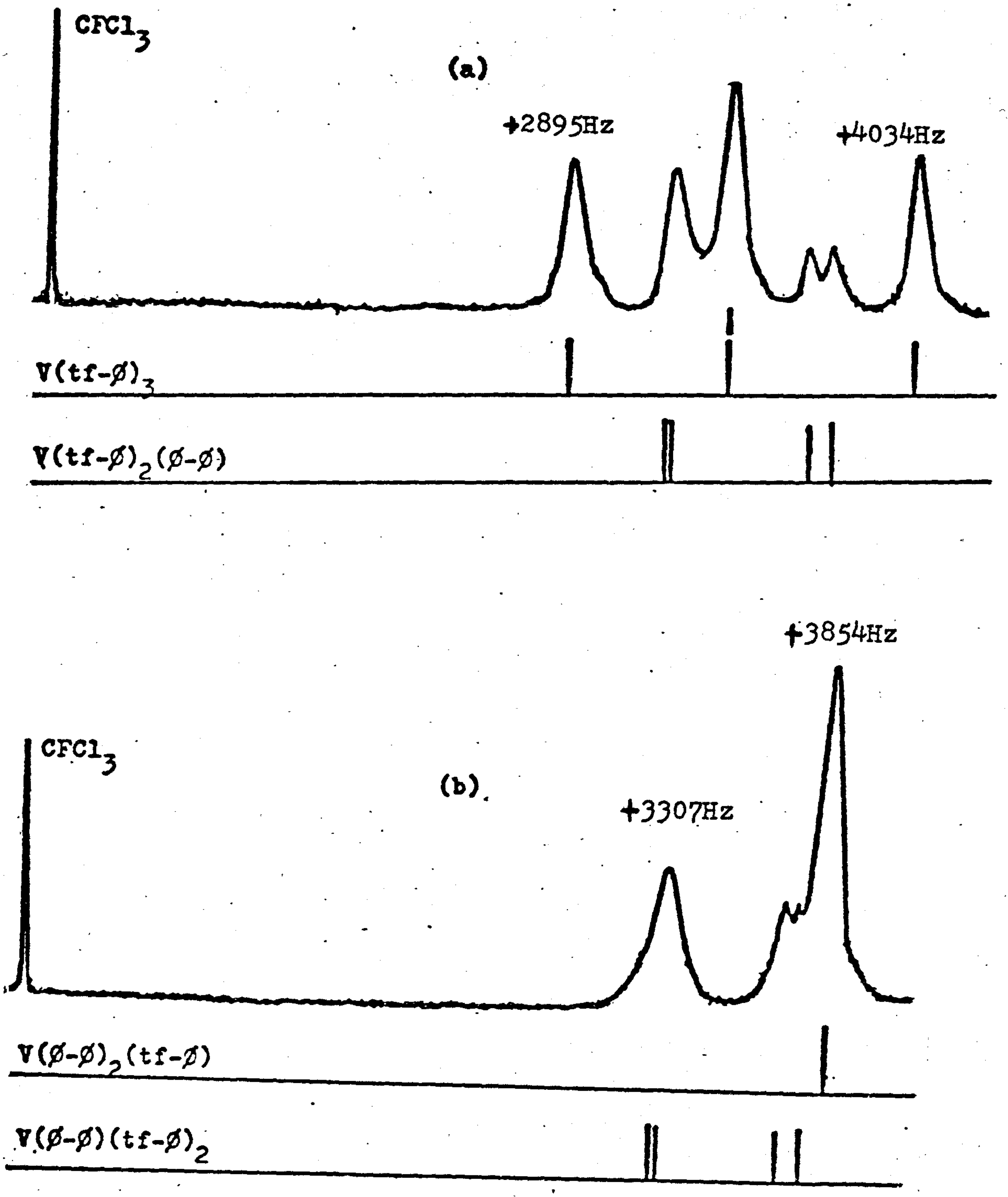


Fig.3-5. ^{19}F NMR spectra of mixtures of (a), V(tf-Ø)$_3$ and HØ-Ø and (b), V(Ø-Ø)$_3$ and Htf-Ø. Solvent CDCl$_3$.

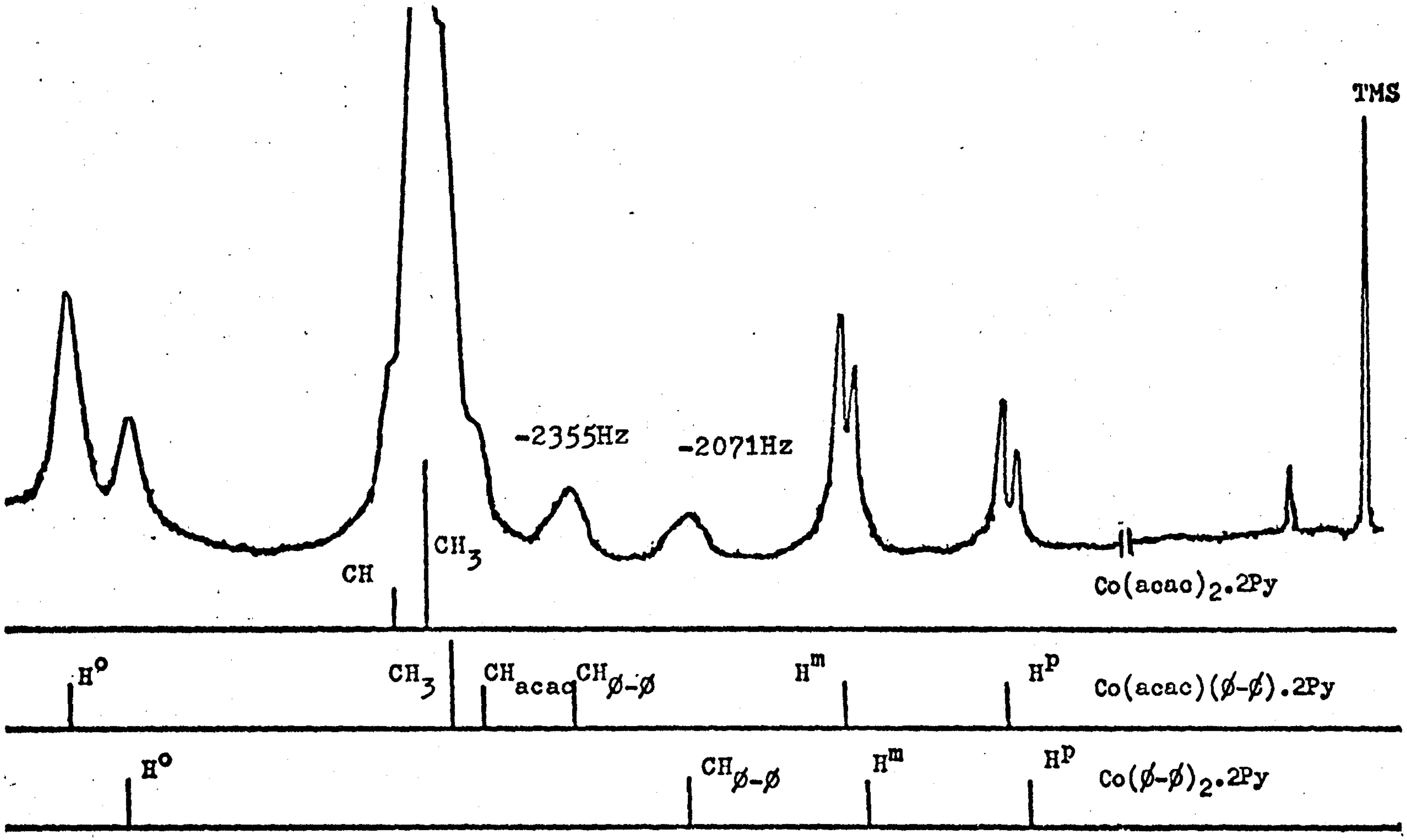


Figure 3-6. ^{1}H NMR spectrum of mixture Co(acac)$_2$, pyridine-d$_6$ and 1,3-Diphenyl-1,3-propanedione in CCl$_4$.

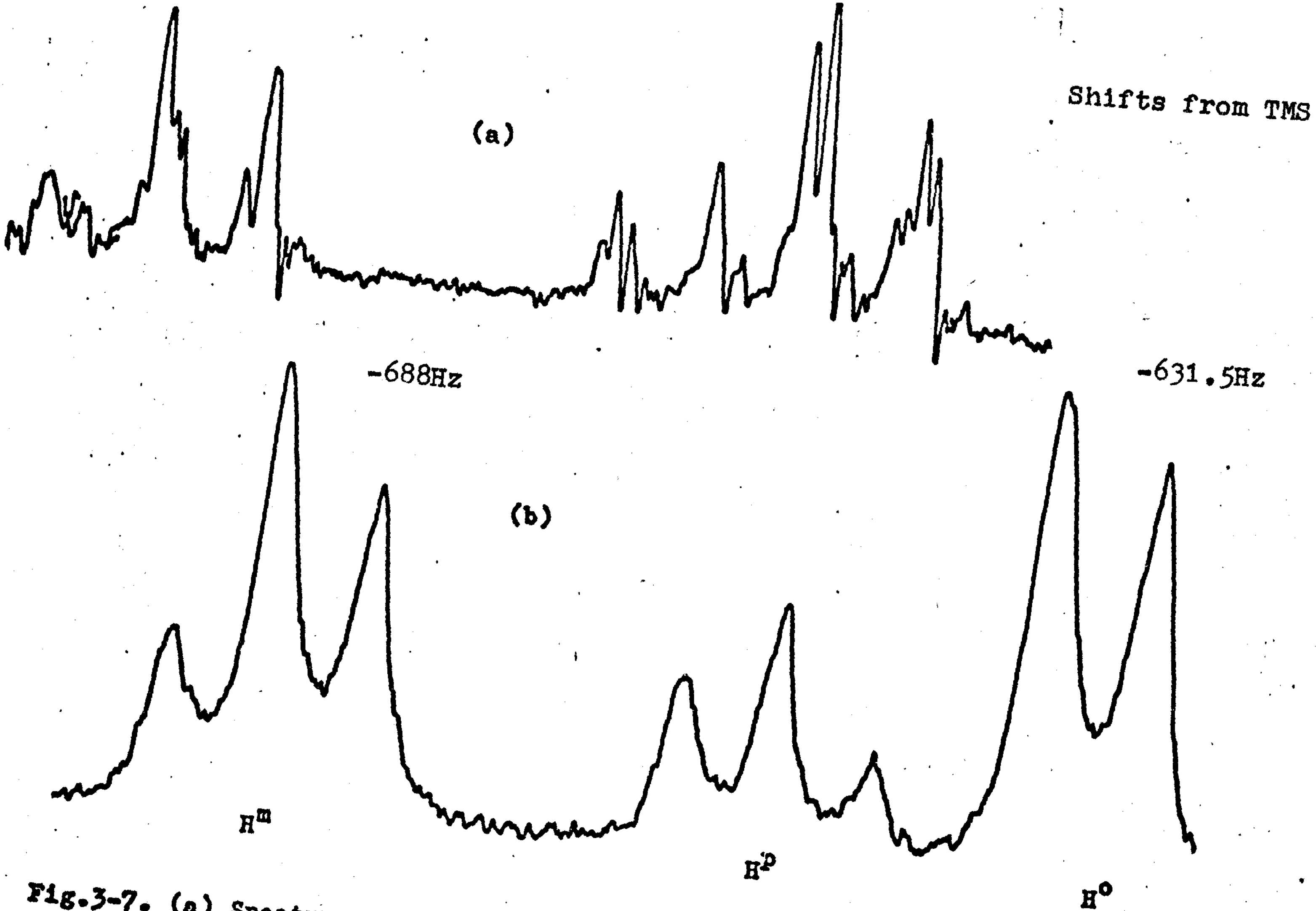


Fig.3-7. (a) Spectrum of aniline in CCl_4 .
(b) Spectrum of mixture of Co(II) tris-pyrazolylborate and aniline.

4. Tris-β-Diketonato Vanadium (III) System.

Preliminary.

The nature of bonding in transition metal complexes has been an extensive field of investigation. A subsection of this field deals with the effect of changes in the structure of one ligand on the bonding of the other ligands. The so-called "trans effect" particularly as it applies to square planer complexes [55] has received most attention . Examples of similar effects in octahedral complexes [28,29] have been less thoroughly studied. In any case, a selective transmission of electronic effects through the central metal atom is involved. There is also a common finding in the studies of mechanisms of homogeneous catalysis and of ligand exchange reactions that rather small changes in the structure of ligands not directly involved in the reaction can considerably change the reaction rates. Attempts to rationalize the results in terms of the concept of electron-withdrawing and donating substituents and of inductive and resonance effects made popular by organic chemists have in many cases proved unsatisfactory. It is therefore desirable to investigate the general problem of how changes in the structure of one ligand affect bonding to other ligands. We have therefore undertaken some studies aimed at elucidating the details of transmission of electronic effects in metal complexes using NMR as a probe.Tris acetylacetonato vanadium(III) is regarded as the parent compound of a series of tris β-diketonato V(III)complexes which are six coordinated compounds with basically octahedral geometry. The NMR spectrum of tris acetylacetonato vanadium(III) has been reported and consists of two lines.[20,45] The relative intensity of the lines distinguishes the CH_3 from the CH resonance. Both signals showed large low field shifts and are well separated from those of an analogous diamagnetic compound or free ligand. The shifts have been attributed to π contact interaction [20,45,51,74] due to admixture of metal d_π and ligand π orbitals leading to delocalization of unpaired electron density in the ligand π system. The basic experiment consists of measuring the change in the isotropic shift of a given proton which occurs when there is a change of substituent on the other ligand(s). The substituent changes observed are large (the total spread is often several thousand Hz at 100 MHz for a given resonance in a series of substituted complexes) so that experimentally the method is quite sensitive. The ab initio calculation of isotropic shifts for transition metal complexes is however fraught with a number of hazards. We have therefore preferred to adopt a more empirical approach to the analysis of the results . The parameters obtained from this analysis reflect substituent effects transmitted across the metal atom. A rather large number of substituent parameters are required in this analysis. A convincing empirical analysis therefore demands a large amount of data. We have attempted to justify our method of analysis by presenting an essentially complete data set for one system where complete analysis of the spectra is possible and have then applied the method to other substituents for which we have less data.

4-1. Application to V(III)/acac/tfac/hfac system.

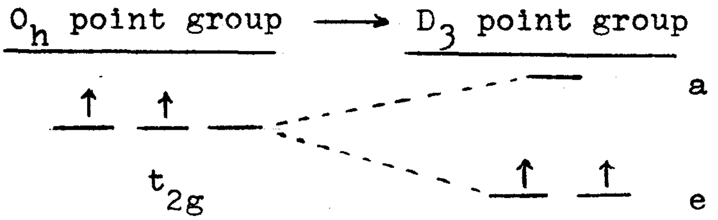
Results: NMR spectra of pure and mixed V(III) complexes were obtained by the method described in the experimental chapter. Consider first the complexes which can be obtained from the systematic substitution of CF_3 groups for CH_3 groups in the compound $V(acac)_3$. We use the abbreviations Hacac = acetylacetone, Htfac = trifluoroacetylacetone and Hhfac = hexafluoroacetylacetone. A total of 16 isomers were obtained which give rise to 32 chemically distinct CH_3 resonances, 32 CF_3 resonances and 36 CH resonances as tabulated in Table 4-1. The structures of all the 16 isomers for the general case with two different substituents X and Y are shown in figure 4-1, which provides the key to the numbering system adopted to present the data. Table 4-2 presents the observed CH_3 isotropic shifts for the system in which $X=CH_3$ and $Y=CF_3$. All 32 CH_3 resonances have been identified and assigned. The isotropic shifts varied from -4054 to -6660 Hz at 100 MHz and 37°C. Table 4-3 gave similar data for the CF_3 isotropic shifts. Again all 32 possible resonances have been observed. The range in this case is from -3410 Hz to -5724 Hz at 100 MHz and 37°C . 35 of the possible 36 CH resonances are reported in Table 4-4. The missing line belongs to one of the isomers of V(acac)(tfac)(hfac) and is in all probability overlapped by stronger CH_3 resonances present in the complex mixtures used. The spread of the shifts is in this case larger ranging from -1330 to -5980 Hz. Thus overall 99 of the possible 100 pieces of data have been obtained. The problem of assignment of lines has been discussed in the experimental chapter.

Temperature dependence studies of the shifts have been carried out for some of the complexes. The results showed a linear relationship in the plot of $\Delta\nu$ versus 1/T. Figure 4-2 shows some of these plots . The nonzero intercepts can arise from a number of sources as discussed by Drago [72].

<u>Analysis of the data:</u> Examination of the experimental results contained in Table 4-2 to 4-4 showed that there are clearly large substituent effects of the type defined in the preliminary discussion, but that there is no simple pattern to the data. The most obvious qualitative feature is that increasing the number of CF_3 substituents

increases the CH_3 shifts whereas increasing the number of CH_3 substituents decreases the CF_3 shifts. The CH shifts generally follow the trend of the CH_3 or CF_3 groups on the same ligand but the changes are proportionately greater. There are however several exceptions and numerous irregularities in this trend. The model adopted for analysing the results is based on the following assumptions:

A. The ground state of all these V(III) β-diketonates are orbitally nondegenerate and arises from e^2 configuration in D_3 symmetry as shown below:



B. The isotropic shifts observed are attributed to contact rather than dipolar interactions. Evidence in favour of these assumptions comes from :

1. The rather closely Curie law dependence of the magnetic susceptibility of all V(III) distorted octahedral complexes reported in the literature. Van Vleck [2] first pointed out if the ground state is orbitally degenerate , considerable deviation from Curie law is to be anticipated. Thus at room temperature, Vanadium alum [25] with a magnetic moment of 2.80 B.M. , very close to spin only value was reported to depart from Curie law only at very low temperature. Detailed analysis of the data fits the theory with the

inclusion of spin-orbit coupling very well and leaves little doubt that the ground state[21] is $^3A_2$ with a splitting of 2000 cm^{-1} due to the trigonal splitting. V(acac)$_3$ has also been examined over the temperature range[25] 80 to 300°K . It obeys the Curie law very well with μ=2.80 B.M. and a Weiss constant θ of only 2°C. In fact the trigonal splitting of many V(III) complexes is very similar and the ground state of V(acac)$_3$ is clearly orbitally non-degenerate.

