MAGNETIC STUDIES OF TRANSITION METAL COMPLEXES IN SOLUTION

A Thesis Submitted for

THE DEGREE OF DOCTOR OF PHILOSOPHY

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by

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ABSTRACT

The temperature dependence of the magnetic properties of a variety of Fe$^{II}$ and Fe$^{III}$ complexes which exhibit a "spin-crossover" have been studied using an n.m.r. method for measuring magnetic susceptibility. Where possible, the data has been analysed to provide thermodynamic parameters for the spin-state equilibrium process.

The n.m.r. method has also been successfully applied to the study of ligand complexation reactions in which the formation of a complex results in a change in the spin state of the central metal ion.
CONTENTS

ABSTRACT 2

CONTENTS 3

LIST OF TABLES AND FIGURES 5

ACKNOWLEDGEMENT 9

ABBREVIATIONS AND SYMBOLS 10

INTRODUCTION - MAGNETIC SUSCEPTIBILITY IN SOLUTION - AN N.M.R. METHOD 13

CHAPTER ONE: VARIABLE TEMPERATURE MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF SPIN EQUILIBRIA FOR IRON(III) DITHIOCARBAMATES IN SOLUTION. 19

A) i) Spin equilibria in d^5 systems 20

ii) Iron(III) Dithiocarbamates 26

B) Results and discussion 31

C) Experimental 51

CHAPTER TWO: VARIABLE TEMPERATURE MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF SPIN EQUILIBRIA FOR IRON(II) COMPLEXES WITH 2-(2'-PYRIDYL)BENZIMIDAZOLE. 56

A) i) Spin equilibria in d^6 systems 57

ii) Fe(II) complexes of 2-(2'-pyridyl)benzimidazole 60

B) Results and discussion 64

C) Experimental 71
CHAPTER THREE: MAGNETIC TITRATIONS AND SPIN EQUILIBRIA
FOR IRON(III) PORPHINE COMPLEXES.

A)  i) Ferric Porphyrins  
    ii) Complexation reactions with nitrogenous 
        bases  
B) Magnetic titrations of ferric porphines  
C) Spin equilibria in ferric porphines  
D) Experimental  

CONCLUSIONS  

APPENDIX 1: Computer Program Four - Magnetic Susceptibilities  
APPENDIX 2: Computer Program Three - Chemical Shifts  
APPENDIX 3: Computer Program Five - Magnetic Titrations  
APPENDIX 4: Kinetics of the A + L₂ ⇄ AL₂ Equilibrium  
APPENDIX 5: Visible Absorption Spectra of Metal Porphines  

REFERENCES:
LIST OF TABLES AND FIGURES

FIGURES:

1.1 Variation of energy with ligand field strength for high-, intermediate- and low-spin states in octahedral transition metal complexes, d⁴-d⁷ 20

1.2 Electronic configurations of high- and low-spin d⁵ complexes 21

1.3 Structure of the Iron(III) dithiocarbamates 26

1.4 Bonding in the Iron(III) dithiocarbamates 29

1.5 Variation of magnetic moments with temperature for Fe(S₂CNBu₂)₃, solid and solution state 33

1.6 Variation of magnetic moments with temperature for Fe(S₂CNPr₂)₃, Fe[S₂CN(CH₂Ph)₂]₂, and Fe(S₂CNPrPh)₃ in toluene 35

1.7 Plot of ln[μ²-μ²_B/μ²_A-μ²] -vs- 1/T for a series of Iron(III) dithiocarbamates in toluene 38

1.8 Variation of magnetic moments with mean Fe-S distances for some known structures 39

1.9 Variation of magnetic moments with temperature for Fe(S₂CNPr₂)₃ in toluene, dichloromethane and chloroform solutions 42

1.10 ¹H-N.M.R. Spectrum of Fe(S₂CNPr₂)₃ in chloroform at 34°C 44

1.11 T₀ -vs- temperature curves for Fe(S₂CNPr₂)₃ in dichloromethane and toluene 46
1.12 Plot of $\ln[C_{L,S} - T6/T6 - C_{H,S}]$ -vs- $1/T$ for Fe(S$_2$CNPr$_2$)$_3$ in dichloromethane and toluene.

2.1 Electronic configurations of high- and low-spin $d^6$ complexes

2.2 Temperature dependence of the magnetic moment of Fe phen$_2$(NCS)$_2$

2.3 Mer- and fac-octahedral symmetry

2.4 Variation of magnetic moments with temperature for Fe(PYB)$_3$(BF$_4$)$_2$ (from ethanol); Fe(PYB)$_3$(BF$_4$)$_2$ (from acetone) and Fe(PYB)$_3$(ClO$_4$)$_2$ (from acetone) in the solid state

2.5 Variation of magnetic moments with temperature for Fe$^{II}$(PYB)$_3$X$_2$ in acetone/water. X = ClO$_4$ or BF$_4$

2.6 $\ln[\mu^2-\mu_B^2/\mu_A^2-\mu^2]$ -vs- $1/T$ for Fe$^{II}$(PYB)$_3$X$_2$ in acetone/water

3.1 Structure of Fe(PPIX)X and Fe(TPP)X

3.2 Configuration of 5-coordinated high-spin ferric porphyrins

3.3 d orbital splitting for the spin states encountered in ferric porphines

3.4 Structure of a six-coordinated low-spin ferric porphyrin

3.5 pH dependence of a ferri-haem undecapeptide

3.6 Magnetic titration curve for the equilibrium

$$Fe(TPP)Cl + 2 \text{Im} \leftrightarrow Fe(TPP)(\text{Im})^+ + Cl^-$$

3.7 Magnetic titration of hemin with imidazole and cyanide
3.8 Magnetic titration of Fe(TPP)Cl with 1-Melm (35°C) 93
3.9 Magnetic titration of Fe(TPP)Cl with 1-Melm at 24.6°C 93
3.10 Magnetic titration of Fe(TPP)Br with 1-Melm at 35°C 97
3.11 Magnetic titration of Fe(PPIX-DME)Cl with 1-Melm at 35°C 97
3.12 Magnetic titration of Fe(TPP)Cl with Me₂N-Py at 35°C 98
3.13 Magnetic titration of Fe(PPIX-DME)Cl with Me₂N-Py at 35°C 98
3.14 Magnetic titration of Fe(PPIX-DME)Br with 1-Melm at 35°C 99
3.15 Magnetic titration of Fe(TMPP)Cl with 1-Melm at 35°C 99
3.16 Magnetic titration of Fe(TPP)I with pyridine at 37.4°C 100
3.17 Magnetic titration of Fe(TMPP)Br with 1-Melm at 35°C 100
3.18 Stabilization of N-H imidazole complexes of ferric porphyrins 102
3.19 Spin equilibrium of Fe(PPIX-DME)(Py)⁺X⁻ in chloroform 108
3.20 Spin equilibrium of Fe(PPIX-DME)(Py)⁺ in chloroform 110
3.21 Temperature dependence of the effective magnetic moments, μ_eff, of hemichrome salts; a) in chloroform b) solid state 111
TABLES

