Solute-Solvent Interactions and High Spin ⇌ Low Spin Transitions in Ferric Dithiocarbamates

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The HS ⇌ LS transition in ferric dithiocarbamates in a number of solvents has been investigated using NMR and is interpreted in terms of preferential solvation or second co-ordination sphere reorganisation effects. These studies clearly demonstrate that neglect of pseudo contact shifts can lead to erroneous conclusions about the spin delocalisation mechanisms. The spin delocalization in these systems is by direct σ-delocalization along the alkyl chain. The A_s values of $^2T_2$ and $^6A_1$ states have the same sign.

Introduction

The characteristics of spin-crossover ($^2T_2 \rightleftharpoons {}^6A_1$) in ferric dithiocarbamates [Fe(dtc)$_3$] are of considerable interest as they may be looked upon as prototypes of iron-sulphur proteins [1]. Many of the haemproteins such as cytochrome P450 also exhibit the high spin ⇌ low spin behaviour which is hypersensitive to the immediate environment, substrate, etc. [2–3]. Magnetic susceptibility measurements on Fe(S$_2$CNPr$^n_2$)$_3$ using NMR have shown that solvent effects on the HS ⇌ LS behaviour are small and insignificant [4]. Temperature dependent NMR on some tris dithiocarbamates in CDCl$_3$ have been interpreted without contributions from pseudo-contact shifts [5]. In an earlier study [6], it has been demonstrated that neglect of the pseudo-contact shift can lead to wrong conclusions on the ground state and spin delocalization characteristics in any system.

As a part of our programme to understand the environmental effects on spin-crossover, we present some observations on the solvent dependence on HS ⇌ LS in ferric dithiocarbamates.

Experimental

Freshly grown crystals (from benzene solutions) of Fe(RR′dtc)$_3$ were dissolved in CDCl$_3$ and CD$_2$Cl$_2$. The PMR spectra were recorded between + 60 °C and − 100 °C on a 90 MHz Bruker NMR spectrometer. A spectrum of the n-butyl derivative dissolved in CD$_2$Cl$_2$ is shown in Figure 1. The spectra for the other derivatives are similar and hence are not presented here. The shifts were measured with respect to TMS as internal standard. The diamagnetic corrections used were as follows:

a) ethyl derivative:
$-CH_2$ -335 Hz, CH_3 -113 Hz.
b) butyl derivative*:
$-CH_{2\text{-}A}$ -325 Hz, $-CH_{2\text{-}B}$ -127 Hz,
$-CH_{2\text{-}C}$ -95 Hz.
c) pyrrolidyl derivative:
$CH_{2\text{-}A}$ -2700 Hz, $-CH_{2\text{-}B}$ -150 Hz.

The plots of the Isotropic Proton Shifts (IPS) vs T, corrected for the diamagnetic part for all the three derivatives in CDCl$_3$ and CD$_2$Cl$_2$ are shown in Figure 2. The Pseudo Contact Shifts (PCS) for the CH$_2$- and CH$_3$- protons in the ethyl derivative were calculated using the magnetic anisotropy and the X-ray data [7–9]. The geometric factors for the methylene protons in twelve conformations were calculated by rotations in steps of 30° along the H$_2$C–N bond. The average value of $(3\cos^2\theta - 1)/R^3$ for the CH$_2$- and CH$_3$- protons over these conformations are -6.17×10^{-3} cm^{-3} and 4.04×10^{-3} cm^{-3} a respectively. This averaging is justified here since no preference for any particular conformation is seen in the PMR spectrum. The PCS calculations were done on the ethyl derivative since the magnetic moments in solid and solution are the same. The IPS for the ethyl derivative in CD$_2$Cl$_2$ solutions

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* On account of technical reasons $CH_{\bar{2}A}$ et al. must be written as $CH_{2\text{-}A}$.