2. The linear relationship of the NMR isotropic shifts versus 1/T as shown in figure 4-2, which parallels that of magnetic susceptibility. It is to be noted that the slopes for all resonances are within experimental error the same. This is not expected for an orbitally degenerate ground state arising from an a_1e configuration. The latter situation has been discussed by LaMar and Van Hecke[64,73] for the case of the Cr(II)(phen)$_3$ system as described in chapter two. For an orbitally non-degenerate state the magnetic anisotropy is expected to be small and dipolar contribution to the isotropic shifts is relatively unimportant. It does not seem feasible that there has been any change in the nature of the ground state in the mixed chelates relative to the symmetric chelates, since in each case the shifts vary linearly with 1/T. It is apparent that the behaviour of the mixed chelates parallels that of V(acac)$_3$.

3. Evidence in favour of contact interaction also comes from other sources:

(i). The observation of the proton isotropic shifts of the phenyl groups in $V(\phi-\phi)_3$ complex at 100 MHz and 37°C indicates that the shifts of the ortho (+740 Hz) , meta (-162 Hz) and para (+735 Hz) protons cannot be accounted for by the dipolar contribution alone as required by the geometrical factors (refer to equation 2-7), where $\phi-\phi$ denotes the anion of the 1,3-diphenyl-1,3-propanedione.

(ii). The proton NMR spectrum of Vanadium (III) tris complex of γ-methylacetylacetone (structure VIII, chapter 3) has been reported by Forman, Murrell and Orgel [20] in 1959. They observed that the shift of γ-CH_3 resonance was opposite in sign to that of the CH shift in $V(acac)_3$ and this was interpreted as evidence for π spin delocalization. On the basis of the temperature dependence of the isotropic shifts of the mixed complexes described above it would appear that the mechanism involved does not change on passing from symmetric to unsymmetric or mixed chelates and hence that the evidence in favour of π delocalization in symmetric chelates also implied π delocalization in the unsymmetric or mixed chelates. However, more direct evidence seems desirable to justify this assumption. Mixed chelates with γ-methylacetylacetone provide this evidence. For π delocalization in an aromatic system McConnell showed that [10,15]

$$a_x = Q_x \rho^{\pi}_{c-x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4\text{-}1)$$

Theory predicts that Q_x will be negative for a hydrogen atom attached to the aromatic carbon and positive for a methyl group so attached, hence the change in sign of the CH and C-CH_3 contact shifts. If Q_x were a true constant in both cases, we would expect the C-CH_3 and CH shifts to be opposite in sign and proportional to each other in magnitude for all mixed complexes provided only contact shifts were involved. Unfortunately, it has been shown that Q_{CH_3} although always positive in sign, can vary in magnitude from compound to compound. Thus if there is π delocalization it is to be expected that the signs of the CH and C-CH_3 shifts will always be opposite and that the magnitudes will still be roughly proportional. Experimentally this is found to be true. Table 4-5 presents the shifts of γ-CH_3 of V(γ-Meacac)$_3$ and a number of mixed complexes. A plot of the observed γ-CH versus γ-CH_3 shifts of the corresponding complexes is shown in figure 4-3. A linear relationship is apparent. The deviation from strict linearity could result either from variations in Q_{CH_3} or from contribution to the shifts from sources other than π delocalization or a combination of both effects. In any event, it appears that the π contact interaction is predominant as we argued.

C. The dominant contact shifts of all Vanadium (III) tris β-diketonates arise mainly from charge donation from metal d_π orbitals to the lowest ligand π^* orbital [45,51,74]. A corollary of this assumption is that the observed shifts are proportional to the π spin transferred according to the well known McConnell relationship.

D. The substituent effects are additive, i.e. the effect on the charge distribution of substituting two CF_3 groups on $V(acac)_3$ at specific positions is the sum of the effects of single substitution at two individual positions. The test of this assumption can only lie in the agreement between observed and calculated shifts which will be described in the following section. It must be expected that the lack of additivity will be one of the factors leading to incomplete agreement between calculated and experimental values.

Consider first the CH_3 shifts. Figure 4-4a illustrates the overlap between the p_π orbital of the oxygen of a ligand in the xy plane and the d_{xz} orbital of Vanadium ion. Based on the above assumptions , the neighbouring CH_3 shift will be proportional to the amount of spin transferred from the d_π orbital to the oxygen p_π orbital. This in turns depends on two factors:

1. The relative population of spin density in the d_{xy} , d_{xz} and d_{yz} orbitals.
2. The ability of the oxygen p_π orbital to accept π electron(s).

Consider the first factor. It is necessary at this stage to examine the form of spin containing orbitals for the O_h and D_3 point groups as given in Table 2-1. If all three ligands are identical as in vanadium (III) $(acac)_3$, the occupied d_π orbitals have the forms:

$$e: \quad \begin{array}{l} 1/\sqrt{2}(d_{xz} - d_{yz}) \\ 1/\sqrt{6}(2d_{xy}-d_{xz}-d_{yz}) \end{array}$$

The charge density in the d_{xz} orbital equals to that in the d_{xy} and d_{yz} orbitals and has a population value of 2/3,i.e.

$$\begin{aligned} q_{xz} &= (1/\sqrt{2})^2 + (1/\sqrt{6})^2 = 2/3 \\ q_{yz} &= (1/\sqrt{2})^2 + (1/\sqrt{6})^2 = 2/3 \\ q_{xy} &= (2/\sqrt{6})^2 \qquad\qquad\quad = 2/3 \end{aligned}$$

for a less symmetric case, the forms of the occupied orbitals are changed and the occupation values of d_{xy} , d_{xz} and d_{yz} are corresponding modified. Thus in the extreme case in which the xy plane is occupied by a symmetric ligand which exerts a tetragonal crystal field distortion very much greater than the trigonal distortion present in all these tris chelates, the appropriate stmmetry is C_{2v} and the correct forms of the orbitals are

$$\begin{array}{ll} a_1: & d_{xy} \\ a_2: & 1/\sqrt{2}(d_{xz} + d_{yz}) \\ b_1: & 1/\sqrt{2}(d_{xz} - d_{yz}) \end{array}$$

This case corresponding to that of the cis isomer of the complex MA_4B_2 . Consider now the case involving both the trigonal and tetrahedral distortions. C_2 symmetry is conserved and there are two orbitals of a symmetry and one of b symmetry. They correlate with the D_3 and C_{2v} case as follows[74]:

$$\begin{array}{lcl|lcl}
D_3 & \longrightarrow & C_2 & C_2 & \longleftarrow & C_{2v} \\
\hline
a_1 & \longrightarrow & a & a & \longleftarrow & a_1 \\
e & \longrightarrow & a+b & a & \longleftarrow & a_2 \\
 & & & b & \longleftarrow & b_1
\end{array}$$

Thus the b orbital in the C_2 point group should be an occupied orbital while one of the a orbitals is unfilled. In all cases the unfilled orbital will be of a symmetry and separated from the next higher orbital by an energy large compared to kT as is shown by the Curie law dependence of the isotropic shifts and magnetic susceptibility discussed above. The form of the unoccupied a orbital will vary in character according to the nature of the substituents.

a. If the three chelating ligands are equivalent, the unfilled d orbital will have the form $1/\sqrt{3}(d_{xy}+d_{xz}+d_{yz})$, a_1 symmetry in D_3 point group.

b. In the extreme case of a very large tetragonal distortion in which the odd ligand occupied the xy plane provides a strong crystal field, the unfilled d orbital will be d_{xy}, a_1 symmetry in C_{2v} point group. The population values in the d_π orbitals will be

$$q_{xy} = 0$$

$$q_{xz} = (1/\sqrt{2})^2 + (1/\sqrt{2})^2 = 1$$

$$q_{yz} = (1/\sqrt{2})^2 + (1/\sqrt{2})^2 = 1$$

In the opposite extreme if the odd ligand in the xy plane is a very strong electron withdrawing substituent the unfilled orbital will be $1/\sqrt{2}(d_{xz}+d_{yz})$, a_2 symmetry in C_2v point group. The population values for the three d_π orbitals will be :

$$q_{xy} = 1$$
$$q_{xz} = (1/\sqrt{2})^2 = 1/2$$
$$q_{yz} = (1/\sqrt{2})^2 = 1/2$$

For the intermediate case, the empty orbital will have the form:

$$a\, d_{xy} + (\sqrt{1-a^2/2}\,)(d_{xz}+d_{yz})$$

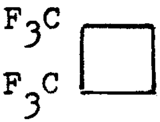
and the half-filled orbital takes the form:

$$\sqrt{(1-a^2)}\; d_{xy} - (a/\sqrt{2})(d_{xz}+d_{yz})$$

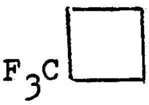
a=1 corresponds to an extreme electron-donating substituent, a=0 to an extreme electron-withdrawing substituent and $a=1/\sqrt{3}$ to the symmetrical case. The parameter a is therefore a measure of the donating or withdrawing properties of the substituent. The value of a can in principle be calculated for a given crystal field by solving the eigenvalue equation provided the basis set, i.e. d_{xy}, d_{xz} and d_{yz} for π bonding do not mixed significantly with those which are involving in σ-bonding. The following qualitative conclusion can therefore be reached: The population of a d_π orbital in a plane occupied by oxygens bearing the more electron-attracting substituent will be increased at the expense of that of the d_π orbitals whose planes containing less electron-attracting substituents. Put in another way the population of a d_π orbital in a plane occupied by oxygens bearing more electron-donating substituents will be decreased to an extent equal to the gain in spin population of the d_π orbitals in planes not bearing such substituents. In general, the relative population values of the three interconnected d_π orbitals depends on the number of substituents, in the present case, the number of CF_3 groups, in each of the three planes. This generalization will then be used for the derivation of a number of equations expressing the effects of the d_π population changes on the contact shifts of the pure and mixed chelates. It is convenient to define ΔS_i as the change of d_π orbital population value in the i^{th} plane ($i = xy$, xz or yz) upon substitution. Since in $V(acac)_3$ the three d_{xy} , d_{xz} and d_{yz} orbitals contain the same number of CH_3 groups, the population values for the three orbitals are expected to be the same. The situation will be different if the three planes contain different number of different substituents as in the mixed or unsymmetric chelates.

The second factor mentioned above, namely the ability of the oxygen to accept electrons will depend on the charge on the oxygen atom. The more positive charge there is on the oxygen, the greater is the electron-accepting ability. We might therefore anticipate an inductive effect whereby an electron-withdrawing substituent operating through σ-bonds will induce positive charge to some extent on the more distant oxygens. The effect will be different for each of the five non-neighbouring oxygens since none are equivalent by symmetry. We therefore introduce the substituent parameters as shown in figure 4-4b. Supposing that we wish to calculate the shift of a CH_3 group located at the X-position. The substituent parameter a, b, c, d or e will appear in an equation if there is substituent other than CH_3 at the appropriate position. We are concerned with CF_3 substituents in this case. Thus the substituent parameters a, b, c, d and e represent the changes in oxygen charge in the five possible positions resulting from the inductive effect of the substituents.

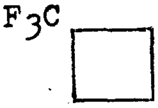
Taking account of the two factors together and with the labelling system of the substituent parameters as shown in figure4-4b and the labels for the distinct groups as shown in figure 4-4c, one may develop empirical equations to correlate the CH_3 isotropic shifts. Consider for example, the complex $V(acac)_2(hfac)$ (compound III of figure 4-1 with $X=CH_3$ and $Y=CF_3$), the three planes capable of π bonding differ in the number of CF_3 groups they contain and the relative changes of d_π orbital population factors are shown below:



$\Delta S_{xy} = +x$



$\Delta S_{xz} = -x/2$



$\Delta S_{yz} = -x/2$

d_{xz} and d_{yz} are equivalent but d_{xy} is unique. Furthermore the xy plane contains two CF_3 substituents which are assumed to be electron-withdrawing, and the xz and yz planes one each. The d_{xy} orbital will therefore gain spin population at the expense of d_{xz} and d_{yz} orbitals. We therefore write the population factor as $(1+x)$ for d_{xy} and $(1-x/2)$ for d_{xz} and d_{yz} orbitals. Since CH_3^A and CH_3^B are equivalent, the substituent factors will be the same and is given by $(1+a+d)$. Also CH_3^C and CH_3^F are equivalent, the substituent factor for either one of these is $(1+b+e)$. Bearing in mind that CH_3^A can π bond with d_{xy} orbital and CH_3^C can π bond with d_{xz} orbital, the respective isotropic shifts are then given by the following empirical equations

$$\Delta v_A = \Delta v_o(1+\Delta S_{xy})(1+a+d) = \Delta v_o(1+x)(1+a+d) \qquad \ldots\ldots\ldots(4\text{-}2)$$

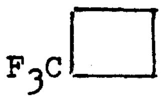
$$\Delta v_C = \Delta v_o(1+\Delta S_{xz})(1+b+e) = \Delta v_o(1-x/2)(1+b+e) \qquad \ldots\ldots\ldots(4\text{-}3)$$

where Δv_o is the shift of $V(acac)_3$. In cis-$V(tfac)_3$, all three CH_3 groups are equivalent and the three π planes contain the same number of CF_3 substituents, therefore $\Delta S_i = 0$ for all three π planes. The substituent factors are the same for all three groups, and is equal to $(1+a+b+c)$. Only one resonance is observed. The equation for this resonance being given by

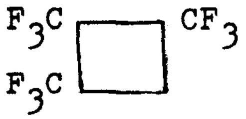
$$\Delta v_A = \Delta v_o(1+0)(1+a+b+c) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4\text{-}4)$$

$$= \Delta v_C = \Delta v_E$$

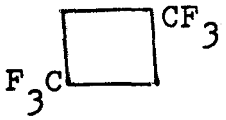
For complexes in which d_{xy}, d_{xz} and d_{yz} all have different population values, two population parameters x and y are required to set up the equations. The trans isomer of $V(tfac)_3$ provides an example of this situation. All three planes contain different number of CF_3 groups as shown below



$\Delta S_{xy} = -x$



$\Delta S_{xz} = +y$



$\Delta S_{yz} = +(x-y)$ or $-(y-x)$

The corresponding empirical equations for the three non-equivalent CH_3 resonances are :

$$\Delta v_A = \Delta v_o(1+\Delta S_{xy})(1+a+c+e) = \Delta v_o(1-x)(1+a+c+e) \quad \ldots\ldots(4\text{-}5)$$

$$\Delta v_B = \Delta v_o(1+\Delta S_{xy})(1+c+d+e) = \Delta v_o(1-x)(1+c+d+e) \quad \ldots\ldots(4\text{-}6)$$

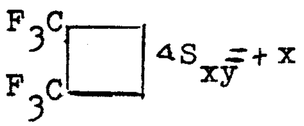
$$\Delta v_C = \Delta v_o(1+\Delta S_{yz})(1+b+c+d) = \Delta v_o(1+(x-y))(1+b+c+d) \ldots.(4\text{-}7)$$

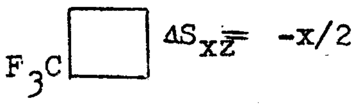
Expressions for all thirty-two distinct CH_3 resonances can be obtained in this way. No y parameter is required as long as any two of the π planes bear the same numbers of CF_3 substituents. These thirty-two expressions are collected and presented in Table 4-6. The next problem is to solve the above equations in order to obtain the approximate values of the population factors and the substituent parameters.

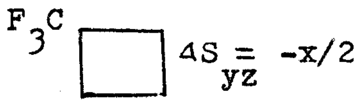
Initially, it was assumed that ΔS_i has a constant value for all d_π orbitals defined by planes which differ by one CF_3 group. The experimental CH_3 frequencies of $V(acac)_2(hfac)$, $V(acac)(hfac)_2$, cis-$V(tfac)_3$ and that of acac of $V(acac)_2(tfac)$ were then used to obtain approximate values for a, b, c, d, e and ΔS_i. The assignments of the CH_3 resonances of the above compounds presented no problems with the aid of deuterated aceylacetone except for $V(acac)_2(hfac)$ where two CH_3 resonances are fairly close in frequency. The actual values of the frequencies of these two CH_3 groups do not greatly affect the values of the substituent parameters obtained. This rough estimate of the parameters indicates that the parameter a is negative whereas the rest are positive with d and e have virtually identical values. In this analysis a value of 0.08 was obtained for ΔS_i. These parameters were further adjusted to give the best fit to all 32 CH_3 resonances. A plot of calculated versus experimental shifts for $\Delta S_{xy} = x = 0.08$ and a=-0.1, b=0.13, c=0.27, d=0.14 and e=0.14 is shown in figure 4-5. It is seen that the agreement between experimental and calculated shifts is rather satisfactory with a standard deviation of 5.6%. The agreement can still be improved by treating ΔS_i as an adjustable parameter for each complex. The possible variations are not large since changes in ΔS_i which improve the agreement for one frequency tend to make it worse for the other frequencies. The final calculated frequencies were obtained by optimizing the values of ΔS_i and then making a further small adjustment to the substituent parameters.Final calculated frequencies also collected in Table 4-2. A plot of final calculated versus experimental shifts is shown in figure 4-6. The standard deviation of the calculated from experimental values is 1.28% of the total spread of the shifts. Of the 1.28% about 0.5% error is attributed to inaccuracies in the measurements and the remainder reflects the inadequacies of the model. Finally it should be mentioned that some of the resonances whose assignments are not obvious were identified by the above method of analysis.

The data for CF_3 groups were treated in exactly the same manner except that the substituent parameter was included for each position bearing a CH_3 group and omitted for each position bearing a CF_3 group. Final calculated frequencies are also collected in Table 4-3. The standard deviation of the calculated shifts from the experimental shifts is in this case 2.19% of the total spread of the shifts. The thirty-two expressions for calculating the distinct CF_3 shifts are similar to those for the CH_3 shifts except that the signs are reversed. A plot of final calculated versus experimental shifts is shown in figure 4-7.