A. Comparison of the three methods for calculating $\mu_{\text{eff}}$ from data obtained by the n.m.r. method

1.1 Magnetic moments of $d^5$ transition metal complexes

1.2 Magnetic moments of Fe(S$_2$CNR'R")$_3$ at room temperature

1.3 Thermodynamic Parameters for Fe(S$_2$CNR'R")$_3$ in toluene solution

1.4 Thermodynamic parameters for Fe(S$_2$CNPr$_2$)$_3$ in various solvents

1.5 Paramagnetic shift data obtained for the -NCH$_2$- protons of Fe(S$_2$CNPr$_2$)$_3$ in toluene and dichloromethane

1.6 Elemental analysis and melting points for tris(N,N-diorganodithiocarbamato)Fe$^{\text{III}}$ complexes

2.1 Magnetic moments of $d^6$ transition metal complexes

2.2 Magnetic moments as a function of temperature for the cation Fe$^{\text{II}}$(PYB)$_3$$^{++}$

3.1 The variation of the molecular weight of Fe(PPIX-DME)Cl with concentration and solvent

3.2 Kinetic data for the equilibrium

$$\text{Fe(P)X} + 2L \rightleftharpoons \text{Fe(P)L}_2^+ + X^-$$

3.3 Magnetic moments of ferric porphyrins in chloroform solution
I would like to express my thanks to Dr. D.F. Evans for his encouragement, guidance and friendship during the period in which this work was undertaken.

My thanks also to Sue Johnson for valuable assistance with the Beckman LM-500 and Dr. D.M.L. Goodgame for the provision of samples of tris[2-(2'-pyridyl)benzimidazole]Iron(II) perchlorate and tetrafluoroborate.

Finally, my thanks to Moira for typing this thesis.
ABBREVIATIONS AND SYMBOLS

The following is a list of abbreviations and symbols used throughout the text.

1) Chemical

Me = Methyl, CH₃-; Et = Ethyl, CH₃-CH₂-
Prⁿ = n-propyl, CH₃-CH₂-CH₂-; Buⁿ = n-butyl, CH₃-CH₂-CH₂-CH₂-
Buᵗ = t-butyl, (CH₃)₃C-; Hxⁿ = n-hexyl, CH₃-(CH₂)₅-
Ph = phenyl, C₆H₅-; CH₂Ph = benzyl, C₆H₅CH₂-

Pyr = Pyrrolidyl, \overline{CH₂-CH₂-CH₂-CH₂-N⁻}; pz = l-pyrazolyl

Py = pyridine
Im = imidazole
1-Melm = 1-Methylimidazole
Me₂N-Py = dimethylaminopyridine
amp = 2-aminomethylpyridine
PYI = 2-(2'-pyridyl)imidazole
PYIM = 2-(2'-pyridyl)imidazoline
PYB = 2-(2'-pyridyl)benzimidazole

tren = tris(2-aminoethyl)amine

papth = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole

PTFE = polytetrafluoroethylene

THF = tetrahydrofuran
DMSO = dimethylsulphoxide
DMF = diemthylformamide
TMS = tetramethylsilane
HMDS = hexamethyldisiloxane

P = Any porphyrin
TPPH$_2$ = Tetraphenylporphyrin
OEPH$_2$ = Octaethylporphyrin
PPIXH$_2$ = Protoporphyrin IX
PPIX-DMEH$_2$ = Protoporphyrin IX - Diethyl Ester
TMPPH$_2$ = tetra(p-methoxyphenyl)porphyrin

2) Others
Å = Angstrom unit
B.M. Bohr Magnetons, 1 B.M. = 9.274 x 10$^{-24}$ J.T.$^{-1}$
$\Delta H$ = Enthalpy change
N.M.R. = Nuclear Magnetic Resonance
P = Pressure
ppm = parts per million
R = Universal Gas Constant = 8.314 J. mol$^{-1}$ K$^{-1}$
$\Delta S$ = Entropy change
T = temperature
$\chi$ = Gram magnetic susceptibility
$\chi'_M = \chi_A$ = Molar magnetic susceptibility corrected for diamagnetism of the ligands
$\mu_{\text{eff}}$ = Magnetic Moment
To TERESA
An n.m.r. method has been described\(^1\) for the measurement of the paramagnetic susceptibilities of compounds in dilute solution. The method involves the measurement of the chemical shift difference between the protons of an inert reference substance in a given solvent and in a solution of the paramagnetic material of known concentration in the same solvent.

The position of the resonance line of a nucleus in a molecule is affected by the bulk diamagnetic shielding of the medium in which the molecule is situated. For two cylindrical samples differing in volume susceptibility by \(\Delta K\) the bulk susceptibility shift is given by the theoretical expression

\[
\frac{\Delta H}{H} = C\Delta K
\]

where \(C = \frac{2\pi}{3}\).\(^2\)

So where \(\Delta f\) is the frequency separation between the two lines (inert reference in solvent and in solution), \(f\) is the oscillator frequency, in Hz, and \(\Delta k\) is the change in volume susceptibility \(k_S - k_o\).

\[
\Delta f = \frac{2\pi}{3} f \Delta k
\]

\[\Delta k = \frac{3}{2\pi} \frac{\Delta f}{f} = k_S - k_o = \chi_S d_s - \chi_o d_o\]

where \(\chi_S\) = mass susceptibility of solution

\(\chi_o\) = mass susceptibility of solvent

\(d_s\) = density of solution

\(d_o\) = density of solvent
\[ \chi_s = \frac{3 \Delta f}{2\pi f} + \chi_o \]  

\[ \chi_s = \frac{3 \Delta f}{2\pi f d_s} + \chi_o \frac{d_o}{d_s} \]  

By Wiedemann's additivity relationship 3

\[ \chi_s = \chi \cdot x + \chi_o (1-x) \]

where \( x \) is the weight fraction of solute, \( x = m/ds \) where \( m \) is g/ml of solute.

\[ \chi_s = x \frac{m}{ds} + \chi_o \left( 1 - \frac{m}{ds} \right) = \frac{3 \Delta f}{2\pi f d_s} + \chi_o \frac{d_o}{d_s} \]

\[ \chi_s = \frac{m}{d_s} = \frac{3 \Delta f}{2\pi f d_s} + \chi_o \frac{d_o}{d_s} - \chi_o \left( 1 - \frac{m}{ds} \right) \]

\[ \chi = \frac{3 \Delta f}{2\pi f m} + \chi_o \frac{d_o}{m} - \chi_o \left( \frac{ds}{m} - 1 \right) \]

\[ \chi = \frac{3 \Delta f}{2\pi f m} + \chi_o \left( 1 + \frac{d_o - ds}{m} \right) \]

\[ \chi = \frac{3 \Delta f}{2\pi f m} + \chi_o + \frac{\chi_o (d_o - ds)}{m} \]  

This full expression has been used to obtain susceptibilities throughout Chapters 1 and 2 of this thesis, and it is an exact expression given \( \Delta f = 2\pi/3 f \Delta k \) and the Wiedemann additivity relationship. Two approximations to the exact expression, which do not require the measurement of densities are
\[ x = \frac{3\Delta f}{2\pi f m} + x_o \]  

(simply omitting the last term)

and

\[ x_A = \frac{3\Delta f A}{2\pi f m'} \]

where A is the atomic weight of the metal, and m' is the mass of the metal in 1 ml of solution. In this expression it is assumed that the volume diamagnetic susceptibility of the complex is the same as that of the solvent. This can more conveniently be written in terms of the magnetic moment \( \mu_{\text{eff}} \) (as \( \mu_{\text{eff}} = 2.8278 \left( \frac{x_A T}{2} \right)^{\frac{1}{2}} \)).

\[ \mu_{\text{eff}} = 0.0618 \left( \frac{\Delta f}{f} \right)^{\frac{1}{2}} \left( \frac{T}{M} \right)^{\frac{1}{2}} \]  

This expression holds for any one metal centre complex, where T is the temperature (°K), f is the oscillator frequency expressed in MHz and M is the molarity of the complex (moles/litre).

