

NMR STUDIES OF PARAMAGNETIC MOLECULES

R. M. GOLDING

*Department of Physical Chemistry, The University of New South Wales,
Kensington, N.S.W. 2033, Australia*

ABSTRACT

In this paper a résumé is given on nmr studies of paramagnetic molecules with specific reference to manganic and ferric dithiocarbamates. The temperature dependence of these spectra is discussed, and the isotropic proton hyperfine interaction constants are examined, yielding information about the electronic configuration in these molecules. The nmr results are complemented by magnetic susceptibility and Mössbauer measurements. The esr results for these compounds are also discussed. The effect of hindered rotation within these molecules is investigated with special reference to the diamagnetic analogues.

1. INTRODUCTION

NMR studies of paramagnetic molecules¹⁻⁴ can yield detailed information about the electronic structure and, in certain cases, the conformation of molecules which may be difficult to ascertain from any other known physical measurements. For instance, we can determine, from the nmr spectra, the magnitude and sign of the various electron-nuclear hyperfine interaction constants throughout a paramagnetic molecule, whereas esr measurements normally yield only the magnitude of the larger hyperfine interaction constants. In this contribution I shall endeavour to outline how nmr studies of paramagnetic molecules can yield an understanding of paramagnetic molecules by considering a series of transition metal ion dithiocarbamates. Other physical measurements may complement the nmr results or be required to fully interpret the nmr data which we shall illustrate by considering the appropriate magnetic susceptibility measurements, esr results and Mössbauer data.

The nmr spectrum of a paramagnetic molecule in a dilute liquid solution normally contains a series of broad peaks which are markedly temperature dependent (see *Figure 1.*) The change in the effective magnetic field, ΔH , due to the unpaired electrons in the molecule at the nmr nucleus for a system in a $2S+1\Gamma$ state is given¹ by

$$\Delta H = - \frac{ahg\beta HS(S+1)}{3g_N\beta_N kT} \quad (1)$$

provided there are zero spin-orbit matrix elements within the electronic state. In equations 1, g and g_N are the electronic and nuclear Landé g -factors

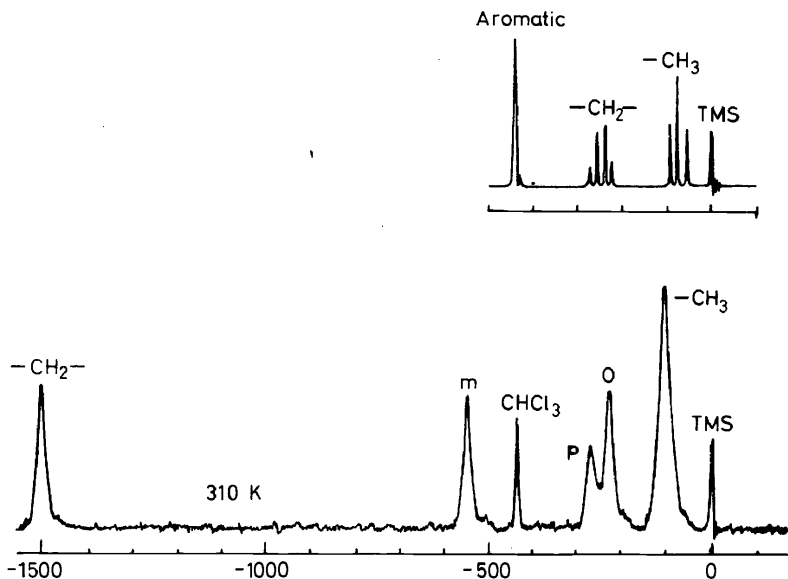


Figure 1. The 60 MHz proton nmr spectrum at 310K of tris(*N*-ethyl-*N*-phenyldithiocarbamato)-iron (III) in a solution of CDCl_3 . The marker peaks of chloroform and TMS are indicated. The insert is the proton nmr spectrum of the diamagnetic cobalt analogue.

respectively, H the applied magnetic field, T the absolute temperature, β and β_N the electronic and nuclear Bohr magnetons respectively, k the Boltzmann constant, h Planck's constant and a is the isotropic hyperfine interaction constant measured in cycles per second.

The electronic ground state for tris(*N,N*-diethyldithiocarbamato)manganese (III) is the ${}^5\text{E}$ state (see later) and hence ΔH from equation 1 is given by

$$\Delta H = -4 \frac{ah\beta H}{g_N\beta_N kT}. \quad (2)$$

A plot of ΔH against $1/T$ should yield a linear relationship where ΔHT is a constant. This is shown in Figure 2 for the most temperature dependent proton peak in the nmr spectrum of a dilute solution of tris(*N,N*-diethyldithiocarbamato)manganese (III).