The CH shifts require a slightly modified procedure. Since spin density can reach the γ-carbon atom equally well through either of the oxygens in each chelating ligand, it is appropriate therefore to include population and substituent factors relating to both oxygens. Thus For example, for the complex $V(acac)_2(hfac)$, the three planes containing the $d\pi$ orbitals are shown below:







(refer to figure 4-1 and figure 4-4c for the labelling of the distinct CH groups where $X=CH_3$ and $Y=CF_3$). The expressions for the acetylcaetonate CH groups are given by the equations

$$\begin{aligned}\Delta v_a &= \Delta v_o^{acac}(1+\Delta S_{xy}+\Delta S_{xz})(1+(a+d)+(b+e))\\ &= \Delta v_o^{acac}(1+x/2)(1+a+b+d+e) \qquad \ldots\ldots\ldots\ldots\ldots(4\text{-}8)\\ &= \Delta v_b\end{aligned}$$

In these equations, ΔS_{xy} and ΔS_{xz} take account of the changes in spin population in the xy and xz planes which can participate in π bonding with the oxygens at A and F positions. The parameters (a+d) and (b+e) represent the substituent factors with respect to oxygens at A and F positions respectively. Δv_o^{acac} is the CH shift of the unsubstituted $V(acac)_3$. Similarly the CH shift of hexafluoroacetylacetonate ligand can be expressed as:

$$\begin{aligned}\Delta v_c &= \Delta v_o^{hfac}(1+\Delta S_{xz}+\Delta S_{yz})(1-(a+b+d+e)-(a+b+d+e))\\ &= \Delta v_o^{hfac}(1-x)(1-2a-2a-2d-2e) \qquad \ldots\ldots\ldots\ldots\ldots(4\text{-}9)\end{aligned}$$

Δv_o^{hfac} in this equation is the CH shift of $V(hfac)_3$. In the situation where the coordinating ligand involves tfac, an average value of CH shifts of $V(acac)_3$, $V(hfac)_3$ and cis-$V(tfac)_3$ was used and dessignated as Δv_o^{ave}. It should also be noted that in the above equations a positive substituent parameter is used to express the substituent effect of a CF_3 group on an oxygen bearing a CH_3 group and an equal but negative value to allow for the effect of a CH_3 substituent on an oxygen bearing a CF_3 group. The 36 expressions so obtained are tabulated in Table 4-7. Examination of these equations shows that the only substituent parameters encountered are the combinations (a+ e) and (b+d). In addition to x and y, we have therefore only two substituent parameters . Analysis then proceeded in the same manner as for CH_3 and CF_3 shifts. The final calculated shifts were collected in Table 4-4. A plot of calculated versus experimental isotropic shifts using the final parameters is shown in figure 4-8. In this case the standard deviation is 1.9% of the total spread.

The various substituent parameters and d orbital population factors thus derived for the CH_3, CF_3 and CH resonances are collected together in Table 4-8 and Table 4-9.

4-2. Results of V(III)/acac/Ø-ac/Ø-Ø and V(III)/Ø-Ø/tfØ/hfac systems.

The analysis described above have been extended to several other mixed chelate systems. Data for systems involving mixed complexes with ligands HØ-Ø , HØ-ac and Htf-Ø (structures III, V and VI as shown in chapter 3) have been obtained. Two additional systems for studying the substituent effect can be obtained with these additional ligands, namely: V(III)/acac/Ø-ac/Ø-Ø and V(III)/Ø-Ø/tfØ/hfac systems.Several investigators [4,5,50] have provided evidence that a phenyl substituent appears to be rather more electron donating than a methyl substituent in the β-diketone ligands and our results on the isotropic shifts of V(III) complexes are consistent with this conclusion. The results for the CH_3 isotropic shifts obtained experimentally and by calculation using the same method as described previously for V(III)/acac/Ø-ac/Ø-Ø system are presented in Table 4-10. Since the shifts are relatively small and analysis has been confined to the CH_3 resonances. 14 of the possible 32 frequencies are obtained. The derived substituent parameters are also collected in Table 4-8. The orbital population factors of the metal d_π orbitals are presented in Table 4-11. Analysis of the shifts of the phenyl ring protons of the mixed chelates has not been attempted since the multiplicity of lines creates a considerable assignment problem.

Data for the CF_3 and CH shifts of V(III)/Ø-Ø/tfØ/hfac system have also been obtained. The calculated and observed values are given in Table 4-12 and Table 4-13. Twenty-six of the possible 32 CF_3 resonances and 30 of the possible 36 CH resonances are reported. Figure 4-9 shows a plot of experimental varsus calculated shifts for the CH resonances. The substituent parameters for CF_3 and CH shifts for this system are also included in Table 4-9 and the d_π orbital population factors are collected in Table 4-14.

4-3. Discussion.

V(III)/acac/tfac/hfac system. The validity of an empirical analysis such as that described above is subject to several criteria.

First of all, it is obviously that the parameters used must reproduce the experimental data with reasonably accuracy. We regard the agreement obtained as satisfactory. The 1 or 2% dicrepancies can very reasonably be ascribed to indequencies of the model.

The second criteria is that the parameters derived should be internally consistent, i.e. if from the CH_3 results we deduce a drift of electron from a cis oxygen bearing the CH_3 group toward an oxygen bearing a CF_3 substituent, the CF_3 results must then indicate enchanced electron density at the CF_3 oxygen obtained from the neighbouring cis-CH_3 bearing oxygen. Such consistency should be reflected in the opposite signs for corresponding parameters derived from the CH_3 and CF_3 analysis. This result is indeed obtained as indicated in Table 4-8, apart from a small inconsistency in the e parameters for the CF_3 results where we obtained small positive values rather than small negative values. However we do not believe that this discrepancy detracts seriously from the overall trend of the results. Similarly, the CH parameters should bear some relationship to the CH_3 parameters. Again the zero value of (a+e) agrees with the opposite signs of a and e found for the individual CH_3 parameters and the positive value of (b+d) is qualitatively expected. The d orbital population value for V(III)/acac/tfac/hfac obtained from the three sets of data are displayed in Table 4-9. If the model were rigiously correct the three values for a given orbital population should be identical. Not surprisingly, this equality does not hold particularly well. However, there is good agreement in signs of the changes in orbital populations with substituent and in the overall magnitude of the effect. The main discrepancy is that the CH shifts indicate larger population changes than do the CH_3 and CF_3 shifts. This implies that the CH shifts are more sensitive to changes in π spin density than the CH_3 or CF_3 shifts. This is reasonable since a larger contribution from σ spin density might be expected for the CH_3 and CF_3 groups due to the smaller number of bonds separating them from the metal atom.

A final criterion for accepting the analysis is that the results should be physically plausible. This aspect is illustrated by the charge distribution shown diagramatically in figure 4-10 for two typical complexes. Consider the mixed complex $V(acac)_2(tfac)$ first, this has a single electron-withdrawing CF_3 substituent. An inductive effect through the σ-bonds of the system is expected to operate . The net results is to increase the positive charge at each of the four cis oxygens (figure 4-10a) , thus increasing their electron accepting ability. This is manifested in the positive values of the substituent parameters b, c, d and e in calculating the CH_3 shifts for the CF_3 substitution effect. The effect at the oxygen belonging to the same chelating ligand (i.e. substitution at c position) is roughly twice as great as at the other positions. This seems reasonably in view of the availability of an alternative pathway through the σ bonds of the ligand. The accumulation of charge at the oxygen bearing the CF_3 group may cause a little negative charge leak across to the oxygen trans to the substituents, this account for the negative values of the a parameters. Although not anticipated prior to the analysis of data, in retrospect these results can be correlated with the many reports of unique trans-effects in transition metal complexes. In addition to this direct inductive effect on the charge distribution in the σ system of the molecule, there is also a polarization of the charge in the metal d_π orbitals not involved in σ bonding. The distribution of charge in the metal d_π orbital is spherical for complexes such as, $V(acac)_3$, $V(hfac)_3$ and cis-$V(tfac)_3$. However for the unsymmetric complexes such as $V(acac)_2(tfac)$ instead of there being a spherical distribution of such charge it tends to accumulate in planes containing the more electron-withdrawing CF_3 group.(figure 4-10b) In the present case, the two d_π orbitals in the planes containing the CF_3 bearing oxygen have gained spin population (about 5% in our analysis) and the d_π orbital in the plane not containing the CF_3 group has lost spin population (about 10%) to the other two planes. Since these are the d_π orbitals involved in π bonding to the different ligands, the result is enhanced

delocalization of unpaired electron to the ligand π orbitals of the ligands not bearing the electron-withdrawing substituent and diminished delocalization to the CF_3 bearing ligand.

The second compound to be considered is $V(acac)_2(hfac)$, this has two CF_3 substituents and the charge distribution arises from the superposition of the inductive and polarization effects of the two CF_3 groups taken individually . The net result is that the two CH_3 bearing oxygens in the same plane as the hfac lose very little negative charge but the two out of this plane lose substantially (figure 4-10c). At the same time the d_π orbitals containing the unpaired electron are polarized leading to gain of spin population (about 12% from our analysis) of the d_π orbital in the plane of hfac and a loss of spin population (about 6%) in each of the other two d_π orbitals in the perpendicular planes.(figure 4-10d) Thus the parameters obtained from the above analysis lead to a plausible rationalization of the effect of substituents on the charge distribution of the transition metal complexes. The good agreement of the calculated and experimental shifts using the above method of analysis has in turn supported the assumption that π

delocalization is the predominant mechanism responsible for the large contact shifts of all tris β-diketonato V(III)chelates. It should be noted that the two effects operate in such a manner that the differences in ligand π spin density distribution in the mixed chelates are enhanced.

Other systems. The substituent parameters for the phenyl substituted compounds follow the pattern discussed above. Those derived from the CH_3 shifts with phenyl group substituents are all opposite in signs to the corresponding parameters obtained with CF_3 substituents confirming that a phenyl group does indeed have an opposite effect to a CF_3 group in these transition metal complexes. It is interesting to note that the trans parameters for phenyl versus methyl is quite large but the cis parameters are all considerably smaller than those obtained for CF_3 substitution. Thus the phenyl group donates electrons to the cis-positions but withdraws from the trans position to such an extent that the net effect is electron withdrawing. This is to be contrasted with CF_3 substituent which withdraws electrons from cis-positions and donates to the trans position but also has a large net withdrawing effect. The parameters obtained from the CF_3 and CH data of V(III)/ø-ø/tf-ø/hfac system reflecting the competition of a phenyl group with a CF_3 group are quite similar to those obtained from the V(III)/acac/tfac/hfac system. The anomaly of a small positive value for e is again observed. (It is interesting to note the similarity in signs of the substituent parameters for the CH_3 shifts of V(III)/acac/ϕ-ac/ϕ-ac/ϕ-ϕ system and that of CF_3 shifts of V(III)/acac/tfac/hfac system except for the small values of e. Both CH_3 and CF_3 groups act as electron-withdrawing groups in the respective systems). The d_π orbital population factors given in Table 4-14 show no new features. They are quite scattered with one or two anomalously high values but the trends relating to the direction of polarization of charge in the metal d_π orbitals are quite clear.

4-4. General remarks.

Finally we add some general remarks on the significance of these results. The substituent parameters should be regarded as qualitative indicators of the charge distribution in the σ system. In this respect they are similar to the various Hammett and Taft parameters for substituted aromatic compounds. The latter parameters are also often derived from NMR chemical shifts and there are parallel hazards in deriving charge density information from measurements of a variable which is only indirectly related to charge. Confidence in the significance of aromatic substituent parameters rests on their ability to correlate a large variety of diverse physical measurements. If obtained by NMR a given substituent parameter is usually derived from the measurement of a single chemical shift. For transition metal complexes data on substituent effects are much less accessible and confidence in the significance of the parameters presented here rests on their ability to correlate a large body of NMR data. Direct proportionality between a substituent parameter and the charge on a ligand atom is not implied and is not required if only qualitative discussion of the charge distribution is intended. Similarly we would not place any reliance on the numerical values for orbital populations but merely regard them as a qualitative indication of the movement of charge around the metal atom. Examination of the results, keeping in mind these reservations, reveals a number of interesting aspects of substituent effects which are unique to transition metal complexes. First of all the movement of charge resulting from unsymmetric substitution is very much greater than that resulting from symmetric substitution. This can be seen most directly by comparing the CH shifts of the symmetric complexes $V(acac)_3$ (-3292 Hz), cis-$V(tfac)_3$ (-3328 Hz) and $V(hfac)_3$ (-3734 Hz) with those of an unsymmetric compounds, e.g. $V(hfac)_2(tfac)$ (-5010 Hz, -4220 Hz and -1916 Hz). In the series of symmetric complexes there is an increasing shift representing more charge transfer to the electron withdrawing ligands. In the unsymmetric compounds the spread of the shifts is nearly an order of magnitude larger than the difference between $V(acac)_3$ and $V(hfac)_3$. Thus the majority of the charge redistribution represents movement from one ligand to another rather than from the metal to the ligands. We believe that this point has major significance with respect to the activation of substrate molecules in homogeneous catalysis. Thus it is a common observation that catalytic efficiency can depend crucially on the nature of ancillary ligands not directly involved in the reaction. The above observation suggests an obvious rationale for such dependence.

The pattern of charge migration from one ligand to another is revealed in the analysis presented. As with aromatic substitution both σ and π effects are involved. For these three dimensional complexes there are inter-relationships between the σ and π systems not found in planar compounds. A result of this is that there is an inherent tendency for charge movement in the σ and π systems to be opposed. Thus in the present case negative charge moves from acac to hfac ligands in the σ system but from hfac to acac in the π system. Basically this arises because there is charge in d orbitals orthogonal to the σ bonding system which has a spherical distribution in a symmetric complex. In the presence of an unsymmetric ligand field this spherical distribution is distorted to a prolate or oblate spheroid and the distortion is such that the more electron donating ligand has π interactions with the high electron density region. It seems that this effect may also have important mechanistic significance. For example in a complex of suitable geometry an electron withdrawing substituent at a remote point could not only diminish the charge density in the σ bond of a coordinated olefin but could concurrently enhance the density in the olefin π^* orbital resulting from back donation. Such a synergistic effect provides an attractive rationale for olefin activation.

A further comparison with aromatic substituent effect is of some interest. Generally an inductively electron-withdrawing substituent will qualitatively, if not quantitatively exert the same influence at the ortho, meta or para-positions of an aromatic molecule. In these transition metal complexes the sign of the effect differs for cis and trans-positions. This difference can again be related to the complexities inherent in a three dimensional system compared to a two dimensional system. Ligands trans to each other utilize common metal orbitals to form σ-bonds. Ligands cis to each other interact with orthogonal metal orbitals. In the latter case the charge distributions in the two metal-ligand bonds are polarized leading to a net inductive movement of charge from one ligand to the other. In the former case the involvement of common metal orbital results in charge gained by the electron-withdrawing ligand being shared with the trans-ligand. This feature could also have considerable significance to substrate activation in catalysis. The implication is that the relative positions of two ligands in a catalytic intermediate may be crucial to the activation process.

In conclusion it seems that the type of qualitative arguments used to rationalize substituent effects on reaction rates and mechanisms in organic chemistry may find application in transition metal chemistry. They must however be used with some sophistication and with due regard to the complications which result from the three dimensional nature of metal complexes.

Table 4-1. No. of isomers of V(III)/acac/tfac/hfac system.

Compound	Isomers	CH_3 Groups	CF_3 Groups	CH Groups
$V(acac)_3$	1	1	-	1
$V(hfac)_3$	1	-	1	1
$V(acac)_2(hfac)$	1	2	1	2
$V(acac)(hfac)_2$	1	1	2	2
$V(tfac)_3$	2	4	4	4
$V(acac)_2(tfac)$	1	5	1	3
$V(acac)(tfac)_2$	3	8	4	7
$V(hfac)_2(tfac)$	1	1	5	3
$V(hfac)(tfac)_2$	3	4	8	7
V(acac)(tfac)(hfac)	2	6	6	6
Total	16	32	32	36

Table 4-2. CH_3 shifts of V(III)/acac/tfac/hfac system.

Compound No.[1]	Calculated shifts(Hz)	Expt'al shifts(Hz)
I	:-4208	:-4208
II	A :-4779 B :-4261 C :-4006 D :-5022 E :-4967	A :-4808 B :-4300 C :-4054 D :-5031 E :-4981
III	A=B:-4826 C=F:-4983	A=B:-4836 C=F:-4982
IV	A=B:-5136 D=E:-5625	A=B:-5120 D=E:-5598
V	C=F:-5829 D=E:-4296	C=F:-5856 D=E:-4330
VI	A :-5702 C :-4735 D :-5106 E :-4608	A :-5740 C :-4756 D :-5110 E :-4610
VII	:-5449	:-5420
VIII	A :-5029 B :-5921 E :-6601	A :-5056 B :-5870 E :-6654
IX	A :-5892 D :-6007 E :-5121	A :-5829 D :-6004 E :-5126
X	C :-5519 D :-4970 E :-4932	C :-5220 D :-4988 E :-4976
XI	A :-6039 C :-5856	A :-5988 C :-5790
XII	A=B:-5901	A=B:-5945
XIII	C=F:-6519	C=F:-6510
XIV	B=C:-5727	B=C:-5734
XV	F :-6597	F :-6640

[1] Refer to figure 4-1 with X = CH_3 Y = CF_3

Table 4-3. CF_3 shifts of V(III)/acac/tfac/hfac system.

Compound No.[1]	Calculated shifts(hz)	Expt'al shifts(hz)
XVI	:-4510	:-4510
II	F :-4159	F :-4152
III	C=D:-4455	C=D:-4152
IV	C=F:-3743	C=F:-3714
V	A=B:-4781	A=B:-4710
VI	B :-4540 F :-3802	B :-4524 F :-3760
VII	:-4158	:-4150
VIII	C :-4162 D :-5021 F :-3390	C :-4080 D :-4998 F :-3394
IX	B :-4236 C :-4218 F :-3790	B :-4240 C :-4228 F :-3394
X	A :-4464 B :-5220 C :-4979	A :-4536 B :-5156 C :-4978
XI	B :-3574 D :-4344 E :-4788 F :-4845	B :-3566 D :-4377 E :-4725 F :-4920
XII	C=F:-4082 D=E:-5792	C=F:-4147 D=E:-5730
XIII	A=B:-4486 D=E:-3732	A=B:-4526 D=E:-3756
XIV	A=D:-4460 E=F:-4505	A=D:-4480 E=F:-4578
XV	A :-4057 B :-4850 C :-5158 D :-4336 E :-3944	A :-3984 B :-4999 C :-5158 D :-4316 E :-3922

[1] Refer to figure 4-1 with X = CH_3, Y = CF_3

Table 4-4. CH shifts of V(III)/acac/tfac/hfac system.