Since extensive density data has been obtained during the course of this work a check has been made of the accuracy of the two approximations to the exact expression, in solvents of varying mass susceptibilities. The results are represented in Table A.

As can be seen in the table both approximations are good to within 1% and the second approximation is not only easier to use, as diamagnetic corrections do not have to be applied, but on balance is the more accurate. It is recommended that for work of moderate accuracy expression (6) should be applied; for variable temperature
Table A. Comparison of the three Methods for Calculating $\mu_{\text{eff}}$ from Data Obtained by the N.M.R. Method.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar Susceptibility</th>
<th>$\mu$ exact expression&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\mu$ approx (1)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% Error</th>
<th>$\mu$ approx (2)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>$-0.729 \times 10^{-6}$</td>
<td>4.658</td>
<td>4.629</td>
<td>0.60</td>
<td>4.663</td>
<td>0.10</td>
</tr>
<tr>
<td>Acetone</td>
<td>$-0.602 \times 10^{-6}$</td>
<td>4.651</td>
<td>4.611</td>
<td>0.85</td>
<td>4.626</td>
<td>0.55</td>
</tr>
<tr>
<td>Chloroform</td>
<td>$-0.517 \times 10^{-6}$</td>
<td>4.552</td>
<td>4.528</td>
<td>0.50</td>
<td>4.531</td>
<td>0.45</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molecular weight of the complex taken to be 542.57; diamagnetic correction for ligands taken to be $267 \times 10^{-6}$ c.g.s. units. $\mu = 2.8278 \left( x_A T \right)^\frac{1}{2}$.
temperature work it is, of course, still necessary to correct for the change in density of the solution with temperature. Expression (6) has been used throughout Chapter 3 of this thesis. The assumption that the volume diamagnetic susceptibility of the complex is the same as that of the solvent is reasonable as it is known that volume diamagnetic susceptibilities of the majority of organic liquids and dissolved solids lie in the region \(0.61 \pm 20\%\).

For variable temperature work three main methods can be used for correcting for the change in density, and hence concentration, of the solution with temperature. 1) Density measurements at various temperatures (see Chapter 1 D) for details. 2) Measuring the depths of liquid in the n.m.r. tube at room temperature and at low temperatures \(^6\) or 3) using accurate density data taken at or around room temperature and extrapolating back to give low temperature densities. Accurate room temperature data are readily available\(^7\) and an expression of the sort

\[d_t = d_0 + at + bt^2\]

can be employed in the extrapolation to give the density \(d\) at any temperature \(t\)°C. This last 'approximation' method is in fact extremely accurate. E.g., density 4% HMDS/96% toluene measured as in Chapter 1 C is 0.95365 g/ml.

Density calculated using reference 7 (values from 0°C - 30°C) and the expression given above is 0.95406 g/ml. - percentage error 0.04%.
The n.m.r. method as outlined above has several great advantages which include its sensitivity (< 0.01 M solutions can be used), the small amount of substance required (a magnetic titration followed by a spin equilibrium study of a metal porphine can be carried out with just 2-3 mgms of material), ready availability of variable temperature measurements and applicability to air-unstable compounds using standard rubber septum cap techniques. This makes it the ideal technique for the study of spin-equilibria, magnetic properties and ligand complexation reactions as described in this thesis.
CHAPTER 1

Variable Temperature Magnetic Susceptibility Measurements of Spin Equilibria For Iron(III) Dithiocarbamates in Solution.
A) i) Spin Equilibria in $d^5$ Complexes.

Octahedral transition metal complexes with configurations $d^4$, $d^5$, $d^6$, or $d^7$ do not have a uniquely defined ground state, but fall into one of two groups depending on the strength of the ligand field.\(^8\) (See Figure 1).

Figure (1.1)

This situation has been interpreted by crystal field theory in terms of the total spin quantum number of the electrons in the complex, $S$.

With weak field ligands $S$ will take its maximum value (high spin) and with strong field ligands $S$ will take its minimum value (low spin). The ground state of the ion changes at the crossover point $\Delta_x$. 
A regular octahedral complex will never have a ground state of intermediate spin.

The magnetic properties of the complex depend mainly on the number of unpaired electrons in the d orbitals of the metal; to a good approximation the spin-only formula \( \mu = 2 \sqrt{S(S + 1)} \text{ B.M.} \) is correct.\(^9\) The high- and low-spin complexes will each possess different magnetic moments as their spin quantum numbers are different.

**Figure (1.2)**

**High spin and low spin \(d^5\) complexes**

**High**

\[ \uparrow \Delta_0 \uparrow \]

\[ \{ \text{e}_g \} \quad d_{z^2}, d_{x^2-y^2} \text{ orbitals} \]

**Electronic configuration** \( t_{2g}^3 e_g^2 \) \( (^6A_1), S = \frac{5}{2} \)

\[ \downarrow \Delta_0 \downarrow \]

\[ \{ \text{t}_{2g} \} \quad d_{xy}, d_{xz}, d_{yz} \text{ orbitals} \]

**Low**

\[ \uparrow \Delta_0 \uparrow \]

\[ \{ \text{e}_g \} \quad d_{z^2}, d_{x^2-y^2} \text{ orbitals} \]

**Electronic configuration** \( t_{2g}^5 \) \( (^2T_2), S = \frac{1}{2} \)
Figure (1.2) represents the case of the d5 configuration, e.g., Fe(III). Examples of weak field- and strong field complexes of Fe(III) are given below (Table 1.1).

Table 1.1. Magnetic Moments of d5 Transition Metal Complexes.

<table>
<thead>
<tr>
<th>Spin State</th>
<th>S</th>
<th>$\mu_{S.0}$</th>
<th>$\mu_{\text{eff}}$</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>5/2</td>
<td>5.92</td>
<td>5.7-6.0</td>
<td>[Fe(H2O)6]3+, [FeF6]3-</td>
</tr>
<tr>
<td>Low</td>
<td>1/2</td>
<td>1.73</td>
<td>2.0-2.5</td>
<td>[Fe(CN)6]3-, [Fe(phen)3]3+</td>
</tr>
</tbody>
</table>

* Taken from reference 9.