If the electronic ground state is orbitally degenerate then, in general, ΔH may be a function of not only H , T and the multiplicity but of ζ , the spin-orbit coupling constant, and the isotropic hyperfine interaction constant for each state, namely,

$$\Delta H = f(H, T, \zeta, a_i). \quad (3)$$

For the case of a transition metal ion in a crystal field of octahedral symmetry ΔH is given by equation 1 when the ground electronic state is ${}^{2S+1}\text{A}_1$, ${}^{2S+1}\text{A}_2$ and ${}^{2S+1}\text{E}$. When the ground state is the ${}^{2S+1}\text{T}_1$ or the ${}^{2S+1}\text{T}_2$ states, then ΔH is of the form of equation 3 where the a_i s arise from the Fermi contact

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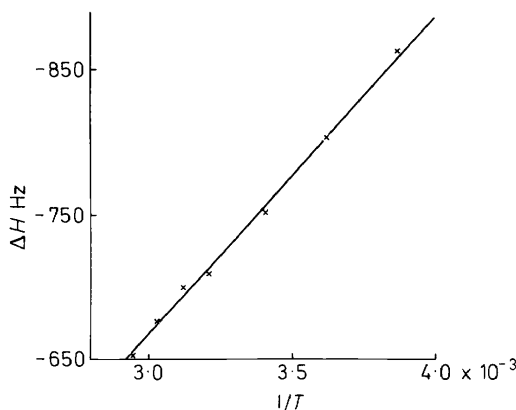


Figure 2. The temperature dependence of ΔH for the $-\text{CH}_2-$ protons in tris(*N,N*-diethyl-dithiocarbamato)manganese(III). The solid line is $T\Delta H = -2.221 \times 10^5 \text{ Hz K}$.

interaction and the ligand dipolar interaction. If the $a_i s$ dominantly arise from the Fermi contact interaction and are all equal then⁵

$$\Delta H = \frac{-ah\beta H \sum_J (2S+1) \langle S_z \rangle_J \exp(-E_J/kT)}{3g_N \beta_N kT \sum_J (2S+1) \exp(-E_J/kT)} \quad (4)$$

where

$$\langle S_z \rangle_J = \frac{(g-\gamma)}{(2-\gamma)} g J(J+1) + 2 \frac{(g-\gamma)(g-2)}{(2-\gamma)} \frac{kT}{\nu}$$

and

$$E_J = \frac{\nu}{2} J(J+1).$$

The g , ν and γ values can readily be determined for any particular $^{2S+1}T_1$ or $^{2S+1}T_2$ states. In general ΔH would be more detailed involving the specific $a_i s$ which would require knowledge of the molecular wave functions.

The expression for ΔH may be further complicated if there are low-lying electronic states. Such an example occurs when a d^5 transition metal ion is in an intermediate crystal field of octahedral symmetry. Here ΔH is given by the expression^{6,7}

$$\Delta H = -\frac{A_2 h H (x+16/3) \exp(x) - (16/3) \exp(-x/2) + 105xZ \exp(-E/kT)}{6g_N \beta_N \exp(x) + 2 \exp(-x/2) + 3 \exp(-E/kT)} \quad (5)$$

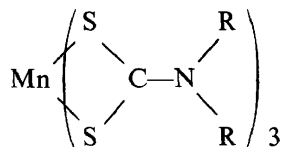
where $Z = A_6/A_2$ and $x = \zeta/kT$. A_6 and A_2 are the isotropic hyperfine interaction constants in the 6A_1 and 2T_2 states respectively where the states are separated by E . (Kurland and McGarvey⁸ have shown that A_2 may be expressed as $(K_0 + 2K_1)/3$ where K_0 and K_1 arise from the spin density at the nmr nucleus through the d_{xy} and the d_{xz} , d_{yz} and appropriate ligand p orbitals respectively.) No account has been taken of the molecular partition

function, configurational mixing and bonding effects in equation 5. All may be readily included.⁹

From the temperature dependence of ΔH the isotropic hyperfine interaction constants can be determined. In the following sections we shall outline the investigation of the nmr spectra of a series of manganic and ferric dithiocarbamates.