Compound No.[1]	Calculated shifts(hz)	Expt'al shifts(hz)
I	:-3292	:-3292
II	A :-2768 B :-3226	A :-2668 B :-3116
III	A=B:-4467 C :-1672	A=B:-4486 C :-1700
IV	A=B:-2387 C :-5865	A=B:-2522 C :-5974
V	A=B:-3738 C :-2732	A=B:-3728 C :-2710
VI	A :-3789 B :-2175 C :-4300	A :-3866 B :-2190 C :-4470
VII	:-3445	:-3310
VIII	A :-1893 B :-3910 C :-4858	A :-1970 B :-3988 C :-4984
IX	A :-4134 B :-1338 C :-5596	A :-4221 B :-1330 C : ?
X	A :-3548 B :-2957 C :-3954	A :-3579 B :-2906 C :-3748
XI	A :-5081 B :-3032 C :-2669	A :-5104 B :-3028 C :-2667
XII	A=B:-3428 C :-3771	A=B:-3551 C :-3610
XIII	A=B:-4288 C :-2126	A=B:-4220 C :-1980
XIV	A=C:-2541 B :-5999	A=C:-2475 B :-5920
XV	A :-5040 B :-4257 C :-1898	A :-5014 B :-4229 C :-1910
XVI	:-3734	:-3734

1. Refer to figure 4-1 with X= CH_3 , Y= CF_3

Table 4-5. $\gamma\text{-}CH_3$ shifts.

$V(III)/\gamma\text{-}CH_3\text{-acac}/Ø\text{-}Ø$		$V(III)/\gamma\text{-}CH_3\text{-acac/tfac/hfac}$	
Compound	Observed shifts	Compound	Observed shifts
$V(\gamma\text{-}CH_3\text{-acac})_3$	:+1588	$V(\gamma\text{-}CH_3\text{-acac})_3$	:+1588
		$V(\gamma CH_3\text{-acac})_2\cdot\text{tfac}$	B:+732 C:+1607
$V(\gamma\text{-}CH_3\text{-acac})_2\cdot Ø\text{-}Ø$	A=B :+889	$V(\gamma\text{-}CH_3\text{-acac})_2\cdot\text{hfac}$	A=B :+1788
		$t\text{-}V(\text{tfac})_2\cdot\gamma CH_3\text{-acac}$	C:+2698
		$c\text{-}V(\text{tfac})_2\cdot\gamma CH_3\text{-acac}$	C:+808
		$c''\text{-}V(\text{tfac})_2\cdot\gamma CH_3\text{-acac}$	C:+1878
$V(Ø\text{-}Ø)_2\cdot\gamma CH_3\text{-acac}$	B:+761	$V(\text{hfac})_2\cdot\gamma CH_3\text{-acac}$	B:+2960

Table 4-6

32 CH_3 expressions for V(III)/acac/tfac/hfac system.

$V(acac)_3$ (I)	$\Delta v = \Delta v_o$
$V(acac)_2.tfac$(II)	$\Delta v_A = \Delta v_o(1-x)(1+c)$
	$\Delta v_B = \Delta v_o(1-x)(1+e)$
	$\Delta v_C = \Delta v_o(1+x/2)(1+a)$
	$\Delta v_D = \Delta v_o(1+x/2)(1+d)$
	$\Delta v_E = \Delta v_o(1+x/2)(1+b)$
$V(acac)_2.hfac$ (III)	$\Delta v_A = \Delta v_o(1+x)(1+a+d) = \Delta v_B$
	$\Delta v_C = \Delta v_o(1-x/2)(1+b+e) = \Delta v_F$
t-$V(tfac)_2.acac$ (IV)	$\Delta v_A = \Delta v_o(1-x)(1+c+e) = \Delta v_B$
	$\Delta v_D = \Delta v_o(1+x/2)(1+d+e) = \Delta v_E$
c-$V(tfac)_2.acac$ (V)	$\Delta v_F = \Delta v_o(1-x/2)(1+c+d) = \Delta v_C$
	$\Delta v_D = \Delta v_o(1-x/2)(1+a+e) = \Delta v_E$
c-$V(tfac)_2.acac$ (VI)	$\Delta v_A = \Delta v_o(1-x/2)(1+b+c)$
	$\Delta v_C = \Delta v_o(1-x/2)(1+a+c)$
	$\Delta v_D = \Delta v_o(1-x/2)(1+d+e)$
	$\Delta v_E = \Delta v_c(1+x)(1+a+b)$
c-$Vtfac)_3$ (VII)	$\Delta v_A = \Delta v_o(1+0)(1+a+b+c)$
t-$V(tfac)_3$ (VIII)	$\Delta v_A = \Delta v_o(1-x)(1+a+c+e)$
	$\Delta v_B\ \Delta v_o(1-x)(1+c+d+e)$
	$\Delta v_E = \Delta v_o(1+x-y)(1+b+c+d)$

Table 4-6. Continued.

t-V.acac.tfac.hfac (IX)	$\Delta v_A = \Delta v_o(1-x)(1+c+e+b)$
	$\Delta v_D = \Delta v_o(1+x-y)(1+d+b+e)$
	$\Delta v_E = \Delta v_o(1+y)(1+a+d+b)$
c-V.acac.tfac.hfac (X)	$\Delta v_D = \Delta v_o(1+x/2)(1+a+d+c)$
	$\Delta v_E = \Delta v_o(1+x/2)(1+a+b+e)$
	$\Delta v_F = \Delta v_o(1+x/2)(1+a+d+c)$
c'-V(tfac)$_2$.hfac (XI)	$\Delta v_A = \Delta v_o(1+x/2)(1+a+b+c+d)$
	$\Delta v_C = \Delta v_o(1- x)(1-a+b+c+e)$
c-V(tfac)$_2$·hfac (XII)	$\Delta v_A = \Delta v_o(1-x)(1+a+c+d+e)$
t-V(tfac)$_2$.hfac (XIII)	$\Delta v_F = \Delta v_o(1-x/2)(1+b+c+d+e)$
V(hfac)$_2$(acac) (XIV)	$\Delta v_B = \Delta v_o(1+x/2)(1+a+b+d+e)$
V(hfac)$_2$(tfac) (XV)	$\Delta v_F = \Delta v_o(1+y-x)(1+a+b+c+d+e)$

Table 4-7

36 CH expressions for V(III)/acac/tfac/hfac system.

$V(acac)_3$	(I)	$\Delta v = \Delta v_o^{acac}$
$V(hfac)_3$	(XVI)	$\Delta v = \Delta v_o^{hfac}$
$V(acac)_2 \cdot tfac$	(II)	$\Delta v_a = \Delta v_o^{ave}(1-x/2)(1-(a+e)-(b+d))$ $\Delta v_b = \Delta v_o^{acac}(1-x/2)(1+a+e)$ $\Delta v_c = \Delta v_o^{acac}(1+x)(1+b+d)$
$V(acac)_2 \cdot hfac$	(III)	$\Delta v_a = \Delta v_o^{acac}(1+x/2)(1+(a+e)+(b+d)) = \Delta v_b$ $\Delta v_c = \Delta v_o^{hfac}(1-x)(1-2(a+e)-2(b+d))$
t-V9tfac$)_2 \cdot acac$	(IV)	$\Delta v_a = \Delta v_o^{ave}(1-x/2)(1-(b+d)) = \Delta v_b$ $\Delta v_c = \Delta v_o^{acac}(1+x)(1+2(b+d))$
c-$V(tfac)_2 \cdot acac$	(V)	$\Delta v_a = \Delta v_o^{ave}(1+x/2)(1-(a+e)) = \Delta v_b$ $\Delta v_c = \Delta v_o^{acac}(1-x)(1+2(a+e))$
c'-$V(tfac)_2 \cdot acac$	(VI)	$\Delta v_a = \Delta v_o^{ave}(1+y-x)(1-(a+e))$ $\Delta v_b = \Delta v_o^{ave}(1-y)(1-(b+d))$ $\Delta v_c = \Delta v_o^{acac}(1+x)(1+(a+e)+(b+d))$
c-$V(tfac)_3$	(VII)	$\Delta v_a = \Delta v_o^{ave}(1)(1) = \Delta v_c = \Delta v_b$
t-$V(tfac)_3$	(VIII)	$\Delta v_a = \Delta v_o^{ave}(1-y)(1+(a+e)-(b+d))$ $\Delta v_b = \Delta v_o^{ave}(1+y-x)(1)$ $\Delta v_c = \Delta v_o^{ave}(1+x)(1-(a+e)+(b+d))$

Table 4-7. Continued.

t-V.acac.tfac.hfac (IX)	$\Delta v_a=\Delta v_o^{ave}(1+y-x)(1+0)$ $\Delta v_b=\Delta v_o^{hfac}(1-y)(1-(a+e)-2(b+d))$ $\Delta v_c=\Delta v_o^{acac}(1+x)(1+(a+e)+2(b+d))$
c-V.acac.tfac.hfac (X)	$\Delta v_a=\Delta v_o^{ave}(1+y-x)(1+0)$ $\Delta v_b=\Delta v_o^{hfac}(1-y)(1-2(a+e)-(b+d))$ $\Delta v_c=\Delta v_o^{acac}(1+x)(1+2(a+e)+(b+d))$
c-V(tfac)$_2$.hfac (XI)	$\Delta v_a=\Delta v_o^{ave}(1+x)(1+(b+d))$ $\Delta v_b=\Delta v_o^{a}ve(1+y-x)(1+(a+e))$ $\Delta v_c=\Delta v_o^{hfac}(1-y)(1-(a+e)-(b+d))$
c-V tfac)$_2$.hfac (XII)	$\Delta v_a=\Delta v_o^{ave}(1-x/2)(1+a+e)=\Delta v_b$ $\Delta v_c=\Delta v_o^{hfac}(1+x)(1-2(a+e))$
t-V(tfac)$_2$.hfac (XIII)	$\Delta v_a=\Delta v_o^{ave}(1+x/2)(1+b+d)=\Delta v_b$ $\Delta v_c=\Delta v_o^{hfac}(1-x)(1-2(b+d))$
V(hfac)$_2$.acac (XIV)	$\Delta v_a=\Delta v_o^{hfac}(1-x/2)(1-(a+e)-(b+d))=\Delta v_b$ $\Delta v_c=\Delta vo^{acac}(1+x)(1+2(a+e)+2(b+d))$
V(hfac)$_2$tfac (XV)	$\Delta v_a=\Delta v_o^{ave}(1+y)(1+(a+e)+(b+d))$ $\Delta v_b=\Delta v_o^{hfac}(1+y-x)(1-(a+e))$ $\Delta v_c=\Delta v_o^{hf}ac(1-x)(1-(b+d))$

Table 4-8. Substituent parameters of different systems.

System	CH_3	CF_3	CH
V(III)/acac/tfac/hfac	a=-0.102 b=+0.135 c=+0.262 d=+0.126 e=+0.125	a=+0.160 b=-0.113 c=-0.125 d=-0.025 e=+0.046	a+e=0.00 b+d=0.18
V(III)/acac/Ø-ac/Ø-Ø	a=+0.132 b=-0.026 c=-0.038 d=-0.012 e=-0.034	-	-
V(III)/Ø-Ø/tfØ/hfac	-	a=+0.127 b=-0.065 c=-0.126 d=-0.020 e=+0.016	a+e=0.07 b+d=0.18

Table 4-9.

d orbital population factors of V(III)/acac/tfac/hfac.

Compound number[1]	CH_3 shifts			CF_3 shifts			CH shifts		
	d_{xy}	d_{xz}	d_{yz}	d_{xy}	d_{xz}	d_{yz}	d_{xy}	d_{xz}	d_{yz}
I	.00	.00	.00	.00	.00	.00	.00	.00	.00
II	-.10	+.05	+.05	-	-	-.02	-.04	+.02	+.02
III	+.12	-.06	-.06	+.15	-.075	-.075	+.30	-.15	-.15
IV	-.12	+.06	+.06	-.12	+.06	+.06	-.31	+155	+.155
V	+.004	-.002	-.002	.004	-.002	-.002	+.17	-.085	-.085
VI	-.03	-.03	+.06	-.02	-.02	+.04	-.13	-.10	+.23
VII	.00	.00	.00	.00	.00	.00	.00	.00	.00
VIII	-.07	+.04	+.03	-.05	+.03	+.02	-.195	+.33	-.135
IX	-.08	+.03	+.05	-.07	+.03	+.04	-.25	-.19	+.44
X	-.04	+.02	+.02	-.02	+.01	+.01	-.018	-.016	+.034
XI	+.01	-.02	+.01	+.04	-.08	+.04	+.13	-.25	+.12
XII	-.006	+.003	+.003	-.13	+.065	+.065	-.01	+.005	+.005
XIII	+.12	-.06	-.06	+.08	-.04	-.04	+.11	-.055	-.055
XIV	+.06	+.06	-.12	+.06	+.06	-.12	+.17	+.17	-.34
XV	-	-	+.014	+.028	-.014	-.014	+.38	-.24	-.14
XVI	.00	.00	.00	.00	.00	.00	.00	.00	.00

1. Refer to figure 4-1 with X= CH_3 , Y= CF_3

Table 4-10. CH_3 shifts of V(III)/acac/Ø-ac/Ø-Ø system.

Compound	Calculated shifts(hz)	Experimental shifts(hz)
V(acac)$_3$	:-4208	:-4208
V(acac)$_2$.Ø-ac	A :-4170 B :-4187 C :-4716 D :-4115 E :-4017	A :-4180 B :-4200 C :-4780 D :-4010 E :-4017
V(acac)$_2$.Ø-Ø	A=B:-3960 C=F:-4272	A=B:-3914 C=F:-4230
c-V(Ø-ac)$_3$	:-4494	:-4480
t-V(Ø-ac)$_3$	A :-4995 B :-4314 E :-4316	A :-4908 B :-4476 E :-4380
V(Ø-Ø)$_2$.acac	D=E:-3724	D=E:-3706
V(Ø-Ø)$_2$.Ø-ac	F :-4322	F :-4280

Table 4-11

d orbital population factors of V(III)/acac/Øac/Ø-Ø system.

Compound[1]	CH$_3$ shifts		
	d$_{xy}$	d$_{xz}$	d$_{yz}$
V(acac)$_3$	.00	.00	.00
V(acac)$_2$.Ø-ac	+.03	-.01	-.02
V(acac)$_2$.Ø-Ø	-.16	+.08	+.08
c-V(Ø-ac)$_3$	.00	.00	.00
t-V(Ø-ac)$_3$	+.12	-.23	+.11
V(Ø-Ø)$_2$.acac	+.33	-.165	-.165
V(Ø-Ø)$_2$.Ø-ac	-.01	+.005	+.005
V(Ø-Ø)$_3$	.00	.00	.00

1. Refer to figure 4-1 with X = Ø , Y = CH$_3$

Table 4-12. CF_3 shifts of V(III)/Ø-Ø/tf-Ø/hfac system.

Compound[1]	Calculated shifts(hz)	Expt'al shifts(hz)
V(Ø-Ø)$_3$	-	-
V(Ø-Ø)$_2$.tf-Ø	F :-3909	F :-3900
V(Ø-Ø)$_2$.hfac	D=E:-3674	D=E:-3660
t-V(Ø-Ø)(tf-Ø)$_2$	C=F:-3957	C=F:-3962
c-V(Ø-Ø)(tf-Ø)$_2$	A=B:-4515	A=B:-4454
c'-V(Ø-Ø)(tf-Ø)$_2$	B :-4465 F :-4407	B :-4440 F :-4014
c-V(tf-Ø)$_3$	:-4221	:-4252
t-V(tf-Ø)$_3$	C :-4198 D :-4908 F :-3701	C :-4274 D :-4859 F: :-3720
c'-V(tf-Ø)$_2$.hfac	B :-3794 D :-4406 E :-4672 F :-4695	B :-3680 D :-4376 E :-4666 F :-4736
c-V(tf-Ø)$_2$.hfac	C=F:-3890 D=E:-5206	C=F:-3990 D=E:-5076
t-V(tf-Ø)$_2$.hfac	A=B:-4215 D=E:-4023	A=B:-4230 D=E:-4048
V(hfac)$_2$(Ø-Ø)	A=D:-4461 E=F:-4593	A=D:-4524 E=F:-4612
V(hfac)$_2$.tf-Ø	A :-4060 B:-4720 C :-4981 D:-4331 E :-4174	A :-4020 B:-4974 C :-5100 D:-4320 E :-4046
V(hfac)$_3$	:-4510	:-4510

1. refer to figure 4-1 with X = Ø , Y = CF_3

Table 4-13. CH shifts of V(III)/Ø-Ø/tf-Ø/hfac system.

Compound[1]	Calculated shifts(hz)	Expt'al shifts(hz)
V(Ø-Ø)$_3$	:-3694	:-3694
V(Ø-Ø)$_2$.tf-Ø	A :-2462 B:-3873 C :-4881	A :-2420 B:-3853 C :-4828
V(Ø-Ø)$_2$.hfac	A=B:-5218 C:-1381	A=B:-5140 C:-1240
t-V(tf-Ø)$_2$.Ø-Ø	A=B:-2647 C:-6179	A=B:-2653 C:-6190
c-V(tf-Ø)$_2$.Ø-Ø	A=B:-3800 C:-3200	A=B:-3860 C:-3260
c'-V(tf-Ø)$_2$.Ø-Ø	A :-3596 B:-2542 C :-4970	A :-3580 B:-2550 C :-4970
c-Vtf-Ø)$_3$	:-3648	:-3513
t-V(tf-Ø)$_3$	A :-2142 B:-4049 C :-4980	A :-2115 B:-4015 C :-4925
c'-V(tf-Ø)$_2$.hfac	A :-5466 B :-3396 C :-2408	A :-5426 B:-3306 C :-2448
c-V(tf-Ø)$_2$.hfac	A=B:-3708 C:-3532	A=B:-3766 C:-3557
t-V(tf-Ø)$_2$.hfac	A=B:-4821 C:-1817	A=B:-5266 C:-2074
V(hfac)$_2$.Ø-Ø	A=C:-2646 B:-6150	A=C:-2636 B:-6165
V(hfac)$_2$.tf-Ø	A :-5289 B:-3993 C :-2112	A :-5244 B:-3974 C :-2062
V(hfac)$_3$	:-3734	

1. Refer to figure 4-1 with X=Ø , Y=CF_3

Table 4-14.

d orbital population factors of V(III)/Ø-Ø/tf-Ø/hfac system.