The transition from a high spin ground state to a low spin ground state involves the transfer of two electrons from the higher energy $e_g$ orbitals to the lower energy $t_{2g}$ orbitals. Hence the orbital energy is enhanced by $2\Delta_0$. This is offset by increased Coulomb forces of repulsion between the $t_{2g}$ electrons and by the loss of quantum mechanical energy upon the spin pairing process.8 The mean pairing energy, $P$, and the ligand field stabilization energy $\Delta_0$ thus determine the ground state. If $\Delta_0 \gg P$ the complex will be low spin, if $\Delta_0 \ll P$ the complex will be high spin. But if $\Delta_0 \approx P$ then the high spin ground state and the low spin ground state will be of about equal energy. As a consequence a temperature and pressure dependent spin state equilibrium is established.

$^6A_1 \rightarrow ^2T_2$
Several factors are known to influence this spin state equilibrium, e.g., chemical modification of the ligands, solid state effects, changes of pressure and changes of temperature.

Chemical Modification of the Ligands:- Minor chemical changes to the ligands can cause large changes in the physical properties of the complex as the ligand field in the crossover region is very sensitive to such changes. This is best illustrated by reference to the magnetic data obtained by White, et al.,\textsuperscript{10} for the ferric dithiocarbamates in solution, at room temperature. The complexes are seen to fall into four distinct groups depending on the substituents $R^1$ and $R^2$ in Fe(S$_2$CNR$^1$R$^2$)$_3$. Group I includes the parent complex Fe(S$_2$CNH$_2$)$_3$ and has a $^6A_1$ ground state, $\mu_{\text{eff}} = 5.8 \pm 0.1$ B.M. Group II contains two n-alkyl substituents, $\mu_{\text{eff}} = 4.3 \pm 0.1$ B.M. In Group III, one of the n-alkyl substituents is replaced by a phenyl substituent, displacing the equilibrium towards a lower spin state, $\mu_{\text{eff}} = 3.5 \pm 0.15$ B.M. and Group IV is almost totally low spin and includes those complexes with two phenyl substituents, $\mu_{\text{eff}} = 2.6 \pm 0.3$ B.M.

Solid State Effects:- Crystal lattice effects can alter the symmetry of the metal ion in the complex, imposing a further distortion onto the intrinsically distorted free molecule.\textsuperscript{11} Also, the ligand field strength may be affected by atoms belonging to near-neighbour molecules in the lattice, thus altering the relative populations of high- and low-spin states present, in an unpredictable way; e.g., take the value $[\mu_{\text{eff}} (\text{solid}) - \mu_{\text{eff}} (\text{solution})]$ for the following complexes:\textsuperscript{10}
\[
\begin{align*}
\text{Fe}(S_2\text{CNBu}^\text{H})_3 & \quad 5.32 \text{ B.M.} - 4.34 \text{ B.M.} = +0.98 \text{ B.M.} \\
\text{Fe}(S_2\text{CNMe}_2)_3 & \quad 4.17 \text{ B.M.} - 4.20 \text{ B.M.} = -0.03 \text{ B.M.} \\
\text{Fe}(S_2\text{CNHx}^\text{P})_3 & \quad 3.52 \text{ B.M.} - 4.42 \text{ B.M.} = -0.90 \text{ B.M.}
\end{align*}
\]

The formation of solid state adducts adds a further degree of complexity to solid state data.\(^1\)\(^2\) Phase changes also occur in certain complexes (see Figure (1.5)).

**Effect of Pressure:** The metal-ligand bond distances of the low-spin ferric complexes \((t_{2g}^5)\) are shorter\(^1\)\(^3\) than the metal-ligand bond distance of the high-spin complex \((t_{2g}^3 e_g^2)\) due to the differences in spatial arrangement of the filled orbitals. Consequently, the equilibrium is pressure dependent, and is related to the accompanying volume change \(\Delta V\).

\[
\left[ \frac{\partial (\ln K)}{\partial P} \right]_T = -\frac{\Delta V}{RT}
\]

where \(K\) is the equilibrium constant.

**Effects of Temperature:** The equilibrium \(^2T_d \rightleftharpoons ^6A_1\) like all other equilibria will depend on the free energy change \(\Delta G^0\) when 1 mole of low-spin species is transformed to 1 mole of high-spin species, each being in their standard states.

\[
\left[ \frac{\partial (\ln K)}{\partial T} \right]_P = \frac{\Delta G^0}{RT^2}
\]

\[\Delta G^0 = -RT \ln K.\]
This standard thermodynamic expression has been used as the starting point for the analysis of the solution state magnetic data in this Chapter (see p. 36). One of the aims of this section of the work is to show that in solution the equilibrium can be analysed on the basis of a simple Boltzmann distribution between the two spin states. Because of solid state effects this has not been possible with previous variable temperature data on ferric dithiocarbamates. Similar analyses have been performed recently for the bis(N-methylethlenediaminesalicylaldiminato)Iron(III) complexes, and with iron(III) chelates derived from triethylenetetramine and various salicylaldehydes.

Apart from variable temperature magnetic measurements, a great many other physical techniques have been used over the years to study the spin-equilibrium phenomenon. Some of the most successful are infra-red spectroscopy, Mossbauer, $^1$H nmr and X-ray photoelectron spectroscopy. There is no doubt, however, that variable temperature magnetic measurements in solution are the most important physical measurements in this field.
ii) **Iron(III) Dithiocarbamates.**

The iron(III) dithiocarbamates, Fe(III) \( (S_2C.NR'R'') \) (Figure 1.3) were first prepared by Delepine in 1908.\(^{24}\)

*Figure (1.3) Iron(III) Dithiocarbamates.*

The anomalous magnetic behaviour of these compounds was first characterised by Cambi and co-workers during the years 1931-1933.\(^{25,26}\) They noted that \( \mu_{\text{eff}} \) was intermediate between the values expected for high- and low-spin Fe(III) complexes and depended on the alkyl groups \( R' \) and \( R'' \). Furthermore, the magnetic properties obeyed neither a
Curie or Curie-Weiss law and Cambi's interpretation was "a thermal equilibrium between two magnetically isomeric forms". White, et al., synthesised nineteen members of the dithiocarbamate series\(^\textsuperscript{10}\) and confirmed the findings of Cambi. Magnetic moments were reported in solid and solution states (benzene and chloroform) using the Gouy technique. This was followed by a variable temperature solid state study of these complexes\(^\textsuperscript{14}\), the moments represented theoretically by\(^\textsuperscript{14,27}\)

\[
\mu_{\text{eff}}^2 = 0.75 g^2 + 8x^{-1} (1 + e^{-3x/2}) + 105 C e^{-(1 + (\epsilon/\zeta))x} / \left(1 + 2e^{-3x/2} + 3 C e^{-(1 + (\epsilon/\zeta))x}\right)
\]

\(x = \zeta/kT\), \(\zeta\) is the one electron spin-orbit coupling constant, an important factor for all low spin \(d^5\) complexes\(^\textsuperscript{28,29}\), \(g\) is the spectroscopic splitting factor applicable to the \(^2T_2\) state and \(\epsilon\) the zero point separation energy of the two states. \(C = Q_a/Q_t\) the ratio of the molecular vibrational partition functions. This formula was also used to give an accurate interpretation of solid state results for the morpholine, 2-methylpiperidine and 3-methylpiperidine derivatives\(^\textsuperscript{30}\).