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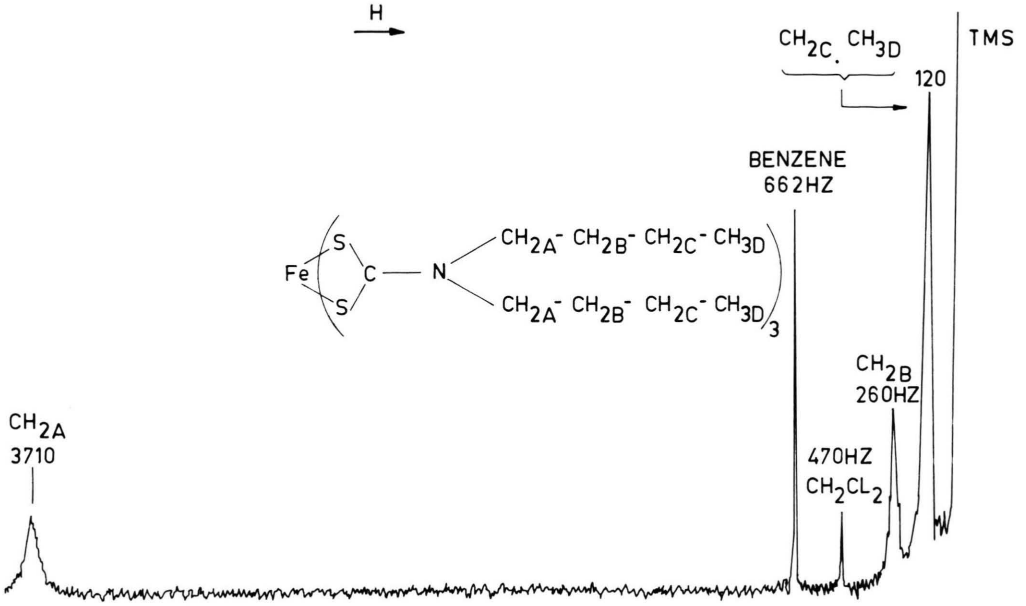

Fig. 1. NMR Spectrum of tris(n-dibutyl dithiocarbamato)Fe(III) in CD_2Cl_2.

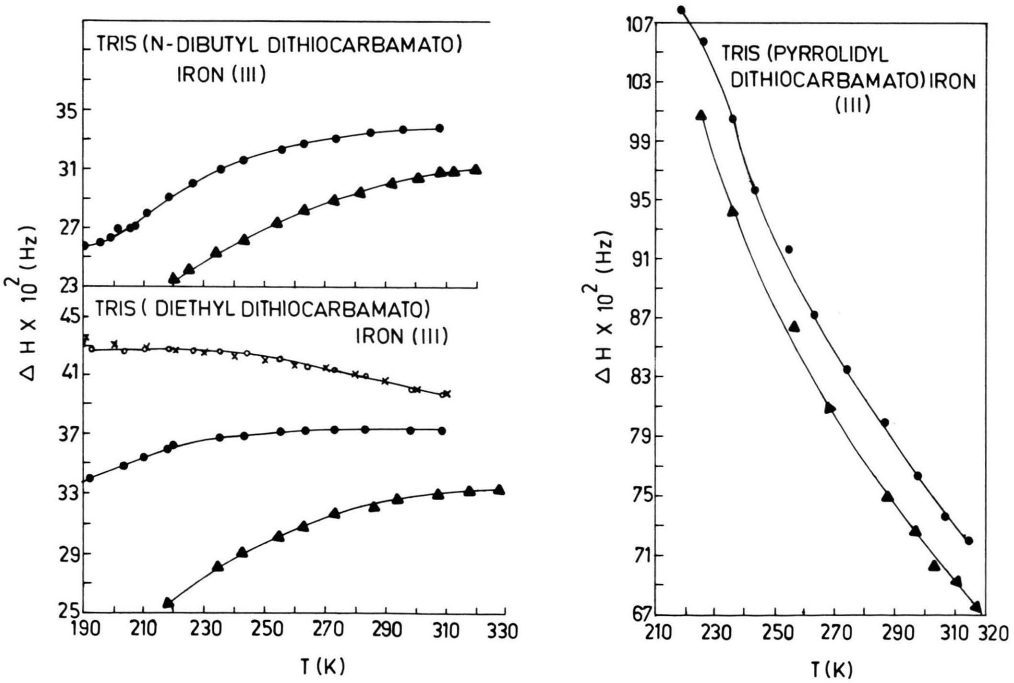

Fig. 2. Isotropic proton shifts (IPS) of proton on α-carbon in Ferric dithiocarbamates. Shifts have been corrected for the diamagnetic contribution.

*** CS calculated from magnetic susceptibility and magnetic anisotropy data.
○ CS of ethyl derivative calculated from IPS and PCS.
▲ IPS in $CHCl_3$.
● IPS in CD_2Cl_2.

were corrected for the PCS. The data in $CDCl_3$ solutions could also be used for this purpose where the temperature dependence of the Contact Shift (CS) would remain the same, except that the actual numbers appear scaled by some factor. Plots of the CS for the ethyl derivative are also given in Figure 2. These calculations were not carried out for the n-butyl and pyrrolidyl derivatives as their magnetic moments in solution and solid state are very different.