Compound[1]	CF_3 shifts			CH shifts		
	d_{xy}	d_{xz}	d_{yz}	d_{xy}	d_{xz}	d_{yz}
V(Ø-Ø)$_2$.tf-Ø	-	-	-.07	-.12	+.10	+.02
V(Ø-Ø)$_2$.hfac	+.46	-.23	-.23	+.26	-.13	-.13
t-V(tfØ)$_2$.Ø-Ø	-.18	+.09	+.09	-.23	+.115	+.115
c-V(tfØ)$_2$.Ø-Ø	+.005	-.0025	-.0025	+.24	-.12	-.12
c'-V(tfØ)$_2$.Ø-Ø	-.03	-.01	+.04	-.09	-.06	+.15
c-V(tf-Ø)$_3$	.00	.00	.00	.00	.00	.00
t-V(tf-Ø)$_3$	-.11	+.07	+.04	-.23	+.34	-.11
c'-V(tfØ)$_2$.hfac	+.04	-.08	+.04	+.14	-.27	+.13
c-V(tfØ)$_2$.hfac	-.02	+.01	+.01	-.10	+.05	+.05
t-V(tfØ)$_2$.hfac	+.05	-.025	-.025	+.24	-.12	-.12
V(hfac)$_2$.Ø-Ø	+.04	+.04	-.08	+.055	+.055	-.11
V(hfac)$_2$.tf-Ø	+.03	-.02	-.01	+.31	-.16	-.15
V(hfac)$_3$	.00	.00	.00	.00	.00	.00

1. Refer to figure 4-1 with X= Ø , Y= CF_3.

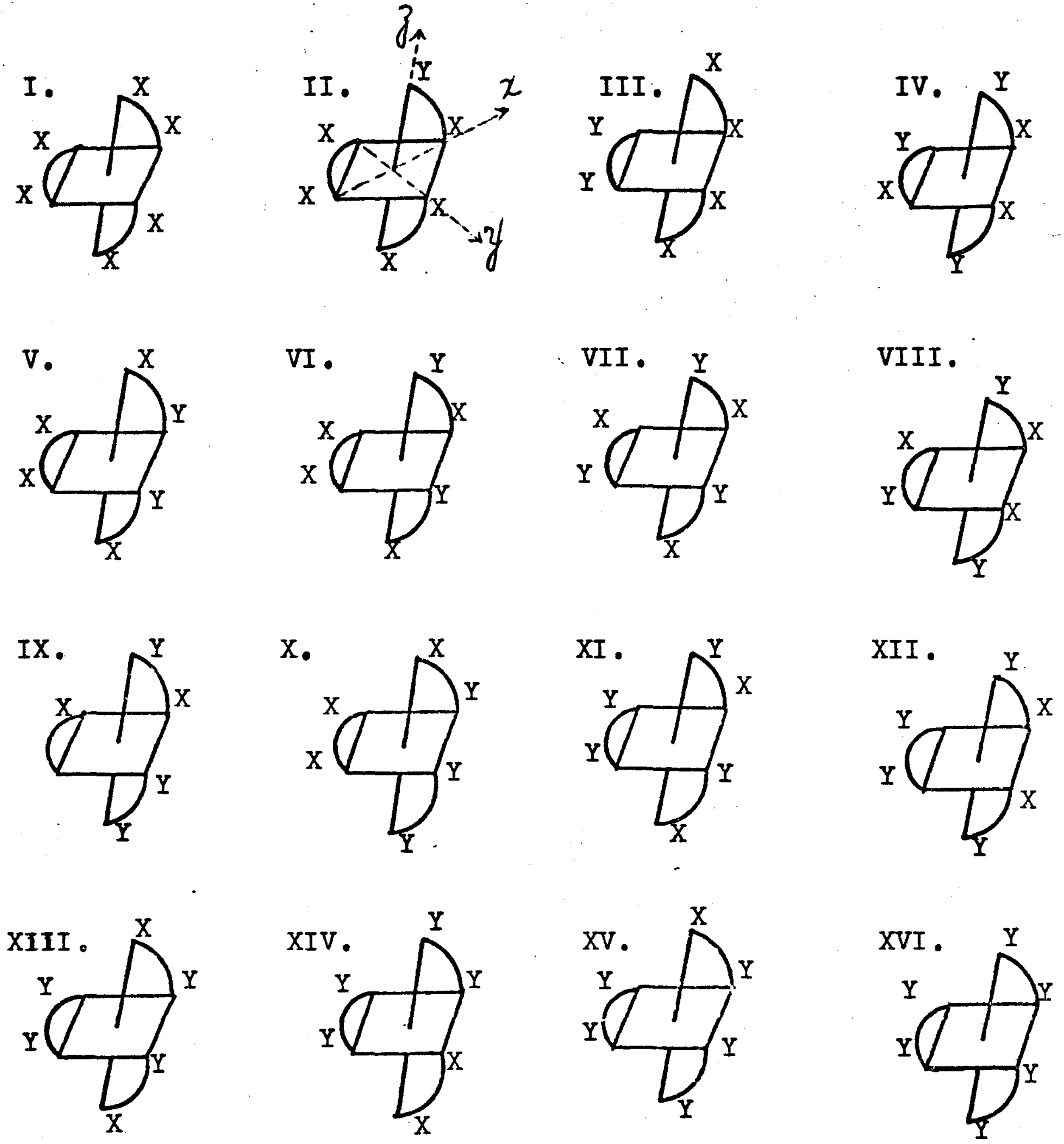


Figure 4-1. 16 possible isomers.

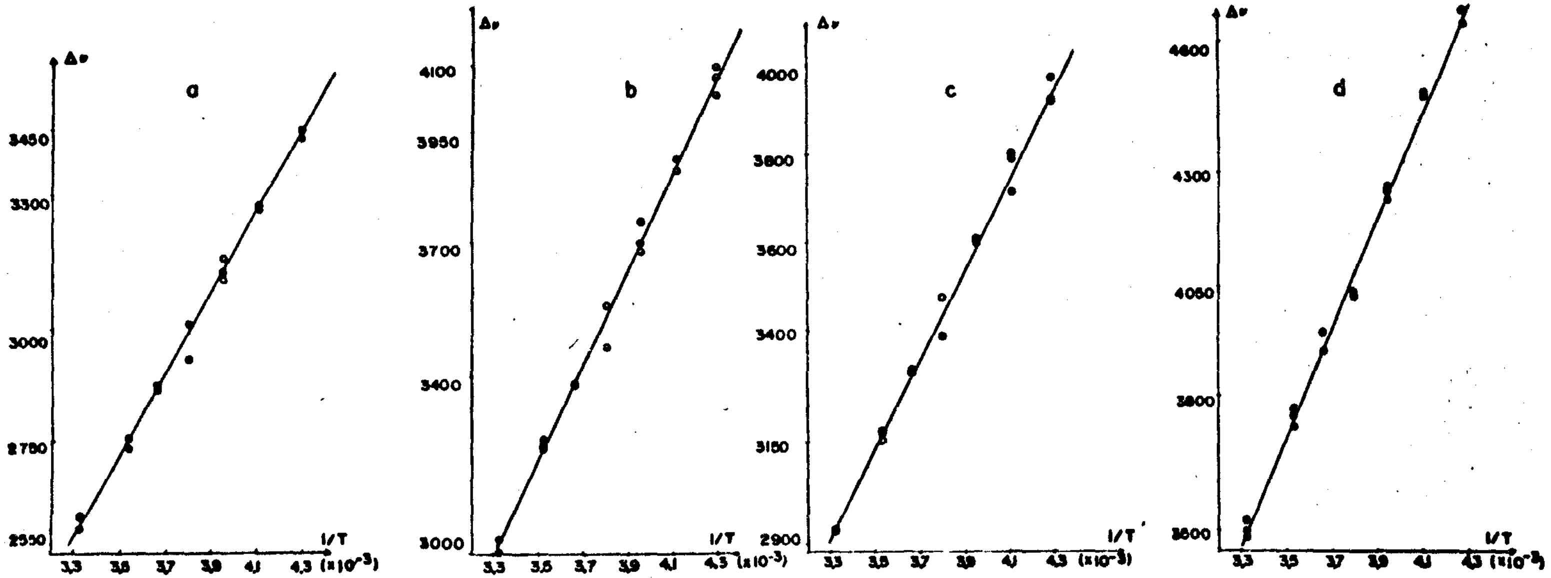


Fig.4-2. Temperature dependence of contact shifts: (a), CH_3 group of $V(acac)_3$; (b) and (c), CH_3 groups of $V(acac)_2(hfac)$; (d), CH_3 group of $V(acac)(hfac)_2$.

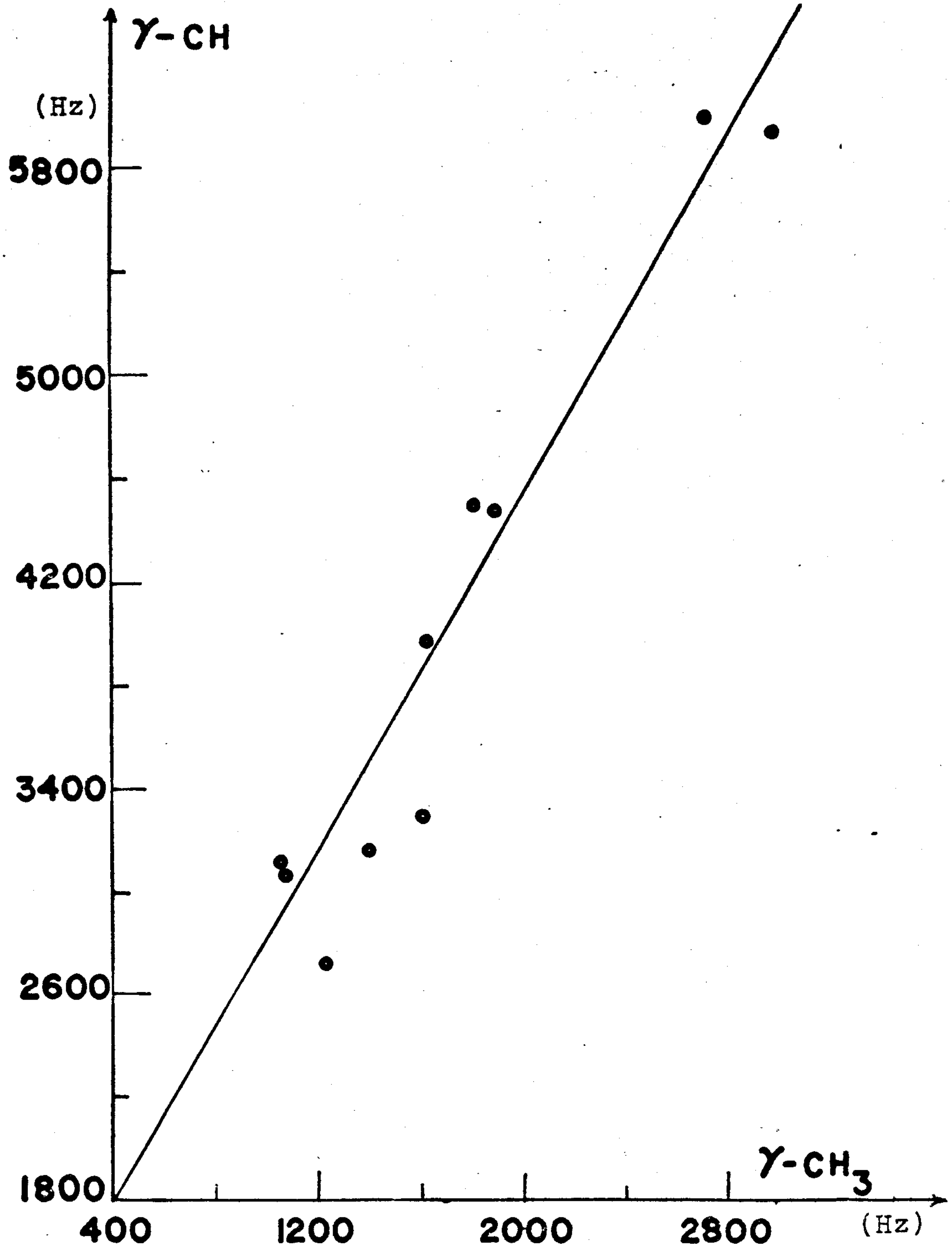
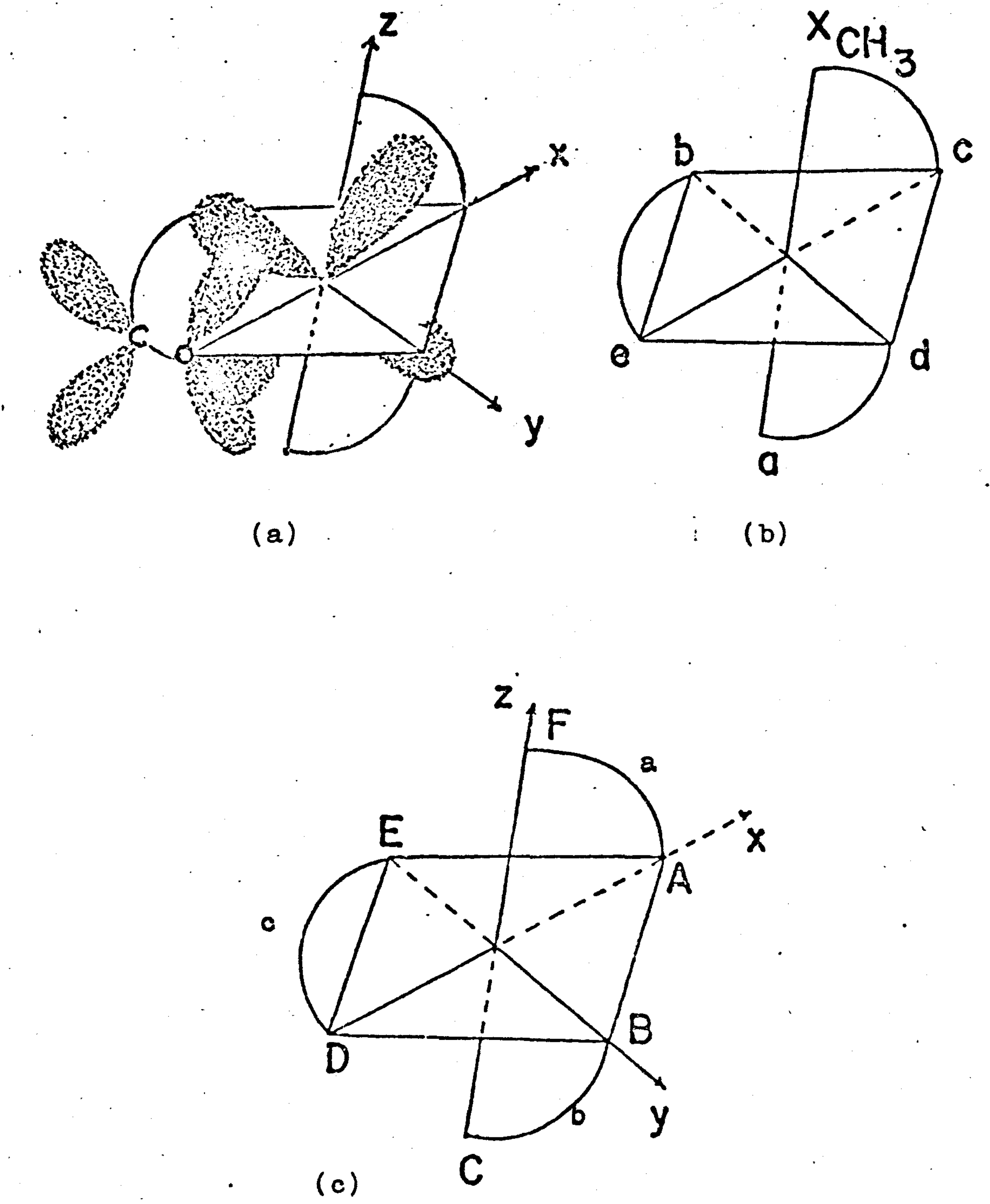


Figure 4-3. γ-CH versus γ-CH$_3$ shifts.



(a) (b)

(c)

Figure 4-4. (a) d_{xz}-p_{π} overlap. (b) Substituent parameters (c) Labels for non-equivalent groups.