2. MANGANIC DITHIOCARBAMATES

The proton nmr spectra of a series of manganic dithiocarbamates of the form



consist of a series of broad proton peaks and the positions of these peaks are markedly temperature dependent.¹⁰ If the transition metal ion is in a strong crystal field of octahedral symmetry, the ground electronic state is the 5E state and ΔH is given, from equation 1, as

$$\Delta H = - \frac{4ah\beta H}{g_N\beta_N kT} \quad (6)$$

The lower-lying excited electronic states 3T_1 and 5T_2 will affect ΔH to a small extent, yielding:

$$\Delta H = - \frac{ah\beta H}{g_N\beta_N kT} \left\{ 4 - \frac{2\zeta}{\varepsilon} - \frac{\zeta^2}{2\varepsilon^2} - \frac{2\zeta^2}{\delta^2} \right\} \quad (7)$$

where as a first approximation $\delta = 6B + 5C - \Delta$ and $\varepsilon = \Delta$; Δ is the crystal field parameter and B and C the usual Racah parameters. (ε and δ are the energies of the 5T_2 and 3T_1 low-lying states above the 5E ground state respectively). Both equations 6 and 7 yield the same temperature dependence of ΔH . A tetragonal component to the crystal field will remove the orbital degeneracy of the 5E state, and if the splitting is 3μ then

$$\Delta H = - \frac{ah\beta H}{g_N\beta_N kT} \left\{ 4 - \left[\frac{3\zeta^2}{4\varepsilon^2} + \frac{\zeta^2}{\delta^2} + \left(\frac{\zeta^2}{4\varepsilon^2} + \frac{4\zeta}{\varepsilon} + \frac{3\zeta^2}{\delta^2} \right) \exp(3\mu/kT) \right] \times [1 + \exp(3\mu/kT)]^{-1} \right\} \quad (8)$$

The terms in curled brackets in equation 7 can only be slightly temperature dependent. A trigonal distortion will not remove the orbital degeneracy of the 5E state and ΔH will be given by equation 7. Therefore, ΔHT for manganic compounds in a strong crystal field should be constant with the possibility of a small departure due to a tetragonal component to the crystal field. These results have been observed for eight manganic dithiocarbamates.

However, from the nmr results we cannot distinguish between equations

6 and 7 leading to an uncertainty in the isotropic proton hyperfine constants. Therefore, we need to establish the energy level scheme. This can be achieved by examining the magnetic susceptibility results. A d^4 ion in an intermediate crystal field of octahedral symmetry will result in the 5E or one of the 3T_1 electronic states as the ground state, the 3T_1 state arising dominantly from the t_2^4 electronic configuration. An analytical expression for the temperature dependence of the magnetic moment in terms of δ , the energy separation of the 3T_1 and 5E states, has been determined¹¹ and the results reproduced in *Figure 3*. The magnetic moments of a series of manganic dithiocarbamates yield results which are slightly temperature dependent from 100 K to 300 K and near 4.82 Bohr magnetons. From *Figure 3* this suggests that the 3T_1 state is about 2000 cm^{-1} above the 5E ground state. The 5T_2 state is therefore

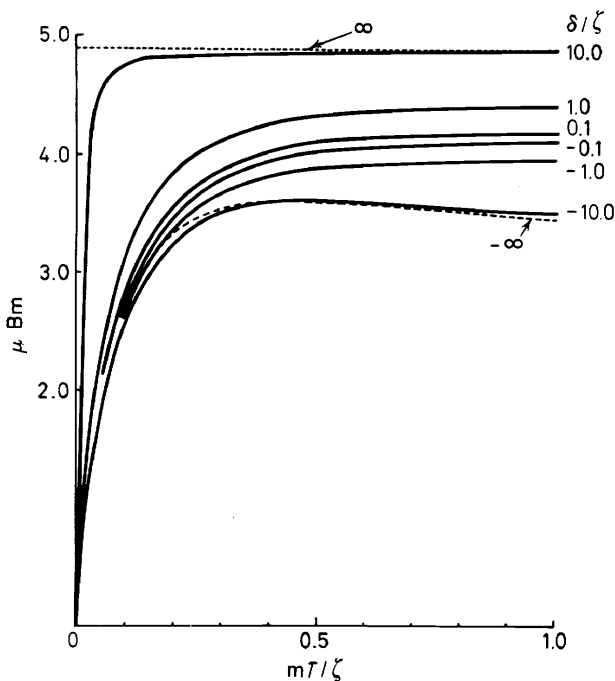


Figure 3. The calculated temperature dependence of the magnetic moment of a d^4 ion in an intermediate crystal field of octahedral symmetry where δ is the energy separation of the 3T_1 and 5E states and ζ the spin-orbit coupling constant.

about $25\,000\text{ cm}^{-1}$ above the ground state. Hence the effect of the excited states on ΔH is less than 1 per cent and equation 6 should be sufficient to interpret the nmr data.