White also noted the importance of lattice effects on solid state results, and his classification of dithiocarbamate complexes in four distinct groups was based on their solution magnetic properties\(^\textsuperscript{10}\).

The crystal structure\(^\textsuperscript{11}\) of the n-butyl derivative, \(\text{Fe(S}_2\text{CNBu}_2)_3\), removed any doubts about the coordination of the dithiocarbamate ligand to the metal\(^\textsuperscript{10}\). The molecular core is Fe-S\(_6\) but the symmetry is nearer to trigonal prismatic than octahedral. Such large deviations
from octahedral symmetry make the theoretical models less appealing.

A $^{57}$Fe Mossbauer study of the Iron(III) dithiocarbamates showed that the high-spin and low-spin spectra are mixed to give a single observable spectrum. This is due to rapid exchange between the states and was confirmed by subsequent work. This situation also arises with some Iron(II) complexes, but with others such as Fe(amp)$_3^{2+}$ and Fe[HB(Pz)$_3$]$_2$ two doublets can be observed at 77°K due to the two spin states. This shows that the rate of exchange between high- and low-spin states is faster than the lifetime of the $^{57}$Fe I = 3/2 state, i.e., faster than $\approx 10^7$ sec$^{-1}$ for the ferric dithiocarbamates. Hence, nmr and Mossbauer spectra are weighted averages, but the e.p.r. signal has both a high- and low-spin constituent. Thus, the rate of exchange is between $10^7$ and $10^{10}$ sec$^{-1}$.

As the vibrational time scale is $10^{-12}$ - $10^{-14}$ sec., i.r. provides another method by which both spin states can be studied simultaneously. The i.r. spectrum of Fe(S$_2$CNET$_2$Ph)$_3$ has been studied at different pressures and it is found that two Fe-S bands are present: one attributed to the $^2T_2$ state and one to the $^6A_1$. The $^2T_2$ band is to higher energy as this is the state with the stronger Fe-S bond. This band increases in intensity as compared to the $^6A_1$ band as the pressure is increased. The isotope shift is also much greater for the $^2T_2$ band than for the $^6A_1$ band. Similar results have been obtained for the compound Fe(S$_2$CNET$_2$)$_3$. 

$^{31}$

$^{32}$

$^{33}$

$^{34}$

$^{35}$

$^{36}$
Eley, et al., found that the $^{57}$Fe Mossbauer isomer shift and $\mu_{\text{eff}}$ were linearly related. The isomer shift declines as the low spin state is approached. This was attributed to bonding differences between the two states; in the low-spin state the d electrons are delocalized to a greater extent, because of increased interaction between the d orbitals and the empty ligand $\pi$ orbitals, arising from the d orbitals of the sulphur atoms. This bonding difference can be expressed by the two limiting forms A and B in Figure (1.4). The low-spin state is favoured by A and the high-spin state by B. Because of the delocalization of d electrons in the low-spin state the S electrons are deshielded from the nucleus and the isomer shift diminishes.

Figure (1.4) Bonding in Iron(III) Dithiocarbamates.

limiting form A

![Limiting form A](image1)

limiting form B

![Limiting form B](image2)

The same bonding picture of greater covalence accompanying the shortening of the Fe-S bond lengths has also been applied by the same author to help explain his findings that a linear relationship occurs between $\mu_{\text{eff}}$ (solution) and $pK_a$ of the parent secondary amine of the ligand.
Many compounds closely related to the tris-dithiocarbamates have also been found to exhibit a spin-state equilibrium. These include the ferric thioxanthates, Fe(S₂C−SR)₃; the bis(dithiocarbamate)-dithiolene complexes, [Fe(S₂CNR₁R₂)₂(S₂C₂R₂)] and the ferric monothiocarbamates, Fe[S(O)CNR₁R₂].

To summarise, it is now known that a ²T₂ − ⁶A₁ spin equilibrium (for assumed octahedral symmetry) is present in the compounds Fe(S₂CNR'R")₃. However, interpretation of the susceptibility data is complicated by solid state effects. Thus, an appreciable number of disposable parameters is necessary to give a reasonable theoretical fit to the observed results. Also, the magnetic moments of a pure complex, its adducts with molecules such as benzene, chloroform and dichloromethane and its solutions (at room temperature) often differ very considerably. Similar differences are also found between closely related pure complexes such as Fe(S₂CNPr₂)₃ and Fe(S₂CNBu₂).  

Although the magnetic moments of a large number of ferric dithiocarbamates have been obtained in solution at room temperature there is only a brief report of one variable temperature measurement. Accordingly, in this work the magnetic moments of four representative ferric dithiocarbamates have been obtained in solution over a wide range of temperature and the data analysed to provide thermodynamic parameters for the spin equilibrium. For one complex, confirmatory data has been obtained from the paramagnetic shifts in the proton resonance spectrum.
### B) RESULTS AND DISCUSSION

#### i) Spin Equilibria in Toluene Solutions:

The magnetic moments as a function of temperature for the four dithiocarbamate complexes studied are given below.

**Tris(N,N-di-n-propyldithiocarbamato)Iron(III)**

<table>
<thead>
<tr>
<th>Temp</th>
<th>97.5</th>
<th>83.2</th>
<th>69.3</th>
<th>49.8</th>
<th>35.3</th>
<th>20.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>7.44</td>
<td>7.44</td>
<td>7.54</td>
<td>7.62</td>
<td>7.56</td>
<td>7.56</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.70</td>
<td>4.60</td>
<td>4.55</td>
<td>4.44</td>
<td>4.32</td>
<td>4.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp</th>
<th>0.4</th>
<th>-19.7</th>
<th>-40.4</th>
<th>-60.4</th>
<th>-80.7</th>
<th>-98.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>7.61</td>
<td>7.40</td>
<td>7.10</td>
<td>6.77</td>
<td>6.42</td>
<td>6.12</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.08</td>
<td>3.87</td>
<td>3.63</td>
<td>3.40</td>
<td>3.14</td>
<td>2.92</td>
</tr>
</tbody>
</table>

**Tris(N,N-di-n-butyldithiocarbamato)Iron(III)**

<table>
<thead>
<tr>
<th>Temp</th>
<th>97.5</th>
<th>83.2</th>
<th>69.3</th>
<th>49.8</th>
<th>34.3</th>
<th>20.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>7.75</td>
<td>7.75</td>
<td>7.75</td>
<td>7.84</td>
<td>8.13</td>
<td>8.22</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.79</td>
<td>4.70</td>
<td>4.61</td>
<td>4.50</td>
<td>4.47</td>
<td>4.40</td>
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</table>

<table>
<thead>
<tr>
<th>Temp</th>
<th>0.4</th>
<th>-19.7</th>
<th>-40.4</th>
<th>-60.4</th>
<th>-80.7</th>
<th>-98.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>7.96</td>
<td>7.72</td>
<td>7.39</td>
<td>7.11</td>
<td>6.72</td>
<td>6.04</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.17</td>
<td>3.96</td>
<td>3.71</td>
<td>3.48</td>
<td>3.22</td>
<td>2.91</td>
</tr>
</tbody>
</table>
### Tris(N,N-dibenzyldithiocarbamato)Iron(III).