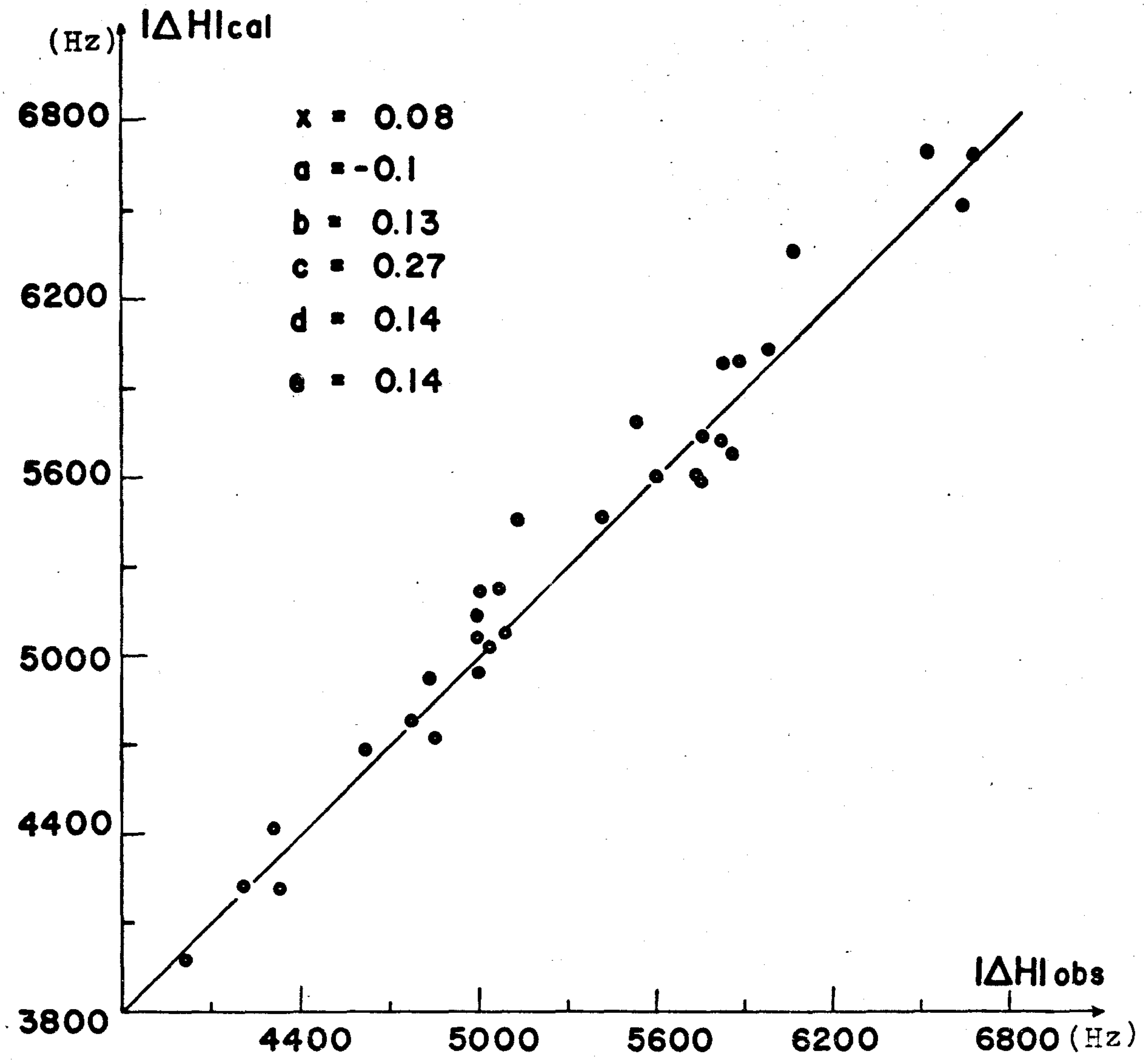


Figure 4-5. CH_3 plot of Cal. versus Expt. shift for a fixed x of V(III)/acac/tfac/hfac system.

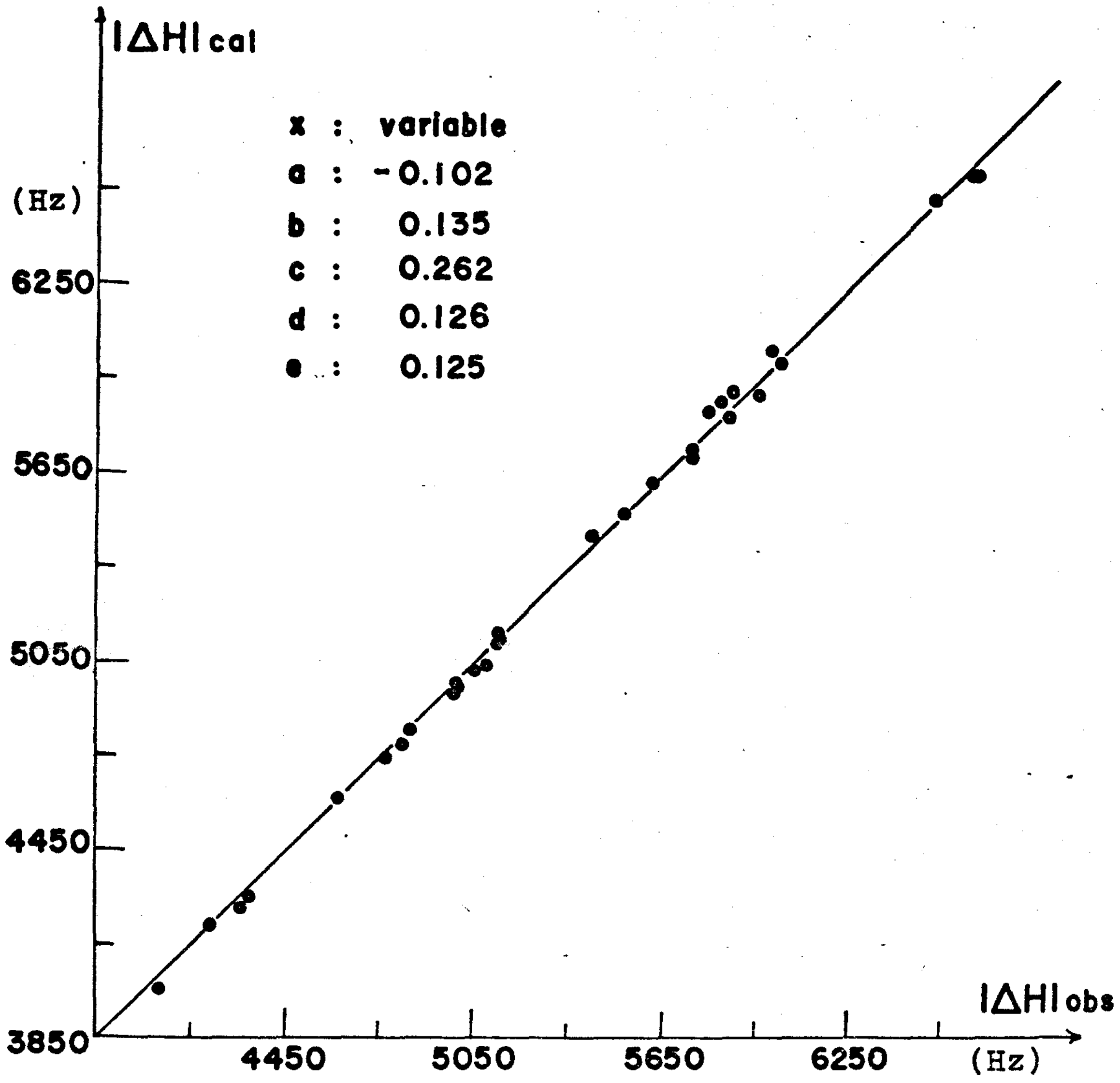


Figure 4-6. CH_3 plot of Cal. versus expt. shifts for variable x of V(III)/acac/tfac/hfac system.

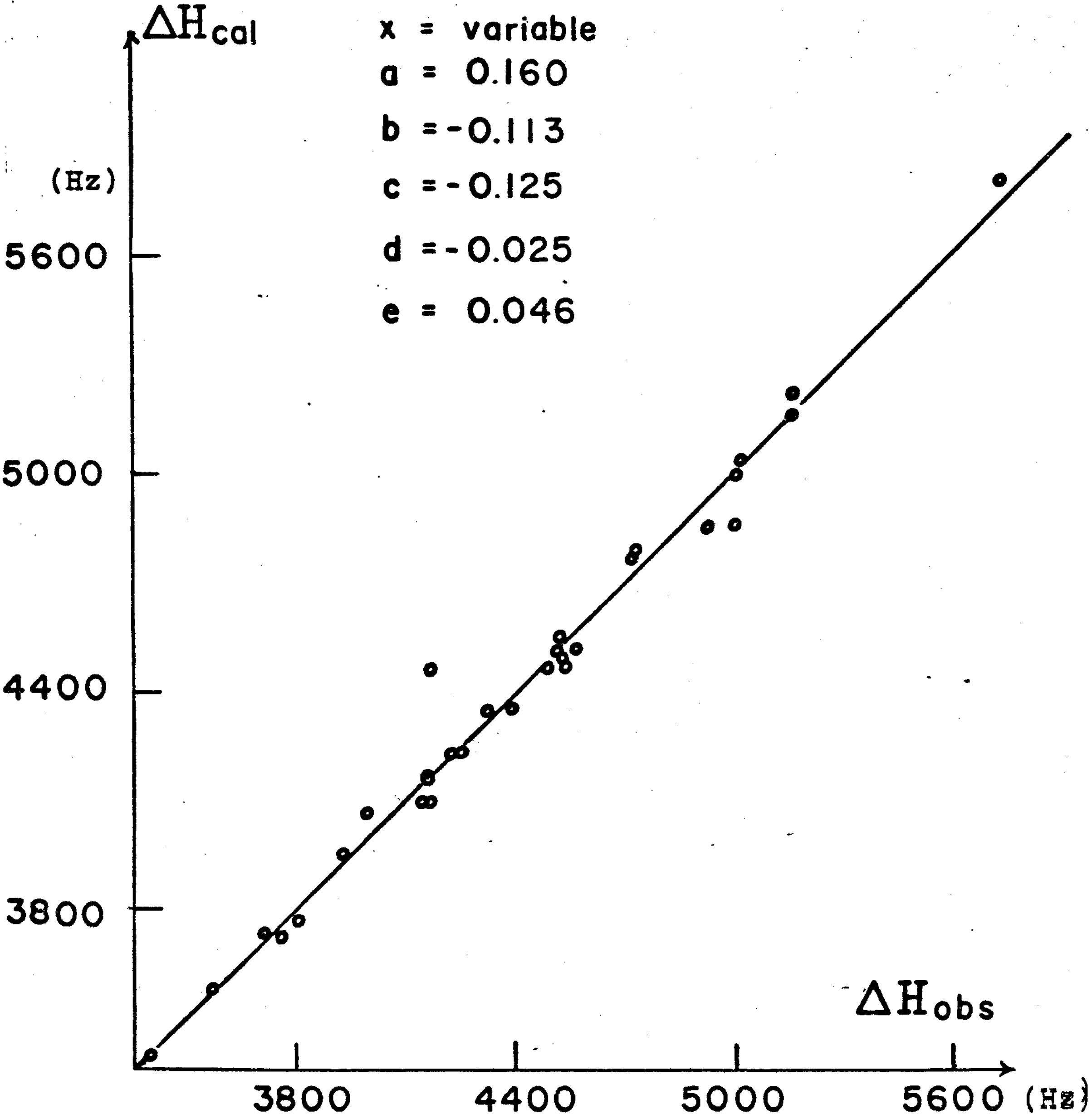


Figure 4-7. CF_3 plot of cal. versus expt. shifts for a variable x of V(III)/acac/tfac/hfac system.

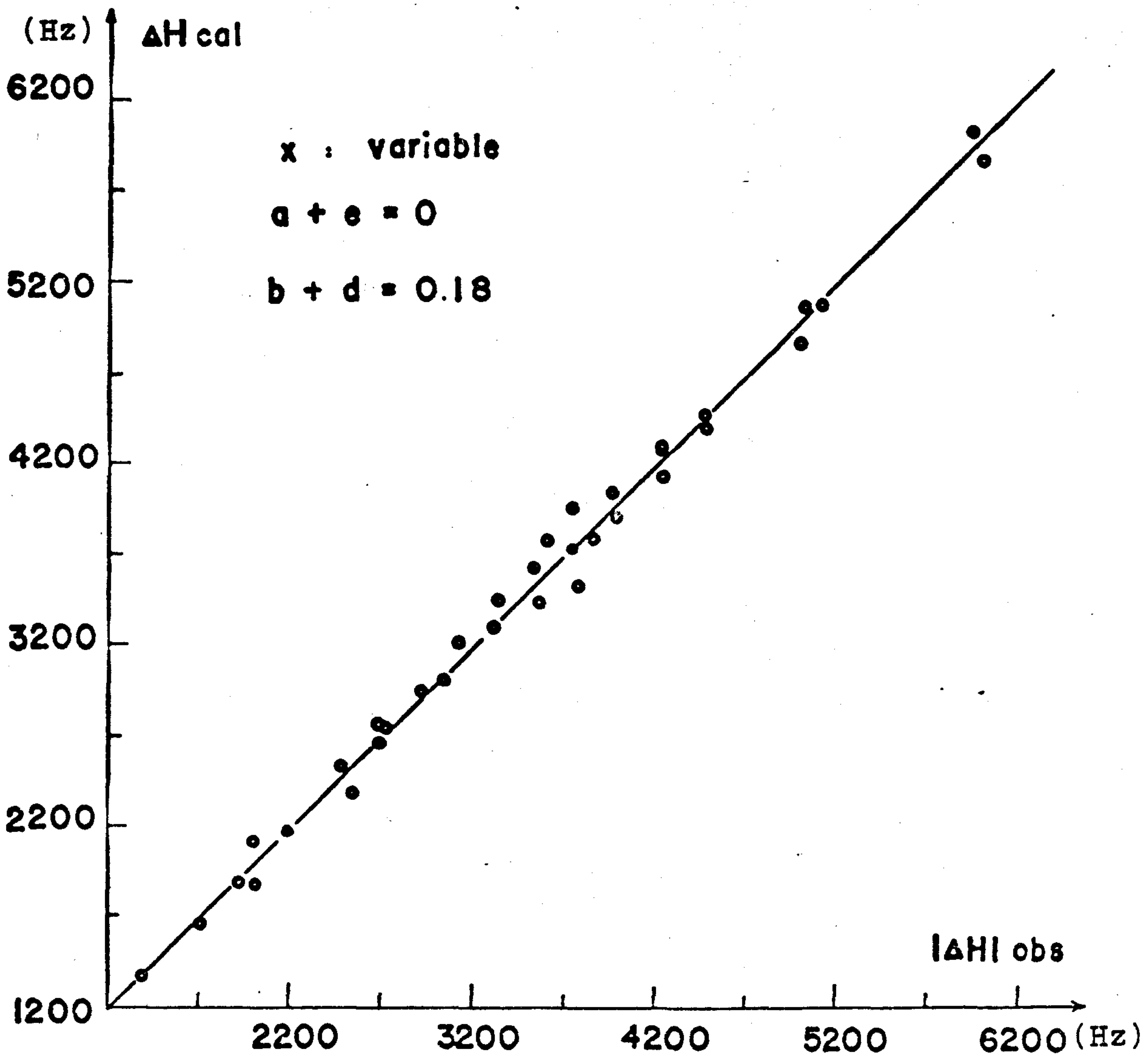


Figure 4-8. CH plot of cal. versus expt. shifts for a variable x of V(III)/acac/tfac/hfac system.

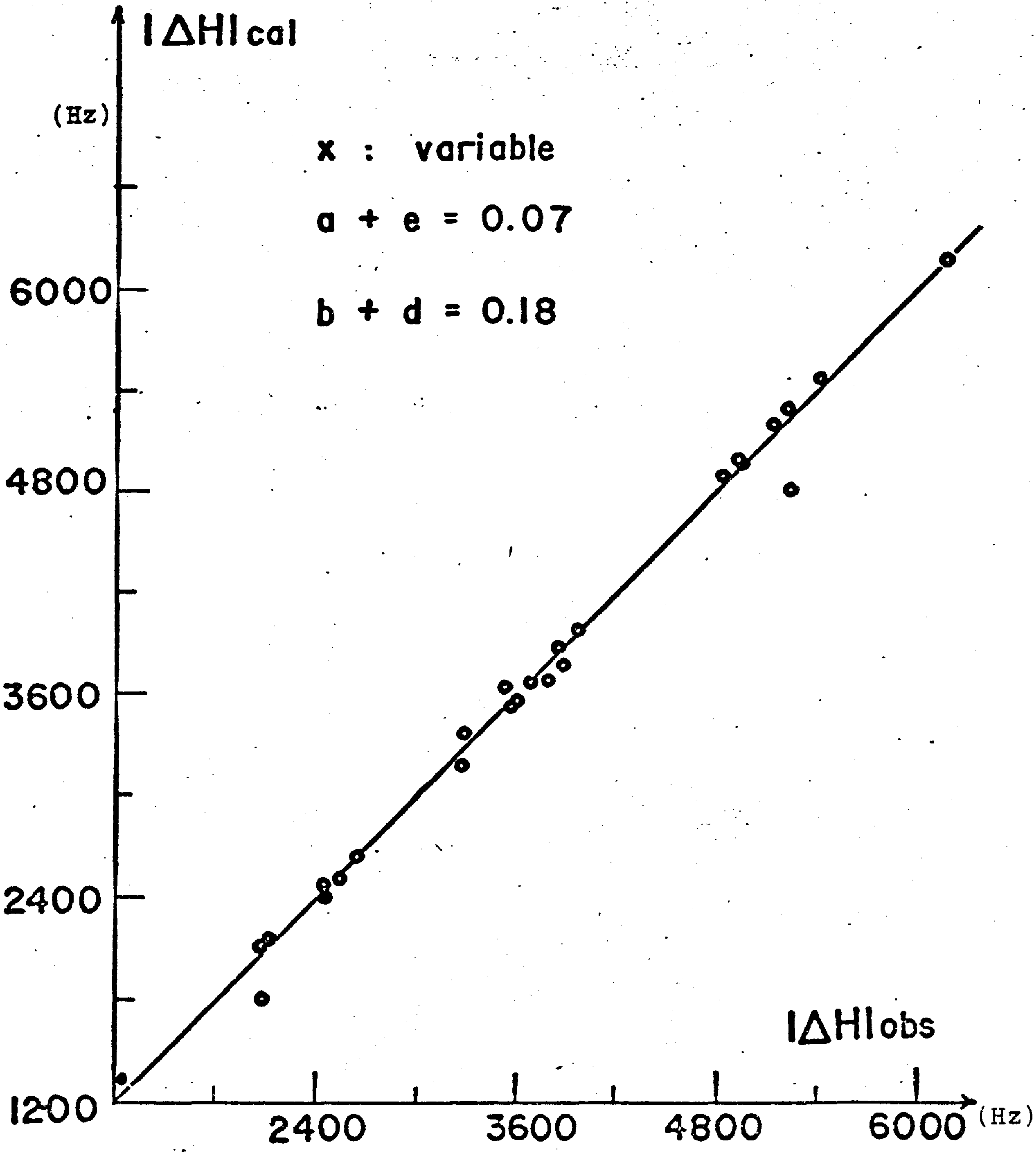


Figure 4-9. CH plot of cal. versus expt. shifts for a variable x of V(III)/Ø-Ø/tf-Ø/hfac system.

