Ligand Induced Spin Crossover in Penta-Coordinated Ferric Dithiocarbamates

P. Ganguli * and R. M. Iyer
Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Bombay 400085, India

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On addition of lewis bases to $Fe(dtc)_2X$, ligand exchange takes place through a SN_2 mechanism, with a parallel spin crossover in the ferric ion. The two species ($S = 3/2$ and $S = 5/2$) formed are in dynamic chemical equilibrium, and a slow decomposition is then initiated.

Introduction

Though extensive investigations on intermediate spin halo bis (diethyl dithiocarbamates), $[Fe(dtc)_2X]$ have been carried out so far [1, 2], little information is available on the effects of axial perturbation on these systems. Solvent effects of DMF, acetonitrile [3] and THF [4] on $Fe(dtc)_2X$, X=Cl, Br have indicated a probable change in the spin state of the ferric ion on solvation. Earlier [1] NMR studies on ferric dithiocarbamates have shown that the proton contact shifts of the methylene protons in the case of spin intermediate $Fe(dtc)_2X$ lie between 19.5 to 28 ppm and for high spin $Fe(dtc)_3$ these shifts are around to 38 ppm. Since the contact shifts of the methylene protons are so sensitive to the spin state of the metal ion, it was thought that NMR could be used as a diagnostic tool to reveal the ligand (pyridine and γ-picoline) induced spin crossover in the $Fe(dtc)_2X$ systems.

Results and Discussion

The large contact shifts and the broadening of the signals corresponding to the α, β and γ-protons of the pyridine or γ-picoline (cf. Fig. 1 and Table 1) indicate that these bases get bound to the ferric ion forming the corresponding adducts in solution. The observation of only one set of pyridine/γ-picoline protons and the base concentration dependence of the contact shifts indicate that the exchange between the bound and free pyridine/γ-picoline is fast on the NMR time scale. All the observed shifts of the base protons in the adducts are down field relative to the free bases. The shifts get attenuated as the number of bonds increase between the paramagnetic centre and the proton which are characteristic of a σ-delocalisation of the unpaired spin from the metal to the base [5].

The observation of two bands for the methylene protons of the dithiocarbamate ligands on addition of the lewis bases to $Fe(dtc)_2X$, clearly indicates the formation of two distinct adducts in solution. Preliminary electrochemical measurements show that on addition of the base to $Fe(dtc)_2X$, the concentration of X^- increases in solution which is attributed to a ligand exchange through an SN_2 mechanism. Such an exchange has also been found in the case of many pentacoordinated metalloporphyrins (6–8). Hence the two possible species in solution are $[Fe(dtc)_2B]^+X^-$ and $[Fe(dtc)_2B_2]^+X^-$. Based on the methylene contact shifts of 22 to 27 ppm and 35 to 37 ppm, it is concluded that an intermediate spin ($S = 3/2$) and another high spin ($S = 5/2$) species formed are in dynamic equilibrium with each other. However, the differences in contact shifts of the methyl protons are too small to reveal the two

Table 1. Proton contact shifts (ppm) in $Fe(dtc)_2X$ + base in $CDCl_3$.

Base	X	Diethyldithio-carbamate			Base		
		CH_2(A)	CH_2(B)	CH_3	α	β	γ
γ-picoline	Cl	36.8	24.0	2.7	8.7	4.4	6.2
	Br	36.5	22.1	2.7	8.3	4.3	5.9
	I	37.0	22.5	2.6	8.1	5.0	4.8
pyridine	Cl	37.8	25.8	2.7	8.2	3.2	0.9
	Br	35.6	25.6	2.6	5.7	3.1	0.5
	I	37.0	27.1	3.1	5.0	2.9	0

1. All shifts are negative and the observed shifts are corrected for diamagnetic shifts. (in dtc: CH_2: -4.18; CH_3: -1.29; γ-pic: α-H: -8.37; β-H: -6.99; γ-H: -2.29; pyridine: α-H: -8.28; β-H: -6.75; γ-H: -7.14).
2. Shifts in $Fe(dtc)_2X$ in $CDCl_3$ at 300 K [Cl : CH_2: -19.50; CH_3: -2.05; Br : CH_2: -22.52; CH_3: -2.41; I : CH_2: -27.82; CH_3: -3.31] from Ref. [1].
3. The shifts for the CH_2 protons are ± 0.2 ppm and those for CH_3, α-H, β-H and γ-H are ± 0.1 ppm.

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* Present address: Hindustan Lever Research Centre Chakala, Andheri East, Bombay 400099, India.

Reprint requests to Dr. R. M. Iyer, Physical Chemistry, Chemistry Devision, Bhabha Atomic Research Centre, Trombay, Bombay 400085, Indien.