A typical set of nmr results is given in *Table 1* for the protons nearest the nitrogen atom in tris(*N,N*-diethyldithiocarbamato)manganese (III).

The proton hyperfine interaction constants can be determined from equation 6 which yields $a = -0.2641 T\Delta H$ where a and ΔH are expressed in the same units.

Table 1. The temperature dependence of ΔH from the nmr spectrum of the $-\text{CH}_2-$ protons in tris(*N,N*-diethylthiocarbamato)manganese (III).

$T(\text{K})$	340.0	330.0	318.5	311.5	293.5	276.2	258.0
$\Delta H(\text{Hz})$	-653	-675	-699	-709	-753	-805	-865
$T\Delta H \times 10^{-5}$	-2.22	-2.23	-2.23	-2.21	-2.21	-2.22	-2.23

Both the nmr and magnetic susceptibility measurements of the magnetic dithiocarbamates have shown that the ground electronic state is dominantly the ^5E state and an esr study was attempted in support of these findings.

The esr study¹² at 77 K of tris(*N,N*-dimethylthiocarbamato)manganese (III) is typical of the esr results of the manganic dithiocarbamate series and the results will be only outlined here. A single crystal esr study of manganic dimethylthiocarbamate diluted in a single crystal of the diamagnetic cobalt analogue resulted in a single paramagnetic species with an anisotropic g -tensor with principal values of 2.122, 2.091 and 2.076 with no fine or hyperfine structure. The esr spectrum of a powdered sample (see Figure 4) was also analyzed by computing simulated spectra using the relationship

$$F(H) = \iint P(\theta, \phi)G(\theta, \phi) \sin \theta \, d\theta d\phi \quad (9)$$

where for Gaussian first derivative lines

$$G(\theta, \phi) \propto -x \exp(-x^2 \ln 2/W^2)$$

$$W = \text{line-width}$$

$$x = H - g_z H_0/g$$

H = magnetic field, H_0 = magnetic field corresponding to g_z

$$g^2 = g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta$$

$$P(\theta, \phi) = g_x^2 + g_y^2 + g_z^2 - (g_x^4 \sin^2 \theta \cos^2 \phi + g_y^4 \sin^2 \theta \sin^2 \phi + g_z^4 \cos^2 \theta)/g^2.$$

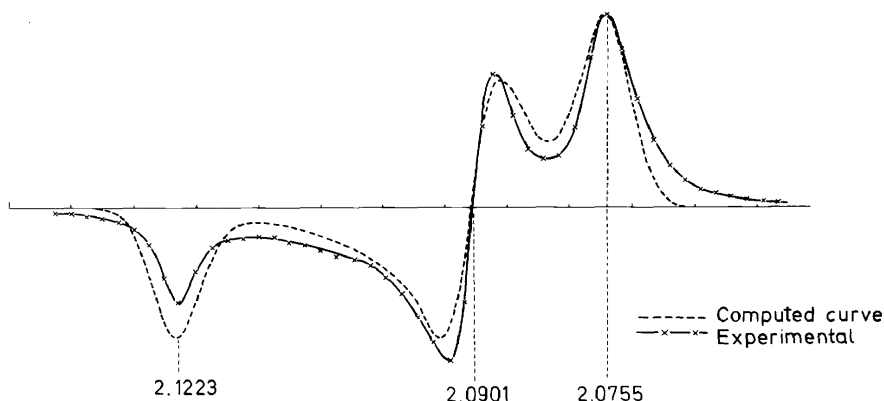


Figure 4. The experimental and computer-simulated esr spectra of a powdered sample of manganic dimethylthiocarbamate. The principal g -values are indicated.

The computer-simulated spectrum of best fit to the experimental power spectrum of 77 K for manganic dimethyldithiocarbamate yielded three principal g -values of 2.122, 2.090 and 2.076 (see *Figure 4*) the results agreeing with the more detailed single crystal studies. The principal g -values of several powdered samples of manganic dithiocarbamates have been determined in this manner¹².

With the absence of any fine structure the esr spectrum arises from an effective $S = \frac{1}{2}$. With no hyperfine structure the unpaired electron cannot be associated with the manganese, nitrogen or proton nuclei. Also, the esr spectrum of these manganese compounds are not only similar to the iron analogues^{13,14} but are very similar to the so-called 'sulphur' pattern observed in sulphur-containing radicals^{15,16}. Therefore, the esr spectrum most likely arises from a radical system where the unpaired electron is associated with the sulphur atoms.