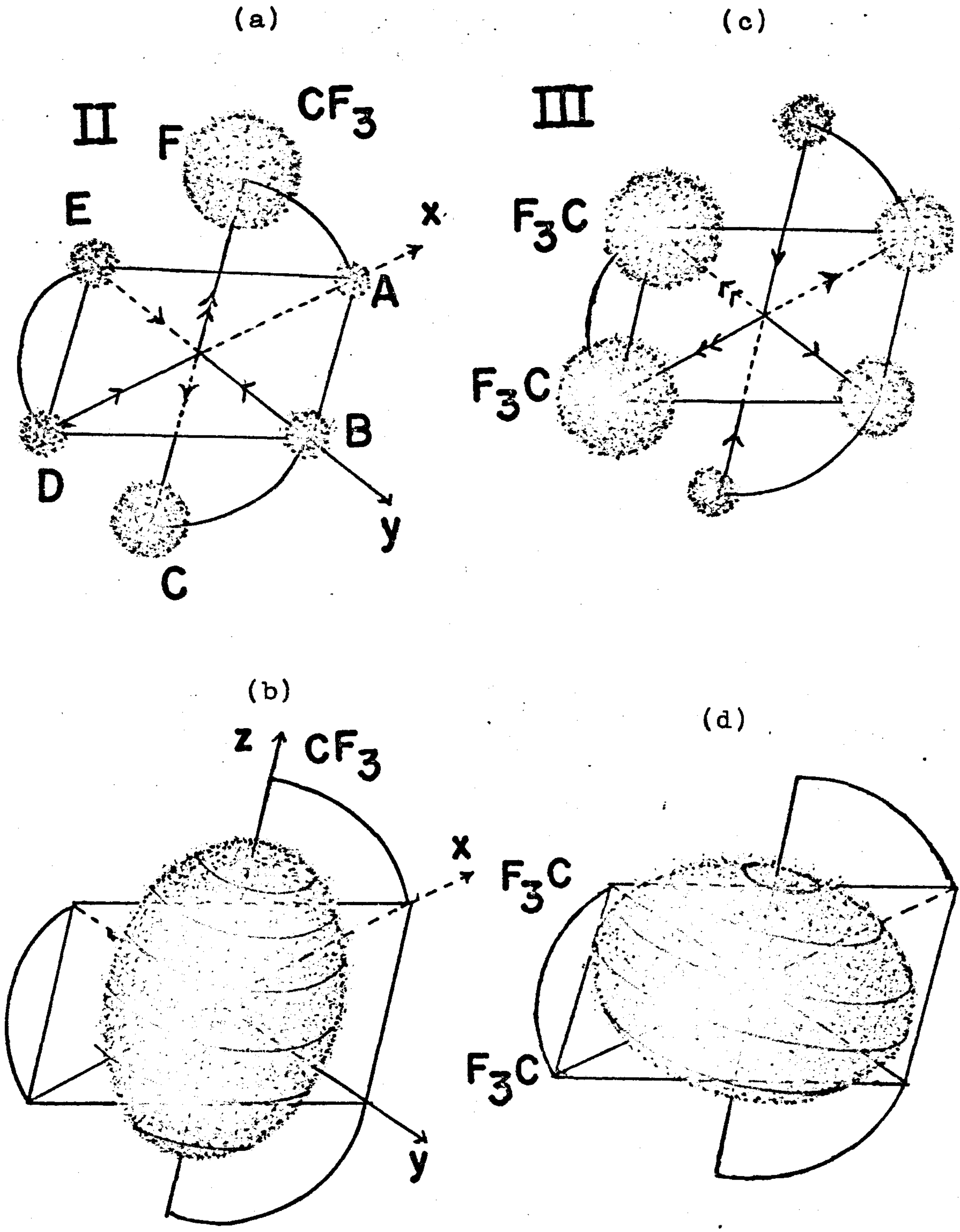


Figure 4-10.(a): σ charge distribution of complex II
(b): π charge polarization of complex II
(c): σ Charge distribution of complex III
(d): π Charge polarization of complex III

5. Di-Adducts of Bis-β-Diketonato Cobalt(II) System.

Preliminary.

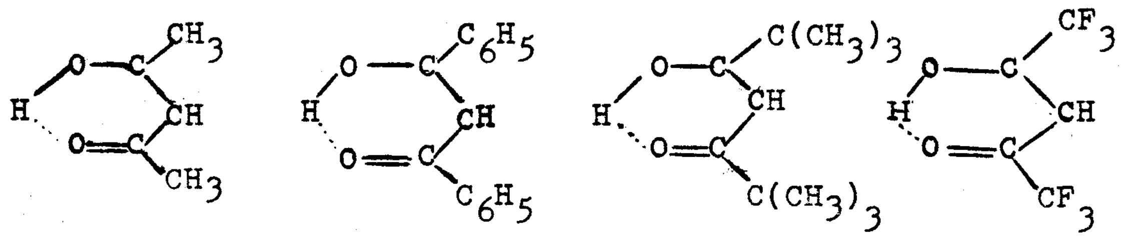
The sensitivity of NMR isotropic shifts in paramagnetic compounds and its application to the studies of transmission of substituent effects in complexes with mixed ligands has been discussed in the previous chapter. Related studies have been reported involving octahedral complexes of Cr(II)[73] and tetrahedral complexes of Ni(II)[44,47]. The detailed interpretation of the results has varied in different cases but all shown the common feature that the effects observed have been attributed to contact rather then dipolar interactions. In principle, the introduction of a substituent in a metal complex can induce a change in the magnetic anisotropy of a molecule and hence cause dipolar shifts. If large, such an effect could invalidate interpretations based on contact mechanisms. It seemed worthwhile to investigate the magnitude of such dipolar shifts by choosing to work with complexes in which magnetic anisotropy is expected to be present. Such a study would at least provide an indication of the errors which could arise from the neglect of dipolar interactions in other systems. The work contained in this chapter provides some results in this area.

Distorted octahedral complexes of Co(II) are known to possess large magnetic anisotropies and therefore to exhibit dipolar shifts.[53] Complexes of stoichiometry Co(acac)$_2$L$_2$ (acac acetylactonate, and L=a variety of monodentate ligands) have been extensively studies.[39,41,56,57,68] Most of these studies have been concerned with the isotropic shifts of protons on the ligands, L. LaMar[61] however has reported large differences in the acac shifts with changes in the ligand L. He concluded that these changes were dipolar in origin. Comparison of the shifts of the protons on L with those on the acac ligand lead to the conclusion that the species in solution had distorted octahedral geometry with the L ligands occupying trans-positions. The shifts of the acac protons were interpreted as arising from a combination of dipolar and contact effects and a series of ligands L was presented in which the contact contribution becomes progressively more dominant. More recently Horrocks and Hall[70] have measured the anisotropy of the magnetic susceptibility of a single crystal of the compound in which L= pyridine and used this data to calculate the dipolar contribution to the isotropic NMR shifts. Their conclusions are consistent with the interpretation presented by LaMar.

5-1. Results.

In the present experiments the intent was to investigate the effect of making a substituent change on one of the β diketone ligands on the isotropic shifts of the other β diketone. By using different mono-dentate ligands L we hoped to vary the proportions of the dipolar and contact contributions to the isotropic shifts and hence deduce whether the substituent changes are predominantly dipolar or contact in origin. It was first necessary to measure the shifts for several symmetric chelates with different substituents on the β diketone. Each chelate was examined with several different axial ligands L. These results are presented in Table 5-1. We then proceeded to examine the mixed chelates to ascertain the substituent effects. Results for mixed chelates are given in Table 5-2.

The β diketone ligands involved in this study have the following structures:



Co(II) chelates of β diketone ligands tend to be polymeric in non-coordinating solvents such as chloroform. This is manifested by the appearance of a complex NMR spectrum. However in coordinating solvents a two line spectrum appears which is assigned to octahedral species such as Co(acac)$_2$L$_2$. With excess of ligand L this is the only species present. Excess can be assured by using L as the solvent. A number of difficulties restricted the systems available for study. For some of the complexes the lines are exceedingly broad. This is particularly true for compounds in which the β diketone has trifluoromethyl substituents. LaMar [61] noted similar linewidth variations, though not so pronounced, and suggested that they arose from varying electron spin relaxation times due to spin orbit interaction with low lying excited states. Relatively slow exchange with ligand L is also possible. Measurement of the temperature dependence of the shifts revealed some deviations from Curie law below -25°C which could be due to slowing down of the fast exchange between free and complex axial ligands. However we would not disagree with LaMar's explanation of the linewidth effects. Measurements in some solvents were also limited by oxidation of the complexes.

5-2. Discussion.

Although the data available is limited we are able to arrive at a relatively unambiguous conclusion regarding the importance of dipolar effects. It is apparent from the results in Table 5-2 that significant substituent effects are observed in some , but not all, cases.

Mixed complexes involving ligands Hacac and HØ-Ø, Hacac and HMe_3C-CMe_3, Hacac and Hhfac and HØ-Ø and HMe_3C-CMe_3 have been examined with L = pyridine and L = dimethylsulphoxide. Significant substituent shifts are observed in all cases with L = pyridine and in the last two cases with L = dimethylsulphoxide. It is not certain whether the inability to observe shifts in the remaining two cases is due to the shifts being too small to observe, to the resonances of the mixed chelates being too broad to observe, or to the failure to form mixed complexes. In cases where the shifts of two or more resonances on the same mixed chelate are observed they are in the same direction relative to the symmetric chelate, e.g. both the CH_3 and the CH resonances of ligand Hacac move to high field in the mixed complex with ligand Hhfac. The most significant observation though is that in each case , resonances on one ligand are shifted in the opposite direction to those on the other ligand in a mixed complex. Thus in the series of mixed complexes with L = pyridine the CH resonance of Hacac is shifted +146 Hz, +200 Hz and +360 Hz from its position in the symmetric $Co(acac)_2L_2$ for the cases in which the second ligand is H∅-∅, $HMe_3C\text{-}CMe_3$ or Hhfac respectively. Examination of the data in Table 5-1 and 5-2 reveals that this pattern holds throughout.

The pyridine ligands of $Co(acac)_2py_2$ are exchanging rapidly with free ligand in solution on the NMR time scale. It is therefore permissible [70] to neglect the orientation of the pyridine molecule with respect to the metal-nitrogen bond when considering the geometry of the $Co(acac)_2py_2$ molecule. Given that the complex has a trans configuration[61] the symmetry of the molecule is therefore D_{2h}. The magnetic susceptibility tensor has three principal axes uniquely defined by the symmetry axes of the molecule. If one of the acacs is replaced by hfac C_{2v} symmetry is retained. The elements of symmetry of the C_{2v} point group (a C_2 axis and two planes) suffice to define three principal axes for the magnetic susceptibility which are identical with those of $Co(acac)_2py_2$. The dipolar shift of a proton is given by the expression[70] (refer to figure 2-2).

$$\left(\frac{\Delta v}{v}\right)^D = -\frac{1}{3N}\left[\chi_z - \frac{\chi_x}{2} - \frac{\chi_y}{2}\right]\left(\frac{3\ \cos 2\theta - 1}{r^3}\right)_{av} - \frac{1}{2N}\left[\chi_x - \chi_y\right]\left(\frac{\sin^2\theta\ \cos\ 2\Omega}{r^3}\right)_{av} \quad \text{.........(5-1)}$$

In this expression θ and Ω are angles relating the position of the proton in question to the principal axes of the magnetic susceptibility tensor. The angular functions in this expression have identical values for the two CH protons of $Co(acac)_2L_2$ since they are equivalent by symmetry, Since both the positions of the CH protons and the directions of the principal axes are unchanged on passing to $Co(acac)(hfac)py_2$ it follows that the angular functions for the two CH protons of this mixed complex are also identical. Any change in the dipolar shift of the two protons resulting from a change in the magnetic anisotropy of the mixed chelate compared with the symmetric chelate must therefore be identical in sign and magnitude for both protons. This is clearly not the case, in fact in every compound examined the two protons in question shift in opposite directions. We deduce therefore that the substituent shifts are predominantly contact in origin and that any dipolar component, if present , is relatively small.

Given this conclusion it becomes valid to compare the present results with those previously reported [74,81] in chapter IV for V(III) complexes which were also interpreted assuming a contact mechanism. Octahedral Co(II) complexes have a T_1 ground state which splits to A and E states* on application of a tetragonal distortion. In the present case the A state is lower and is separated from the excited E state by the tetragonal distortion energy ξ . The V (III) complexes also have a non-degenerate ground state. The type of effects predicted [40] for mixed complexes arising from an orbitally degenerate ground state and with Cr(II) compounds [13] are not to be anticipated. Consider specifically the CH resonances which are common to all the ligands used. LaMar[61] suggested that the shift of this proton in the Co(II) complexes resulted from the combination of a downfield dipolar shift and an upfield contact shift with the dipolar shift becoming progressively less important as the tetragonal splitting ξ becomes larger. In the A ground state of the molecule the unpaired electrons occupy the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals. The results in Table 5-1 show that the CH shifts of the symmetric complexes with ligands HØ-Ø, HMe_3C-CMe_3 and Hhfac are all to high field of those for

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* The E state maybe further split if the symmetry is D_{2h} rather than D_{4h} .

ligand Hacac with the same axial ligand L (the shift for $Co(acac)_2$ in CD_3CN appear to be anomalous in this respect) and hence we deduce that ξ is larger for these ligands and that mixing of the A state with excited states through spin-orbit coupling less important. If we consider only the ground state configuration direct delocalization of spin to the π orbitals of the β diketonate ligand cannot occur since none of the spin containing orbitals $\left(d_{xy}, d_{x^2-y^2} \text{ or } d_{z^2}\right)$ have the correct symmetry to mix with the π orbitals of ligands in the xy plane. If the spin is in the π system, as the most recent analyses has concluded [75], an indirect or polarization mechanism must be involved. According to the model originally proposed by Orgel [23] such a mechanism will lead to a preference for electrons of α spin in the d_{xz}, d_{yz} orbitals and a corresponding preponderance of β spin delocalized to the ligands. The situation in the V (III) complexes is exactly the opposite with the unpaired electrons being contained in d orbitals with the correct symmetry to interact with ligand π orbitals leading to α spin delocalization. In this manner the opposite signs of the contact shift in the two cases may be rationalized.

Consider now the results for the mixed complexes contained in Table 5-2. In the V(III) case in mixed complexes of acac and hfac, the CH of the acac is shifted to low field and that of the hfac to high field [74]. In the Co(II) case, the acac resonance moves to high field and the hfac resonance to low field. If α spin delocalization is involved in the first case and β spin delocalization in the second case the results are clearly equivalent. Our analysis of the V(III) system involved two factors; the first dependent on the populations of the various spin containing d orbitals and the second on the ability of a ligand oxygen to accept an electron, i.e. on its charge. These factors usually acted in concert to enhance the shifts. In the Co(II) case the first factor is inapplicable since the interacting d orbitals are in all cases fully populated. The second factor however remains operative and reflects the movement of charge in the σ-system brought about by substituent changes on other ligands. It may be significant that the substituent shifts are on the whole smaller in the Co(II) compounds than in the V (III) compounds. The implication is that they cannot be amplified by changes in d orbital populations.

5-3. Remarks.

It would not be advisable to extend this analysis in a quantitative manner. It suffers from all the limitations discussed previously in the V (III) case plus the added complications that dipolar effects, although not predominant, may still be of some importance. The significant point is perhaps the observation of substituent effects of the same type as those previously observed in V (III) complexes in a system involving a different metal and a different delocalization mechanism. We would suggest that such effects may be of quite general importance in transition metal chemistry and that isotropic NMR shifts may provide a very convenient probe.

Table 5-1

Isotropic NMR shifts[1] of Symmetric Co(II) Complexes.

Compound		Solvent L			
Co(XCO.CH.COX)$_2$L$_2$	Group	Pyridine	CD$_3$CN	DMSO	Dioxane
X = CH$_3$	CH$_3$	-2518	-878	-1992	-
	CH	-2151	-656	- 7	-
X = C$_6$H$_5$	Ortho	-2629	-2369	-2294	-
	Meta	- 886	- 856	- 812	-
	para	-564	- 614	- 474	-
	CH	-1390	-1645	80	-
X = C(CH$_3$)$_3$	C(CH$_3$)$_3$	-1740	-1190	-1290	-
	CH	-1316	- 671	1461	-
X = CF$_3$	CF$_3$	-3400	-4065	-3279	-3092
	CH	2460	- 274	2536	3582

1. Shifts in Hz at 100 MHz 37°C.

Table 5-2. Isotropic NMR shifts[1] of Mixed Co(II) Complexes.

Compound Co(XCOCHCOX)(YCOCHCOY)L_2	group	L= Pyridine	L= DMSO
X= CH_3 Y= C_6H_5	CH_3	-2454	a
	CH_X	-2005	
	CH_Y	-1674	
	ortho	-2704	
	meta	- 920	
	para	- 594	
X= CH_3 Y= $C(CH_3)_3$	CH_3	-	a
	CH_X	-1951	
	CH_Y	-2418	
	$C(CH_3)_3$	-1949	
X= C_6H_5 Y= $C(CH_3)_3$	$C(CH_3)_3$	-1850	-1538
	CH_X	-1724	948
	CH_Y	-	-
	ortho	-2478	-1834
	meta	- 864	- 669
	para	- 492	- 326
X= CH_3 Y= CF_3	CH_3	-2100	-1910
	CH_X	-1891	897
	CH_Y	901	1746
	CF_3	a	a

[1] Shifts in Hz at 100 MHz 37°C a. Not observed.

6. Second Coordination Sphere Studies of Transition Metal Complexes: Solvent Effects

The structure of the second or outer coordination sphere of metal complexes has been the subject of interest for many years, it obviously plays an important role in the understanding of the mechanisms of ligand exchange reactions. Earlier work [62,76,77] in this laboratory has ultilized the NMR isotropic shifts of the weak second coordination sphere complexes formed between coordinately saturated tris-pyrazolylborate Co(II) compound and other ligands present in solution . These studies have also been extended to include the structure of ion pairs formed by analogous tris-pyrazolylmethane complexes. The motivation underlying this research is the belief that the efficiency of ligand exchange processes depends intimately on the ability of a metal complex to hold incoming ligands in a second coordination sphere where they are readily available for further reaction. The efficiency of a sequence of such ligand exchange reactions determines the overall efficiency of homogeneous catalysis. The tris-pyrazolylborate Co(II) comprise a particularly favorable substrate system for studies of this kind since the strongly bonded tridentate ligands cannot be replaced by the monodentate ligands added which, if they are going to interact at all, can therefore only occupy positions in the second coordination sphere. Further, the large magnetic anisotropy of these Co(II) complexes give rise to dipolar shifts in the NMR spectra surrounding molecules and hence provides a probe to investigate the structure of such a second sphere. Previous stydies have demonstrated that anions tend to occupy positions close to the three-fold axis of the complex whereas neutral molecules such as aniline and pyridine are located perpendicular to this axis and have preferred orientations ehich may or may not be favourable for a subsequent ligand exchange reaction. It is apparent that the solvent plays a part in determining the detailed structure of the second sphere. Thus it was argued previously [77] that anions occupy positions on the symmetry axis because the more favourable positions perpendicular to the axis are preferentially taken by the dipolar solvent molecules. similarly the observed NMR shifts of neutral molecules depend strongly on the solvent used, indicating competition between added ligands and solvent molecules for the limited number of places in the second sphere. The present note reports some further studies with tris-pyrazolylborate Co(II) aimed at clarifying solvent effects.