<table>
<thead>
<tr>
<th>Temp</th>
<th>97.5</th>
<th>83.2</th>
<th>69.3</th>
<th>49.8</th>
<th>34.3</th>
<th>20.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>6.24</td>
<td>6.19</td>
<td>6.10</td>
<td>5.94</td>
<td>5.69</td>
<td>5.53</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.30</td>
<td>4.20</td>
<td>4.09</td>
<td>3.92</td>
<td>3.74</td>
<td>3.61</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Temp</th>
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<th>-19.7</th>
<th>-40.4</th>
<th>-60.4</th>
<th>-80.7</th>
<th>-98.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>5.28</td>
<td>4.84</td>
<td>4.47</td>
<td>4.07</td>
<td>3.84</td>
<td>3.66</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>3.40</td>
<td>3.13</td>
<td>2.88</td>
<td>2.63</td>
<td>2.43</td>
<td>2.26</td>
</tr>
</tbody>
</table>

### Tris(N-n-propyl-N-phenyldithiocarbamato)Iron(III).

<table>
<thead>
<tr>
<th>Temp</th>
<th>97.5</th>
<th>83.2</th>
<th>69.3</th>
<th>49.8</th>
<th>34.3</th>
<th>20.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>5.76</td>
<td>5.75</td>
<td>5.67</td>
<td>5.44</td>
<td>5.26</td>
<td>5.10</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.13</td>
<td>4.05</td>
<td>3.94</td>
<td>3.75</td>
<td>3.60</td>
<td>3.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp</th>
<th>0.4</th>
<th>-19.7</th>
<th>-40.4</th>
<th>-60.4</th>
<th>-80.7</th>
<th>-98.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_M'$</td>
<td>4.89</td>
<td>4.56</td>
<td>4.21</td>
<td>3.94</td>
<td>3.73</td>
<td>3.45</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>3.27</td>
<td>3.04</td>
<td>2.80</td>
<td>2.59</td>
<td>2.39</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Units: Temp, °C; $\chi_M' \times 10^3$ x cgs units; $\mu_{\text{eff}}$, B.M. Range of concentration studied 10 - 22 mM.

The magnetic moments compare well with those obtained in previous studies by the Gouy method at room temperature (see Table 1.2).
Figure 1.5: Variation of Magnetic Moments with temperature for Fe(S$_2$C$\text{N}$Bu$_2$)$_3$. Solid data calculated from eq. (1) ref. 10. Solution data X - experimental pts. / - calculated curve eq. (9) page 36.
Table 1.2: Magnetic Moments of Fe(S₂CN'R''₆)₃ at Room Temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref. 37ᵃ</th>
<th>Ref. 10ᵇ</th>
<th>This workᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(S₂CNPr₂n)₃</td>
<td>4.14</td>
<td>4.24</td>
<td>4.22</td>
</tr>
<tr>
<td>Fe(S₂CNBu₂n)₃</td>
<td>4.53</td>
<td>4.34</td>
<td>4.40</td>
</tr>
<tr>
<td>Fe[S₂CN(CH₂Ph)₂]₃</td>
<td>3.60</td>
<td>3.60</td>
<td>3.61</td>
</tr>
<tr>
<td>Fe(S₂CNPr₂n,Ph)₃</td>
<td>3.75</td>
<td>3.55</td>
<td>3.46</td>
</tr>
</tbody>
</table>

ᵃ Chloroform solution at room temperature.
b Benzene solution at 23°C.
c Toluene solution at 20.9°C.

All four complexes clearly exhibit a temperature dependent spin state equilibrium in solution, similar to that already shown to exist in the solids.¹⁴ However, large differences can occur between solid and solution as illustrated for Fe(S₂CNBu₂n)₃ in Figure (1.5). Curves representing the solution state results obtained with Fe(S₂CNPr₂n)₃, Fe[S₂CN(CH₂Ph)₂]₃ and Fe(S₂CNPr₂n,Ph)₃ are shown in Figure (1.6). In contrast to the solid state results¹⁰,¹⁴ the magnetic moments of Fe(S₂CNPr₂)n₃ and Fe(S₂CNBu₂)n₃ in toluene solution are quite similar.

In the absence of solid state effects (crystal lattice effects, phase changes) the spin equilibrium between the high spin ⁶A₁ and the low spin ⁵T₂ ground states can be treated as a simple thermal equilibrium, the high spin state (⁶A₁) becoming increasingly populated
Figure 1.6: Variation of Magnetic Moments with temperature for Fe(s₂CNPh)₃ X 3Fe(s₂CN(CH₂Ph)₃)

- Fe(s₂CNPh-Ph)₃ 0, in toluene. The solid lines are calculated from eq. (9) page 36.
as the temperature is increased according to a Boltzmann distribution.

For the equilibrium $^{2}T_{2} \rightleftharpoons ^{6}A_{1}$

$$\Delta G = \Delta H - T \Delta S = -RT \ln [A]/[B]$$

(see p. 24 *)

where $[A]$ is the mole fraction present in the high spin state and $[B]$ the mole fraction present in the low spin state.

$$\therefore R \ln ([A]/[1 - [A]]) = \Delta S - \Delta H/T$$

(7)

$$\mu^2 = \mu^2_A [A] + \mu^2_B [1 - [A]]$$

where $\mu_A$ is the magnetic moment of the high spin form, $\mu_B$ is the magnetic moment of the low spin form and $\mu$ is the magnetic moment of the high spin - low spin equilibrium mixture.

$$\therefore \mu^2 = (\mu^2_A - \mu^2_B) [A] + \mu^2_B$$

$$\therefore [A] = \mu^2 - \mu^2_B / \mu^2_A - \mu^2_B$$

(8)

$$\therefore \text{from (7) and (8)}$$

$$\ln[(\mu^2 - \mu^2_B)/ (\mu^2_A - \mu^2)] = \Delta S/R - \Delta H/RT$$

(9)

$\mu_A$ can be taken as $\sqrt{35}$ B.M. independent of temperature without appreciable error. $\mu_B$ will be ca. 2.0 B.M. but would be expected to vary slightly with temperature. In one previous interpretation of the solid state magnetic susceptibilities theoretical expressions derived for octahedral $T_{2g}$ complexes were applied. However, it is known that the iron(III) dithiocarbamates show considerable distortion
from true octahedral symmetry. Accordingly, in treating the present results, $\mu_B$ was assigned a value which in each case gave the best least squares fit to expression (9). The values of $\mu_B$ are in the expected range (see Table 1.3) although clearly no great significance can be attached to them. Details of the computer program used for the analysis of these results can be found in Appendix 1.