3. FERRIC DITHIOCARBAMATES

The proton nmr spectra of a series of ferric dithiocarbamates^{6,17} and the fluorine nmr spectra of fluorine substituted ferric dithiocarbamates⁹ are markedly temperature dependent and the measured ΔH s are usually not proportional to $1/T$. Often the magnitude of ΔH increases with increasing T . The nmr spectra of several series of ferric dithiocarbamates have been interpreted where the d^5 ion is in an intermediate crystal field of octahedral symmetry.^{6,9,17} The energy separation of the 6A_1 and 2T_2 states can be very small in these compounds. Mössbauer spectroscopy^{18,19} has established that the splitting of the 2T_2 state is between 200 and 400 cm^{-1} . Without more detailed information about the energy level scheme and the molecular wave functions equation 5 has been successfully used to determine A_2 , A_6 and E : a more detailed analysis would require more unknown hyperfine interaction constants.

A typical proton nmr spectrum of an iron dithiocarbamate, tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron (III), is given in *Figure 1*. All the peaks are temperature dependent, the most temperature dependent peak being the low field peak. ΔH for all the proton peaks can be determined and *Figure 5* illustrates the temperature dependence of the ΔH s. This spectrum has been analyzed¹⁷ by determining the best value of E to yield the best least mean square fit of equation 5 for the temperature dependence of the low field proton peak. The sensitivity of the E value may be demonstrated by plotting the standard deviation against E (see *Figure 6*.) Once E is known, A_2 and A_6 can be determined from the experimental data for each nmr nucleus.

The magnetic moment of the series of iron dithiocarbamates can also be determined⁶ and with the same approximations as above

$$\mu^2 = \frac{(8/x + 3) \exp(x) - (8/x) \exp(-x/2) + 105 \exp(-E/kT)}{\exp(x) + 2 \exp(-x/2) + 3 \exp(-E/kT)} \quad (10)$$

From the nmr results for tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron (III) the E value is 165 cm^{-1} which yields a predicted magnetic moment value at room temperature, from equation 10, of 3.25 Bohr magnetons. The experi-

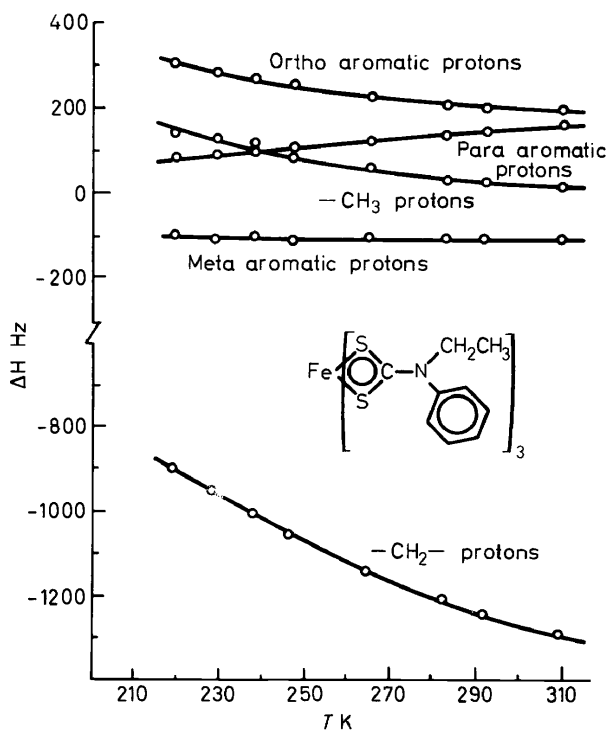


Figure 5. The temperature dependence of ΔH for all the protons in tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron(III).

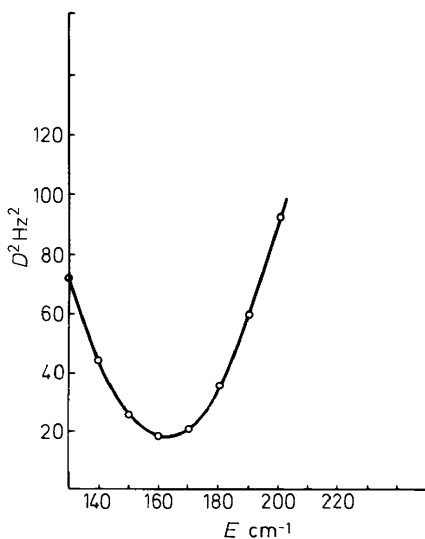


Figure 6. A plot of the square of the standard deviation, D^2 , against E for the methylene protons for tris(*N*-ethyl-*N*-phenyldithiocarbamato)iron(III).

mental result in a chloroform solution is 3.65 Bohr magnetons.¹⁷ This comparison is most encouraging when we consider the approximations embodied in equations 5 and 10 and the usual difficulties in measuring the magnetic moment of a compound in a dilute liquid solution.