The crux of the method used for studying second sphere structure lies in the equation [16]

$$\Delta v_o = - D \frac{(3\cos^2\theta-1)}{r^3} (g_{\parallel} - g_{\perp}) \quad \text{............(6-1)}$$

which relates the dipolar NMR shift of a magnetic nucleus to its position in space relative to the cobalt chelate.Unfortunately this equation (or more sophisticated versions thereof)[65] cannot be used directly since it is impossible to disentangle Δv_o from the equilibrium constant K of a reaction:-

$$X + L \rightleftharpoons XL$$

which determines the fraction of the ligand L complexed to the chelate X. Only the product $K\Delta v_o$ is experimentally accessible . This limitation determined the strategy of the present experiments. We wish to determine the relative tendencies of different solvents to occupy positions in the second sphere, i.e. the relative values of K for the above equilibrium. The direct approach would be to observe the dipolar shifts of the solvent molecules. Unfortunately not all solvents contain hydrogen or other nuclei suitable for NMR experiments and even if they do the observed shifts will depend on both K and Δv_o which will both vary from solvent to solvent. We have therefore adopted the procedure of measuring the extent to which a given solvent will displace a common ligand from the second coordination sphere.

Aniline was chosen as the common ligand and carbon tetrachloride as the common solvent. Previous results have shown that the aniline shifts are larger in carbon tetrachloride than in other solvents indicating that carbon tetrachloride has the least tendency to displace aniline from the second coordination sphere. Aliquots of solvent were therefore added to a standard solution of aniline plus Co(II) tris-pyrazolylborate in carbon tetrachloride and the NMR shifts of the aniline protons measured as a function of the concentration of added solvent. The frequency shifts obtained for the ortho-proton are collected in Table6-1. Other positions behave similarly but the shifts are somewhat smaller. In order to determine the isotropic shift due to the second sphere interaction, which is defined as the difference between free ligand frequency and complexed ligand frequency it is necessary to determine the aniline chemical shifts in the various solvent mixtures used. A plot of Δv_o versus the mole-fractions of various solvents is shown in figure 6-1. Consider the equilibria:

$$XS + L \rightleftharpoons XL + S \qquad K_1 \qquad \ldots\ldots\ldots(6\text{-}2)$$

and

$$XS + S' \rightleftharpoons XS' + S \qquad K_2 \qquad \ldots\ldots\ldots(6\text{-}3)$$

in which X represents the Co(II) complex, L is aniline, S is carbon tetrachloride and S' the added solvent. The observed NMR shift is the weighted average of the shift for complexed and that for free aniline, i.e.

$$\Delta v = \frac{[XL]}{[XL] + [L]}\,\Delta v_o \qquad \ldots\ldots\ldots\ldots\ldots(6\text{-}4)$$

where Δv_o is the frequency of the complexed aniline. Assuming the degrees of association of L and S' in equations (6-2) and (6-3) are small it may be readily shown that:

$$\Delta v = \frac{K_1 x}{S + K_1 x + K_1 l} \Delta v_o \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6\text{-}5)$$

and

$$\Delta v' = \frac{K_1 x}{S + K_1 x + K_1 l + K_2 S'} \Delta v_o \qquad \ldots\ldots\ldots\ldots\ldots\ldots(6\text{-}6)$$

where Δv is the aniline shift in the absence of a second solvent, $\Delta v'$ is the shift in the presence of the second solvent, x is the concentration of cobalt complex, l is the concentration of aniline, S is the concentration of carbon tetrachloride and S' that of the added solvent. Part of the difference between Δv and $\Delta v'$ is due to the dilution of the solution on adding the second solvent. It is therefore appropriate to compare the shift produced by adding the second solvent ($\Delta v'$) with that produced by adding an equal amount of Carbon tetrachloride ($\Delta v''$). Substitution in equation (6-6) together with the approximation that $S \gg S'$, x and l gives: (for CCl_4 , K_2 equals to 1)

$$\frac{\Delta v''}{\Delta v'} = 1 + (K_2 - 1)\frac{S'}{S} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6\text{-}7)$$

plots of $\Delta v''/\Delta v'$ versus the mole fraction of S' should therefore be linear with slopes equal to $(K_2 - 1)$, such plots are shown in figure 6-2 for several solvents and the resulting values of K_2 are collected in Table 6-2.

It is concluded from the data of Table 6-2 that the interactions responsible for binding in the second coordination sphere are essentially Van der Waals forces. The equilibrium constant clearly increases with the dipole moment of the ligand. Ligands for which hydrogen bonding with the nitrogen of the first sphere pyrazolyl ligands would be feasible do not appear to have anomalously high positions in the series. All of the non-polar molecules show a relatively small tendency to form second sphere complexes. Cyclohexane proves to be a somewhat worse second sphere ligand than carbon tetrachloride. The above conclusion is consistent with the values of 2-3 Kcal previously obtained for the enthalpy of formation of the aniline second sphere complex[62]. Perhaps the most significant point though is that the range of equilibrium constants obtained shows that there are very marked preferences for different molecules in the second coordination sphere, which must be reflected in the ease of substitution in the first sphere.

Table 6-1.

NMR shift of ortho-proton in a mixture of aniline and Co(II)-trispyrazolylborate.[1]

Solvent	Ortho-proton shift No. of moles of solvent				
Cyclohexane	-631.5 (.0)	-632.0 (.10)	-632.6 (.19)	-633.0 (.27)	
CCl_4	-631.5 (.0)	-631.9 (.04)	-632.7 (.10)	-633.4 (.17)	-634.8 (.28)
Cyclohexene	-631.5 (.0)	-632.2 (.09)	-633.0 (.16)	-633.6 (.20)	-633.9 (.24)
Benzene	-631.5 (.0)	-630.7 (.09)	-630.0 (.176)	-629.5 (.26)	-629.1 (.30)
CH_2Cl_2	-631.5 (.0)	-632.5 (.027)	-637.0 (.167)	-640.8 (.265)	-642.6 (.32)
MeOH	-631.5 (.0)	-637.8 (.064)	-645.8 (.22)	-648.4 (.294)	-651.7 (.41)
CH_3COCH_3	-631.5 (.0)	-634.0 (.018)	-639.8 (.108)	-642.0 (.17)	-645.7 (.286)
CH_3CN	-631.5 (.0)	-637.5 (.057)	-643.0 (.168)	-645.1 (.24)	-649.1 (.36)

1. CCl_4 is used as a common solvent in all cases.

Table 6-2

Relative Equilibrium Constants for Second Sphere Coordination

Ligand	$K_2 - 1$	K_2	Dipole Moment
CH_3CN	7.2	8.2	3.92
$(CH_3)_2CO$	7.2	8.2	2.88
CH_3OH	3.7	4.7	1.70
CH_2Cl_2	1.0	2.0	1.60
C_6H_6	0.25	1.25	0
C_6H_{10}	0.18	1.18	0
C_6H_{12}	-0.48	0.52	0

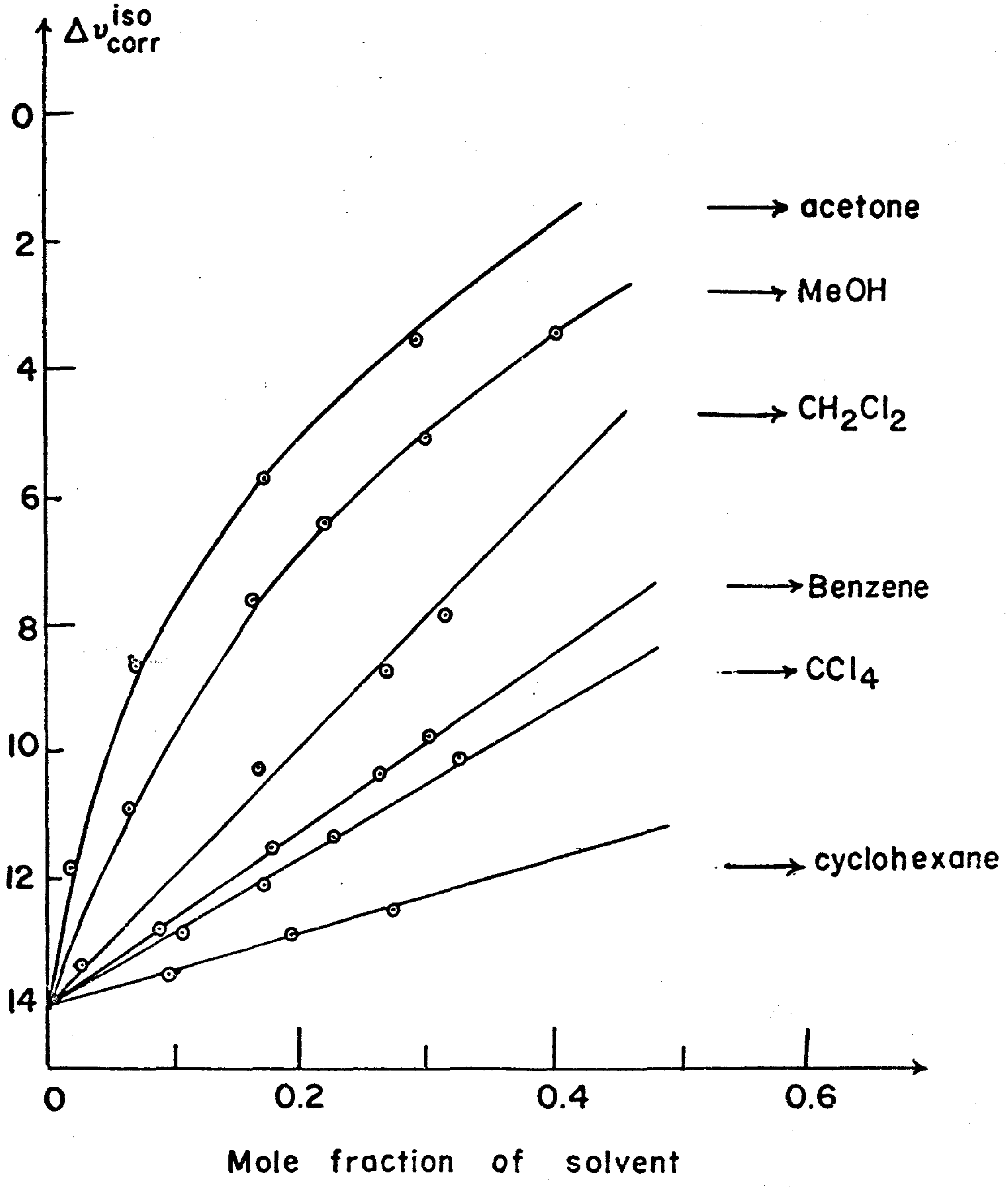


Figure 6-1. Plot of isotropic shift versus mole fraction of the solvent.

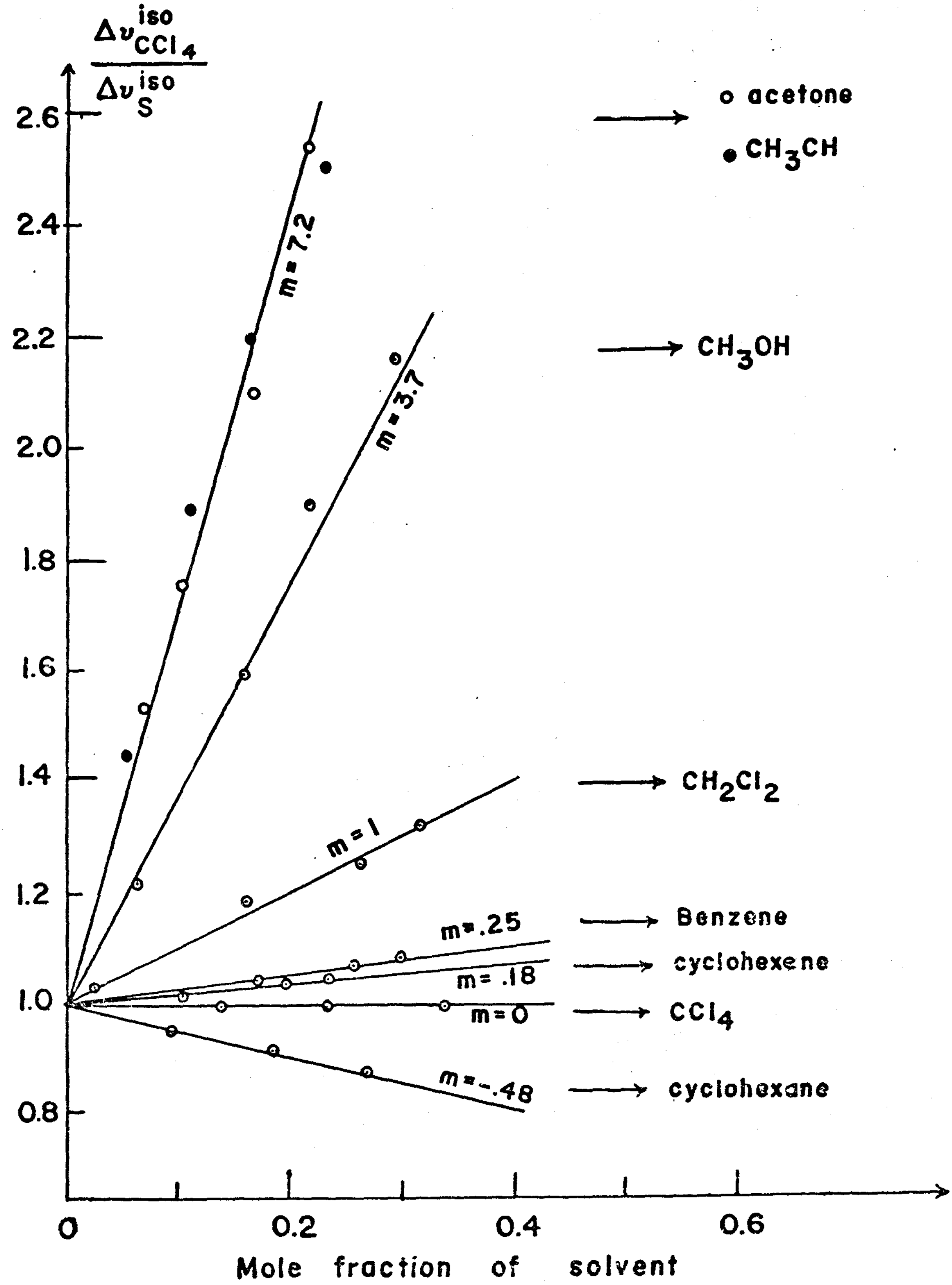
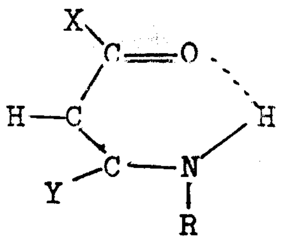


Figure 6-2. Plot of $\Delta V^{iso}_{CCl_4}/\Delta V^{iso}_{S}$ vs. Mole fraction of Solvent.

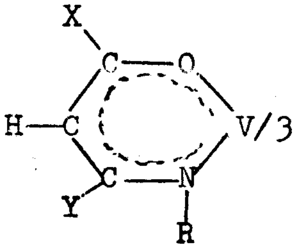
Appendix

Tris-β-Ketoamino-Vanadium (III) Complexes.

It would be of interest to extend the studies on tris(β-diketonato) Vanadium(III) complexes discussed in chapter four to other chelating ligands. With this in mind a number of complexes derived from Vanadium(III) and β-ketoamine ligands which have the following general structure (A) were prepared.



(A)



(B)

Proton NMR isotropic shifts ^{52} of such tris(β-ketoamino) Vanadium(III) complexes which have the structures as shown in (B) have been reported. The resonances show both large high and low field isotropic shifts similar to that of tris(β-diketonato) V(III) complexes. It was concluded that unpaired electron(s) delocalization via metal-to-ligand parallel spin transfer is the primary mechanism responsible for the observed shifts. Since our main 'interest in this study rest on the NMR investigation of the mixed complexes, systems which provide simple NMR spectra are desirable. Initially ligand exchange experiments with tris(4-phenylamino-1,1,1-trifluoro-3-en-2-ono) Vanadium(III), which has the structure as shown in (B) with $X=CF_3$, $Y=CH_3$ and R Phenyl group and other β-diketone or β-ketoamine ligands were attempted. Two types of reactions were tried.

Firstly, we intended to obtain the mixed chelates by adding acetylacetone to tris(4-phenylamino01,1,1-trifluoropent-3-en-2-ono) V(III) complex. However, proton NMR spectra indicates that either degradation or oxidation reaction of the compounds has taken place. Evidence in favour of this also comes from the fact that upon addition of acetylacetone to 4-phenylamino-1,1,1-trifluoropent-3-en-one, a pale yellow precipitate developed and then dissolved again in the solvent, $CDCl_3$. The resulting NMR spectra were not analysable.

The second experiment that has been tried was to add other β-ketoamine ligands e.g. $X=CH_3$, $Y=CH_3$ and R Phenyl group or p-Cl-phenyl group to tris(4-phenylamino-1,1,1-trifluoropent-3-en-2-ono)V(III) complex. No additional lines have been observed with increasing the amount of ligand added. The absence of additional lines upon addition of β-ketoamine ligand to the tris (β-ketoamino) V(III) complex may be attributed to either the exchange reaction having a unfavorable equilibrium constant or to the substituent shifts being too small to observe. The first explanation seems to be most likely.

Preparation of the compounds:

β-ketoamine ligands and their tris-Vanadium(III) complexes were prepared in the manner described by R.E.Ernst and R.H.Holm.[52]

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