Results and Discussions

In the present study of the ethyl and n-butyl derivatives the measurements were extended to 190 K and the signal due to the methylene protons did not show evidence of a kinetic process either due to a restricted rotation around the S_2C-N bond or the trigonal twist seen in some of the ferric dithiocarbamates such as Fe(EtEtdtc)$_2$phen (177 K), Fe(EtEtdtc)$_2$bipy (172 K), Fe(pyrrolidyl dtc)$_3$ (186 K) etc. [10–11]. The temperatures in the brackets show temperatures below which a splitting of the CH_2 resonance is observed.

Figure 1 shows that when the crystals of the benzene solvate of the n-butyl derivative are dissolved in CD_2Cl_2, a peak due to the benzene appears at 663 Hz. As the benzene protons are not contact shifted, the benzene does not chemically bind with the complex in solutions. Tables 1–3 show that the IPS have striking solvent dependence. In all the three derivatives, the shifts in CD_2Cl_2 solutions are higher than those in $CDCl_3$. Since the chloroform or methylene dichloride peaks do not get contact shifted (7.24 ppm in $CHCl_3$ and 5.33 ppm in CD_2Cl_2), the solvent does not get co-ordinated with the dithiocarbamate complex. Also, any conformational change on the alkyl group of the dithiocarbamate ligand seems to be absent. The solvent dependence may, therefore, be interpreted in terms of preferential solvation or second co-ordination sphere reorganization effects [12]. The observation of a marked solvent dependence of the IPS in Fe(RR′dtc)$_3$, is in agreement with our earlier observation that the magnetic susceptibilities are sensitive to the solvated molecules in the lattice [1].

Spin-delocalization mechanism

The sign of the IPS shows some interesting trends. The sign of the IPS of the $CH_{2\text{-}A}$ protons in all the three compounds is negative. The IPS of the subsequent CH_2 protons in the n-butyl and pyrrolidyl derivatives are also negative, in contrast to the positive IPS of the CH_3 protons in the ethyl derivative. This seems to suggest that the spin delocalization in the case of n-butyl and pyrrolidyl derivatives is by direct σ-delocalization, whereas in the case of the ethyl derivative it might be via a spin polarization mechanism. The spin delocalization mechanisms are not expected to vary in these compounds,

Table 1. NMR results on tris(diethyldithiocarbamato)iron(III) at 90 MHz.

T/K	Solvent CD_2Cl_2							Solvent $CDCl_3$	
	CH_2			CH_3				CH_2	CH_3
	IPS + [Hz]	PCS [Hz]	CS [Hz]	IPS + [Hz]	PCS [Hz]	CS [Hz]	T/K	IPS + [Hz]	IPS + [Hz]
309	−3730	245	−3984	20	166	−146	328	−3340	0
298	−3730	297	−4027	30	194	−164	318	−3340	10
283	−3740	360	−4100	50	235	−185	307	−3300	20
273	−3740	401	−4141	70	262	−192	294	−3270	40
263	−3730	432	−4162	–	291	–	286	−3220	–
255	−3720	482	−4202	–	315	–	273	−3170	70
243	−3700	542	−4242	–	355	–	263	−3090	–
235	−3680	589	−4269	–	395	–	255	−3020	–
226	−3640	636	−4276	−180	416	−236	243	−2910	–
218	−3600	684	−4284	−220	447	−227	235	−2810	180
210	−3540	736	−4276	−270	481	−221	218	−2565	210
203	−3480	784	−4264	−290	512	−222			
192	−3410	865	−4275	−330	566	−236			

Shifts have been corrected for diamagnetic corrections.

Table 2. NMR results on tris(n-dibutyldithiocarbamoto)-iron(III) at 90 MHz.

T/K		Solvent CD_2Cl_2	
	$CH_{2\text{-}A}$	$CH_{2\text{-}B}$	$CH_{2\text{-}C} \cdot CH_{3\text{-}D}$
	IPS [Hz]	IPS [Hz]	IPS [Hz]
308	−3385	−120	−25
296	−3370	−110	−25
285	−3340	−100	−15
273	−3320	−90	−15
263	−3280	−90	−15
255	−3230	−80	−10
243	−3160	−60	−10
235	−3090	−50	0
226	−3000	−40	0
218	−2900	−30	10
211	−2800	−10	20
207	−2750	10	30
205	−2700	10	
201	−2690	20	
198	−2620	30	
195	−2590	40	
190	−2565	50	40

Shifts have been corrected for diamagnetic correction.