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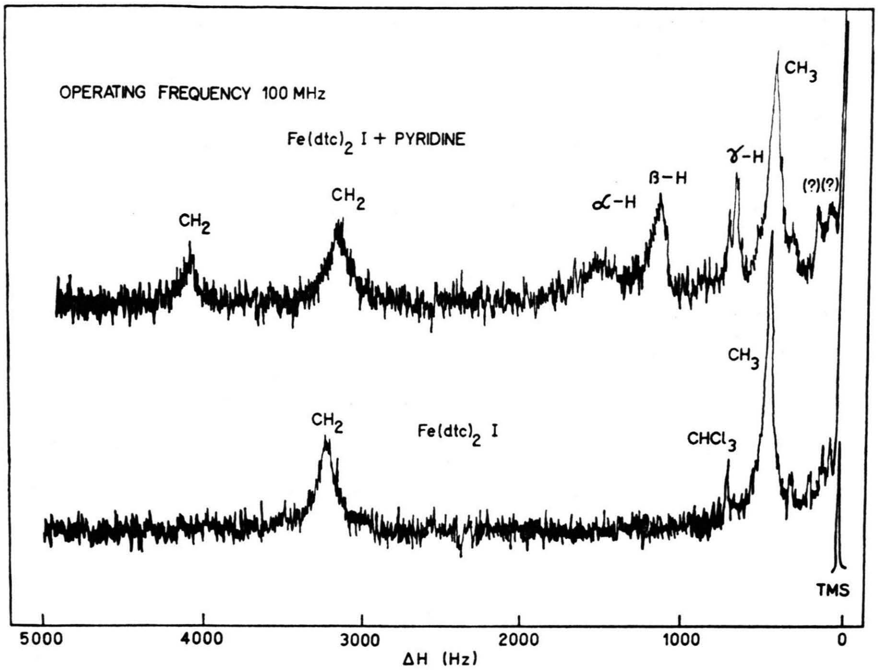

Fig. 1. Proton NMR spectra of $Fe(dtc)_2I$ before and after the addition of pyridine.

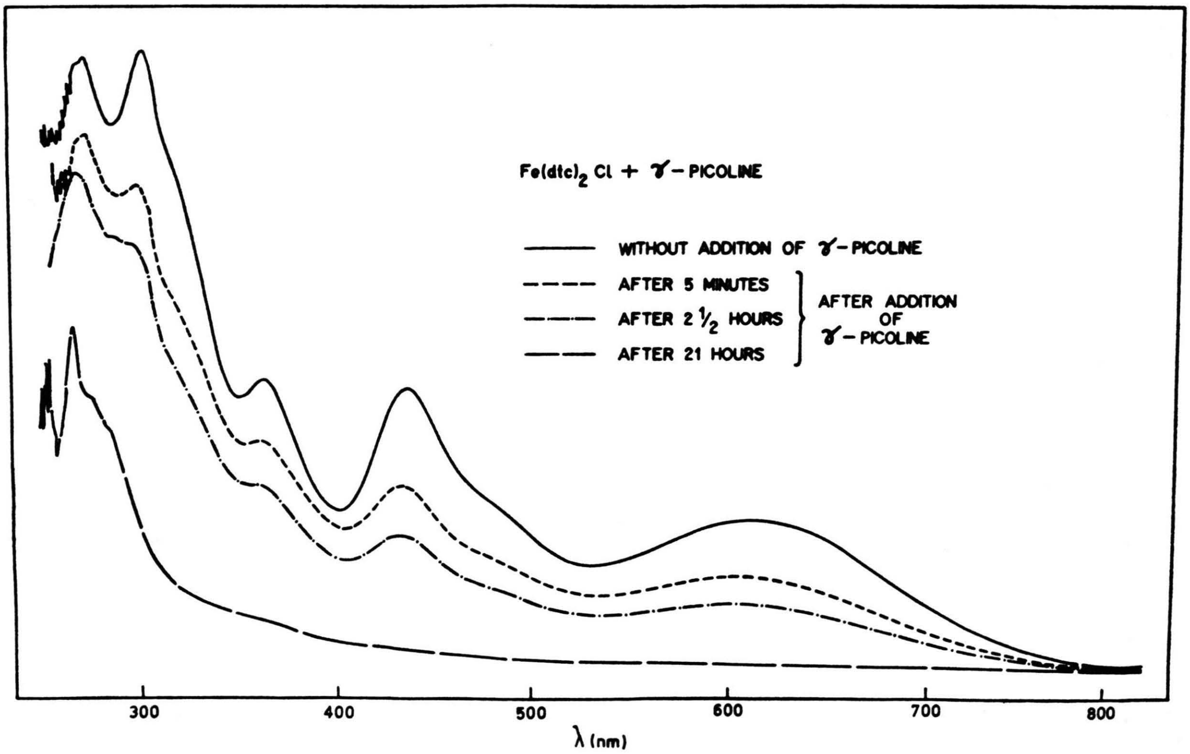

Fig. 2. Electronic absorption spectra of $Fe(dtc)_2Cl$ before and after the addition of γ-picoline.

species. The additional peak around 1.2 ppm on addition of the base to Fe(dtc)$_2$X in $CDCl_3$ suggests the formation of some diamagnetic species like thiuram disulphide. Similar observations have earlier been made by McLeverty et al. [9] during their studies on the adduct formation of some nickel dithiocarbamates. Optical studies of the decomposition process in chloroform solutions (Fig. 2) show that the rate is very strongly dependent on the base concentration. Also the absence of the characteristic IR bands of Fe(dtc)$_2$X or of possible adducts in solutions kept for 21 hours after base addition confirmed that these bases catalyse the decomposition of the complex after adduct formation.

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