It can be seen from Figures 1.5 and 1.6 that the assumption of a simple Boltzmann distribution between high and low-spin forms gives an excellent fit to the observed susceptibility data.

The graph of $1/T$ against $\ln[\mu^2 - \mu_B^2/\mu_A^2 - \mu^2]$ is a straight line over the entire temperature range for all four complexes (Figure 1.7).

The derived thermodynamic parameters are given in Table 1.3, together with $\Delta H$ for the compound Fe(S$_2$CNMe$_2$)$_3$, the only previously reported value from solution work.

Table 1.3 Thermodynamic Parameters for Fe(S$_2$CNR$_1$R$_2$)$_3$ in Toluene Solution.

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^n$</td>
<td>Pr$^n$</td>
<td>6.55</td>
<td>19.6</td>
<td>2.34</td>
</tr>
<tr>
<td>Bu$^n$</td>
<td>Bu$^n$</td>
<td>6.00</td>
<td>19.8</td>
<td>1.97</td>
</tr>
<tr>
<td>CH$_2$Ph</td>
<td>CH$_2$Ph</td>
<td>8.87</td>
<td>22.8</td>
<td>2.02</td>
</tr>
<tr>
<td>Pr$^n$</td>
<td>Ph</td>
<td>8.00</td>
<td>19.1</td>
<td>1.91</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>6.70$^a$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Reference 42 solvent not specified.
Figure 1.7: \( \ln a \) against \( 1/T \) for a series of iron(III) dithiocarbamates in toluene.

\[ a = \left[ \mu^2 - \mu_0^2 \right] / \left[ \mu_0^2 - \mu^2 \right] \]
ΔH values range from 6-9 kJ mol\(^{-1}\). The main contribution to ΔH arises from the changing Fe-S bond lengths and energies that accompany the spin transition. The low spin \(^3\)T form has shorter Fe-S distances and therefore greater Fe-S bond strengths than the \(^6\)A high spin form. X-ray structural data on the compound Fe(S\(_2\)CNEt\(_2\))\(_3\)\(^{13}\) at 297 and 79°K shows that the Fe-S bond distance changes by \(\sim 0.05\) Å while \(\mu_{\text{eff}}\) changes from 4.3 B.M. to 2.2 B.M. For a complete high spin to low spin transition the change will be about 0.11 Å.

**Figure (1.8). Variation of Magnetic Moment with Mean Fe-S Distance for Some Known Structures.**

1. Fe(S\(_2\)CSBu\(^t\))\(_3\), 2. Fe(S\(_2\)CNEt\(_2\))\(_3\) (78°K), 3. Fe(S\(_2\)CNMePh)\(_3\), 4. Fe(S\(_2\)CNEt)\(_3\), 5. Fe(S\(_2\)CNEt\(_2\))\(_3\), 6. Fe(S\(_2\)CNPyr)\(_3\), 7. Fe(S\(_2\)CNBu\(^t\))\(_3\), all reference 13.
8. Fe[S\(_2\)CN(CH\(_2\))\(_4\)O]\(_3\).C\(_6\)H\(_4\)Cl\(_2\), 9. Fe[S\(_2\)CN(CH\(_2\))\(_4\)O]\(_3\).2C\(_6\)H\(_6\) both reference 43.
10. Fe(S\(_2\)CNBu\(^t\))\(_3\).C\(_6\)H\(_4\) reference 44. 11 and 12. Fe[S\(_2\)CN(C\(_2\)H\(_4\)O)]\(_2\) at 295°K and 150°K reference 45. 13 and 14 Fe(S\(_2\)CNMe\(_2\))\(_3\) at 295°K and 150°K reference 46.
The $\Delta S$ parameter is approximately constant at ca. $20 \text{ J} \text{ K}^{-1} \text{ mol}^{-1}$. Since the degeneracy (spin and orbital) of the high- and low-spin forms are the same (i.e., the electronic entropy change $= R \ln 6 - R \ln 6 = 0$), the larger entropy of the high spin forms can be attributed to their "looser" nature, in agreement with previous work.47,48

ii) **Solvent Effects on the Spin Equilibria**:

The iron(III) dithiocarbamates readily form solid adducts with a variety of solvents and these adducts often show large differences in magnetic susceptibility. In particular it has been shown by Butcher, Ferraro and Sinn12,43 that the CHCl$_3$ and CH$_2$Cl$_2$ adducts of tris(morpholyldithiocarbamato)Iron(III) not only have generally higher magnetic moments than the pure compound but also that the low spin forms are apparently $^4T_1$ states with three unpaired electrons. This was attributed to hydrogen bonding by the CHCl$_3$ or CH$_2$Cl$_2$ which stabilizes the higher spin forms.

The magnetic moments as a function of temperature for Fe(S$_2$CNPr$_2$)$_3$ in chloroform and dichloromethane are given below and Figure (1.9) represents a comparison of the data obtained for the three solvents, toluene, chloroform and dichloromethane.

Fe(S$_2$CNPr$_2$)$_3$ in Chloroform Solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>X$^M$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.7</td>
<td>7.33</td>
<td>4.38</td>
</tr>
<tr>
<td>40.1</td>
<td>7.26</td>
<td>4.26</td>
</tr>
<tr>
<td>25.7</td>
<td>7.22</td>
<td>4.15</td>
</tr>
<tr>
<td>10.6</td>
<td>7.12</td>
<td>4.02</td>
</tr>
<tr>
<td>-4.6</td>
<td>6.82</td>
<td>3.83</td>
</tr>
</tbody>
</table>
### Fe(S₂CNPr₂)₃ in Dichloromethane Solution

<table>
<thead>
<tr>
<th>Temp</th>
<th>-19.7</th>
<th>-35.1</th>
<th>-50.4</th>
<th>-60.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_M)</td>
<td>6.64</td>
<td>6.45</td>
<td>6.22</td>
<td>6.10</td>
</tr>
<tr>
<td>(\mu_{\text{eff}})</td>
<td>3.67</td>
<td>3.51</td>
<td>3.33</td>
<td>3.22</td>
</tr>
</tbody>
</table>

### Fe(S₂CNPr₂)₃ in Dichloromethane Solution

<table>
<thead>
<tr>
<th>Temp</th>
<th>-34.3</th>
<th>20.9</th>
<th>0.4</th>
<th>-19.7</th>
<th>-40.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_M)</td>
<td>7.52</td>
<td>7.54</td>
<td>7.43</td>
<td>7.30</td>
<td>7.25</td>
</tr>
<tr>
<td>(\mu_{\text{eff}})</td>
<td>4.30</td>
<td>4.21</td>
<td>4.03</td>
<td>3.85</td>
<td>3.67</td>
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<table>
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<th>-102.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_M)</td>
<td>7.09</td>
<td>6.91</td>
<td>6.69</td>
</tr>
<tr>
<td>(\mu_{\text{eff}})</td>
<td>3.47</td>
<td>3.26</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Units: Temp, °C; \(\chi_M\) 10³ x cgs units; \(\mu_{\text{eff}}\) B.M.