From the nmr results we have been able to investigate the effect of the various dithiocarbamate ligands on the energy separation of the 6A_1 and 2T_2 states. For example, in tris(*N,N*-di-isopropylthiocarbamato)iron (III), the ground state is the 2T_2 state and the 6A_1 state has a negligible effect, if any, on the nmr results. In a series of phenyl substituted¹⁷ tris(*N*-ethyl-*N*-phenylthiocarbamato)iron (III) compounds, the 6A_1 state is only slightly higher in energy than the 2T_2 ground state, whereas, the 6A_1 state is the ground state for tris(*N,N*-piperidylthiocarbamato)iron (III) and the 2T_2 state has a negligible effect, if any, on the nmr results. Therefore, the various dithiocarbamate ligands may substantially change the crystal field environment of the transition metal ion effecting the physical properties of the compound especially when the transition metal ion is in an intermediate crystal field region near the 'cross-over'. In the next section we shall examine the hyperfine interaction constants and indicate what information can be gained.

4. THE HYPERFINE INTERACTION CONSTANTS

The analysis of the temperature dependence of the nmr spectra of paramagnetic molecules in dilute liquid solutions results in a series of isotropic hyperfine interaction constants. The isotropic hyperfine interaction constants arise through the dipolar and the Fermi contact interactions. The dipolar contribution to the isotropic hyperfine interaction constant is known as the pseudo-contact term and depends on the anisotropy of the *g*-tensor, whereas the Fermi contact contribution to the hyperfine constant depends on the electron spin density at the particular nmr nucleus. If the transition metal ion is in a crystal field of octahedral symmetry, the *g*-tensor is isotropic. However, any small crystal field distortion will result in *g* anisotropy yielding a pseudo-contact contribution to the isotropic hyperfine interaction constant. This term will become important, especially in the ${}^{2S+1}T_1$ and ${}^{2S+1}T_2$ orbitally degenerate states, due to small crystal field distortions. Without detailed knowledge of the *g*-tensors in these states, we cannot estimate the dipolar contribution to the hyperfine interaction constants. Therefore, here we shall only consider the isotropic hyperfine interaction constants in the 5E and the 6A_1 electronic states, since the isotropic hyperfine interaction constants in these states will dominantly arise from the Fermi contact term. Hence, the hyperfine interaction constants in the 5E and 6A_1 states indicate the magnitude and sign of the electron spin density at the nmr nucleus.

The electron spin density may arise at the particular nmr nucleus in two ways. First, the unpaired electrons in the molecule may be delocalized in such a way that at the nmr nucleus there is positive or negative electron spin density. For example, if an unpaired electron is in a *p*-like atomic orbital on an atom adjacent to an aliphatic fragment, then electron spin density will occur at the hydrogen nucleus arising from delocalization of the unpaired electron by overlap of the hydrogen 1 *s* and the *p*-orbital. Therefore, an isotropic proton hyperfine interaction constant will be observed. The second

mechanism is due to spin-polarization. This arises through the Coulomb repulsion interaction resulting in electron spin density at the particular nucleus.

A general expression has been derived²⁰ for the isotropic proton hyperfine interaction constant arising from electron spin density ρ at the carbon atom, $C-C_{n-1}-H$ due to spin polarization. When $n = 1, 2$ and 3 , the isotropic proton hyperfine interaction constants have been estimated as $-65 \times 10^6 \rho$, $-4.4 \times 10^6 \rho$ and $0.15 \times 10^6 \rho$ Hz respectively, an alternation of sign along the fragment. Usually, the delocalization of the unpaired electrons into the ligand give rise, through the Fermi contact term to the dominant contribution to the isotropic ligand hyperfine interaction constants. When delocalization cannot occur, the observed hyperfine interaction constants may be due to the spin polarization mechanism.

As examples, the measured isotropic proton hyperfine interaction constants for two manganic and ferric dialkyldithiocarbamates in the 5E and 6A_1 electronic states respectively, are given in *Table 2*. The various proton groups are labelled in alphabetical order from the nitrogen atom.