Table 3. NMR results on tris(pyrrolidyldithiocarbamato)-iron(III) at 90 MHz.

T/K	Solvent CD_2Cl_2	
	$CH_{2\text{-}A}$	$CH_{2\text{-}B}$
	IPS [Hz]	IPS [Hz]
315	−7210	−410
307	−7370	−430
298	−7640	−430
287	−8000	−440
274	−8350	−450
263	−8720	−460
255	−9170	−470
243	−9570	−490
236	−10050	−500
226	−10570	−520
218	−10770	−540

Shifts have been corrected for diamagnetic corrections.

since the nature of bonding does not change along the series from ethyl to pyrrolidyl derivatives. However, after the IPS of the CH_3 protons are corrected for the PCS at various temperatures, the signs of the CS of the CH_3 protons and the CH_2 protons in the ethyl derivative become the same (i.e. negative). It should also be noted that in the butyl derivative, the IPS of the $CH_{2\text{-}B}$ and $CH_{2\text{-}C}$ are negative at 300 K but become positive after 218 K and 207 K respectively. Since the temperature dependence of the CS is expected to be much smaller than the PCS (the temperature variation of PCS will be same as the temperature variation of magnetic anisotropy) [1], the dominant contribution to the IPS at low temperatures is expected to come from the PCS. Since the PCS is expected to be positive in these systems (assuming that the sign of PCS for the $CH_{2\text{-}B}$ and $CH_{2\text{-}C,D}$ protons is same as that of the CH_3 protons in ethyl), the change in sign of the IPS for $CH_{2\text{-}B}$ and $CH_{2\text{-}C,D}$ in the n-butyl case at low temperatures is not surprising. We therefore conclude that the spin delocalization mechanism in these three compounds and in $Fe(EtEtdtc)_2X$ is similar as has been discussed in detail in reference [13]. These calculations again demonstrate that the neglect of PCS in the analysis of the paramagnetic shifts in PMR studies can lead to erroneous conclusions about the spin delocalization mechanisms. This feature has also been stressed by Ganguli et al. [13] in the analysis of PMR data of $Fe[dtc]_2X$, and by Happe and Ward [14] in their analysis of paramagnetic shifts in $M(acac)_2L_2$, where $M = Co$, Ni and $L =$ pyridine type ligand.

Calculation of the PCS for the α-carbon in the diethyl derivative shows that this contribution to IPS is only 3.23 ppm compared to the IPS of −384.3 ppm for the α-carbon in ^{13}C NMR. Thus, a neglect of the PCS in the analysis of IPS of ^{13}C shifts will not lead to much error. Gregson and Doddrell [12] interpreted the spin delocalization in these systems as arising from direct σ-delocalization along the alkyl chain, which is in agreement with our interpretation of the proton NMR data.

Using the model based on the Boltzmann distribution between $^2T_2$ and $^6A_1$ states as outlined earlier [1], the contact shifts for the CH_2 protons in the ethyl derivative was fitted using different values of A_s for the $^2T_2$ (hyperfine interaction constant) and $^6A_1$ states. The same ligand parameters which fitted the magnetic susceptibility and magnetic anisotropy data on the same systems [1] were used in the present calculations. The best fits [using the parameters from our earlier work: δ_1 (trigonal distortion) $= -255\ \text{cm}^{-1}$, δ_2 (energy separation between the $^2T_2$ and $^6A_1$) $= 600\ \text{cm}^{-1}$, ξ (spin orbit coupling) $= 340\ \text{cm}^{-1}$ and q (mixing coefficient of $^2T_2$ levels in the t_{2g} manifold with the cited $^4T_1$ levels) $= 0.555$] for $A_s(^2T_2)$ and $A_s(^6A_1)$ were found to be 19×10^5 Hz and 1.8×10^5 Hz respectively (cf. Fig. 2), in contrast to the results of Golding et al. [5]. We find that the contact shifts cannot be fitted with different signs of $A_s(^2T_2)$ and $A_s(^6A_1)$ in contrast to the results of Golding et al. [5] who have claimed excellent fit to the IPS data. As expected, $A_s(^2T_2) > A_s(^6A_1)$ indicating a higher covalency in the low spin state compared to that in the high spin state. This is in accordance with the X-ray investigations where the M-L bond lengths in the LS are smaller than that in the HS state.

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