Table 2. The measured isotropic proton hyperfine interaction constants, in 10^4 Hz, for two manganic and ferric dialkyldithiocarbamates in the 5E and 6A_1 states respectively.

Transition metal ion	Dithiocarbamate	a	b	c
Fe	diethyl	49.5	3.9	
Mn	diethyl	5.87	-0.39	
Fe	di- <i>n</i> -propyl	46.9	6.5	3.1
Mn	di- <i>n</i> -propyl	5.84	-0.39	-0.13

The largest proton hyperfine interaction constants observed in this series are for the proton group adjacent to the nitrogen atom. This interaction arises from partial delocalization of the d -electrons into the ligand resulting in a positive spin density at the nitrogen atom. (The Mössbauer data¹⁹ has shown that there is partial delocalization of the iron d -electrons into the ligand.) In the iron series, the proton hyperfine interaction constants are all positive and have been interpreted as arising from partial delocalization along the aliphatic chain, the effect being observed up to eight bond lengths from the iron nucleus⁶. In the manganic series, the magnitude of the proton hyperfine interaction constants is much less and consequently it appears that the extent of d -electron delocalization into the ligand is less. Also, there is a sign change of the hyperfine constants along the alkyl chain suggesting that this isotropic proton hyperfine interaction arises mainly by a spin polarization mechanism.

An nmr study of a series of phenyl substituted tris(*N*-ethyl-*N*-phenyl-dithiocarbamato)iron (III) has shown¹⁷ that the substituent in the phenyl ring has very little effect on the energy separation of the 6A_1 and 2T_2 states. From the proton hyperfine interaction constants in the 6A_1 state, it follows that the electron-attracting dithiocarbamate ligand, not the substituent in the ring, governs the electronic configuration. This is illustrated in *Table 3* by comparing four *meta* substituted derivatives.

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Table 3. The measured isotropic proton hyperfine interaction constants, in 10^5 Hz, in the 6A_1 state for all the protons in several phenyl substituted tris(*n*-ethyl-*N*-phenyldithiocarbamato)iron (III) complexes

Compound	<i>ortho</i> H	<i>meta</i> H	<i>para</i> H	—CH ₂ —	—CH ₃	substituent
<i>N</i> -ethyl- <i>N</i> -phenyl	0.163	0.182	-0.635	3.84	0.523	—
<i>N</i> -ethyl- <i>N</i> - <i>m</i> -methylphenyl	0.180	0.239	-0.763	4.64	0.637	-0.055
<i>N</i> -ethyl- <i>N</i> - <i>m</i> -methoxyphenyl	0.185	0.175	-0.687	3.99	0.527	-0.011
<i>N</i> -ethyl- <i>N</i> - <i>m</i> -chlorophenyl	0.300	0.151	-0.866	4.98	0.818	
<i>N</i> -ethyl- <i>N</i> - <i>m</i> -fluorophenyl	0.125	0.141	-0.748	3.94	0.559	

However, the substituent influences the methylene proton isotropic hyperfine interaction constants in the 6A_1 state (see Table 3.). These results have been interpreted¹⁷ as arising from changes in the π character of the *N*-phenyl bond due to the degree of hindered rotation with the aromatic substituent. For example, the methylene proton hyperfine interaction constants for the σ -methoxy, *m*-methoxy and *p*-methoxy derivatives are 4.70, 3.99 and 3.88×10^5 Hz respectively. The *ortho* substituent creates the greatest degree of hindered rotation about this bond. For example, in the σ -methyl derivative, the N—CH₂-bond is locked in a specific orientation, giving rise to two proton hyperfine interaction constants.

The hyperfine interaction constants can yield substantial information about the electronic configuration in the molecule, for instance, the effect of different transition metal ions on the extent of delocalization of the *d*-electrons into the ligands and the effect of substituents on the molecular and electronic structure. However, care must be taken in analyzing and interpreting the nmr spectra of paramagnetic molecules with an understanding and an appreciation of the approximations used.

5. HINDERED ROTATIONS

In a few paramagnetic transition metal ion dithiocarbamates we have observed marked changes in the nmr spectra over a narrow temperature range where a peak due to a specific proton group splits into two or more peaks. We have attributed these changes to hindered rotations within the molecule. To explore the effect of hindered rotation on the nmr spectrum we have examined first the diamagnetic analogues in more detail²¹ and by way of illustration, I shall outline the interpretation of the different temperature dependent proton nmr spectra observed for tris(*N,N*-dibenzylidithiocarbamato)cobalt (III) and tris (*N,N*-di-isopropylidithiocarbamato)cobalt (III).

The proton nmr spectrum of the —CH₂— protons in tris (*N,N*-dibenzylidithiocarbamato)cobalt (III) is an *AB* spectrum of four sharp lines over the temperature range -30°C to 60°C where the only change with temperature is the chemical shift difference of the two protons (see Figure 7.). On the other hand, the nmr spectra of the —CH— protons in tris(*N,N*-di-isopropylidithiocarbamato)cobalt (III) yield the expected seven lines with the usual intensity pattern 1:6:15:20:15:6:1 at temperatures above 60°C . As the

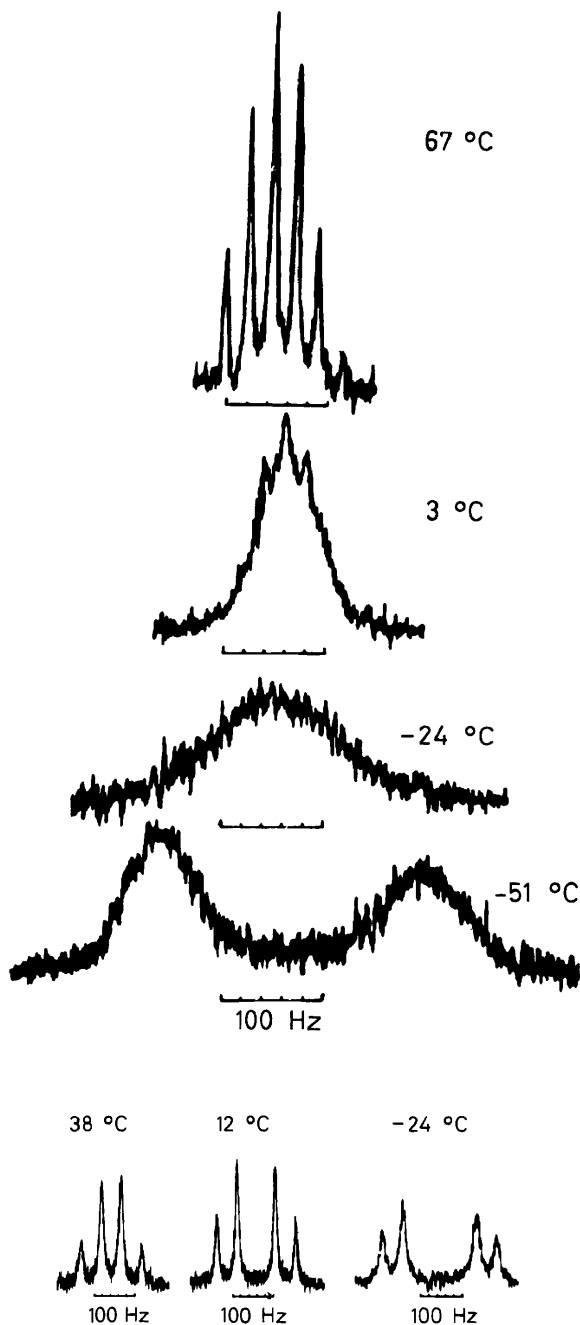


Figure 7. The temperature dependence of part of the 60 MHz proton nmr spectra of (a) tris(*N,N*-dibenzyldithiocarbamato)cobalt (III) and (b) tris(*N,N*-di-isopropylthiocarbamato)cobalt (III).

temperature is lowered the —CH region loses its fine structure and broadens. At -50°C two broad well-separated peaks appear (see *Figure 7*).

We have successfully interpreted these temperature dependent nmr spectra as arising from two stable configurations due to restricted rotation of the N—C bond with an energy difference, ΔE . If the lifetimes of both these states are sufficiently large to have no effect on the nmr spectrum and ΔE is nonzero we would observe a temperature dependent well-resolved nmr spectrum where the observed chemical shifts and coupling constants are averaged over both states. The tris(*N,N*-dibenzylidithiocarbamato)cobalt (III) nmr spectrum over the temperature range measured can be interpreted by this model where ΔE is 250 cm^{-1} . The nmr spectrum of tris(*N,N*-diisopropylidithiocarbamato)cobalt (III) is interpreted when the lifetimes of the two states do affect the nmr spectrum with an energy of activation of 1750 cm^{-1} and ΔE about 10 cm^{-1} .

The nmr spectra of the paramagnetic analogues of these compounds have been interpreted by the model.

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