Range of concentration studied 12-15 mM.

As Figure (1.9) shows the solvent effect on this system is small and there is no evidence that hydrogen bonding by CHCl₃ or CH₂Cl₂ is important in solution (the magnetic moments in CHCl₃ are slightly smaller than in toluene). Similarly, the values of \(\mu_{\text{eff}}\) at 34°C for tris(morpholyldithiocarbamato)Iron(III) were found to be 4.66 (toluene), 4.65 (acetone) and 4.55 (chloroform), and it has previously been reported that a number of Iron(III)dithiocarbamates have the same magnetic moments at room temperature in benzene and chloroform. These results bring into doubt the conclusions of Butcher, et al.,
Figure 1.9: Variation of Magnetic Moment with temperature for Fe(S₂CNPr₂)₃ in Toluene ○; Dichloromethane × and Chloroform •. The solid lines are calculated from eq. (9) page 36.
that hydrogen bonding between the solvent molecules and the complex plays an important part in the magnetic properties of the complex.

As an additional check an infrared method for studying hydrogen bonding in solution was applied. The O-H stretch of the methanol monomer was measured in CCl₄ (5 x 10⁻³ M CH₃OH) and in CCl₄ containing Fe(S₂CNPr₂)₃ (0.092 M). A negligible shift to lower frequencies of 4 cm⁻¹ was observed (3646 cm⁻¹ to 3642 cm⁻¹).

Therefore, it has been shown that in dichloromethane and in chloroform the spin equilibrium is \( ^{2}T_2 \rightleftharpoons ^{6}A_1 \), and it is not noticeably affected by hydrogen bonding, but there are some small solvent effects. The thermodynamic parameters obtained for the equilibrium for Fe(S₂CNPr₂)₃ are given in Table 1.4.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \Delta H ) (kJ mol⁻¹)</th>
<th>( \Delta S ) (J k⁻¹ mol⁻¹)</th>
<th>( \mu_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>6.55</td>
<td>19.6</td>
<td>2.34</td>
</tr>
<tr>
<td>Chloroform</td>
<td>~ 8.0</td>
<td>~ 22.9</td>
<td>2.46</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>6.33</td>
<td>17.7</td>
<td>2.58</td>
</tr>
</tbody>
</table>

The equilibrium data was analysed in the same way as that obtained in toluene solution. Due to the limited temperature range covered in chloroform solution (54.7°C to -60.4°C) the thermodynamic parameters obtained are only approximate. It was found to be
particularly important to cover as much of the low temperature region as possible, hence toluene and dichloromethane are preferable to chloroform as solvents because of their very low melting points.

iii) Chemical Shift Determination of Spin Equilibria.

Spin equilibria in solution can also be studied by measuring the paramagnetic shifts, $\delta$, in the n.m.r. spectrum as a function of temperature. The temperature dependence of the proton n.m.r spectra of a series of Iron(III) dithiocarbamates had already been studied by R.M. Golding, et al. 21

For the purposes of this work the n.m.r. spectrum of the di-n-propyl derivative has been studied, the spectrum is shown in Figure (1.10).

Figure (1.10). $^1$H NMR Spectrum of Fe(S$_2$CNPr$_2$)$_3$ in Chloroform at $34^\circ$C.
It was intended to show that the simple Boltzmann distribution between high spin and low-spin states could give a good theoretical fit to the observed temperature dependence of the paramagnetic shift of the \(-\text{N-CH}_2-\) protons. The paramagnetic shift, \(\delta\), was calculated using the equation:

\[
\delta = \delta_e - \delta_d
\]

where \(\delta_e\) is the experimentally measured shift from the internal reference substance, hexamethyldisiloxane, in ppm; and \(\delta_d\) is the chemical shift for analogous protons in a diamagnetic compound. \(\delta_d\) was taken to be 2.95 ppm\(^{21}\) (the equivalent to 3 ppm from T.M.S.). Figure (1.11) shows the variation of \(T\delta\) with temperature for the \(-\text{N-CH}_2-\) protons in two solvents, toluene and dichloromethane.

If it is assumed that

\[
\delta_{\text{L.S.}} = \frac{C_{\text{L.S.}}}{T}
\]

and

\[
\delta_{\text{H.S.}} = \frac{C_{\text{H.S.}}}{T}
\]

then

\[
\delta = \left[ (1 - x) \frac{C_{\text{H.S.}}}{T} \right] + x \frac{C_{\text{L.S.}}}{T}
\]

(10)

where \(C_{\text{L.S.}}\) and \(C_{\text{H.S.}}\) are constants and \(x\) is the mole fraction of the low spin form at a temperature \(T^\circ\text{K}\). For a simple Boltzmann distribution between the states \(^2\text{T}_2 \leftrightarrow ^6\text{A}_1\), then

\[
\Delta H - T\Delta S = -RT \ln[(1 - x)/x]
\]

(11)

from equation (10)

\[
T\delta = (1 - x)C_{\text{H.S.}} + xC_{\text{L.S.}}
\]

\[
+ \quad T\delta = C_{\text{H.S.}} + (C_{\text{L.S.}} - C_{\text{H.S.}}) x
\]

\[
+ \quad x = \frac{T\delta - C_{\text{H.S.}}}{C_{\text{L.S.}} - C_{\text{H.S.}}}
\]
Figure (1.11): T8 vs. temperature curves for Fe(S₂CNH₂)₃ in x dichloromethane and toluene. The solid lines are calculated from eq. (12) page 48.
Figure 1.12: $\ln b$ vs $1/T$ for $\text{Fe(S}_2\text{CNR}_2^n)\text{_3}$ in $\text{X}$ dichloromethane and $\bullet$ toluene

$$b = \left( C_{l.s} - TS \right) / \left( TS - C_{H.s} \right)$$
substituting for $x$ into eq. (11) leads to

$$\Delta H - T \Delta S = -RT \ln \left[ \frac{C_{L.S.} - T \delta}{T \delta - C_{H.S.}} \right]$$

$$\ln \left[ \frac{C_{L.S.} - T \delta}{T \delta - C_{H.S.}} \right] = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

A computer program varied $C_{L.S.}$ and $C_{H.S.}$ over all possible values to give the best least mean squares fit to equation (12). Details of the computer program used for the analysis of these results can be found in Appendix 2.

The plots of $\ln \left[ \frac{C_{L.S.} - T \delta}{T \delta - C_{H.S.}} \right]$ vs. $1/T$ for the di-n-propyl derivative in both toluene and dichloromethane are shown in Figure 1.12. Both give good straight lines over the entire temperature range. Table 1.5 give the results obtained in each solvent.

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>δ ppm</th>
<th>Tδ k. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>370.7</td>
<td>36.48</td>
<td>13522</td>
</tr>
<tr>
<td>356.4</td>
<td>36.83</td>
<td>13125</td>
</tr>
<tr>
<td>342.5</td>
<td>37.07</td>
<td>12695</td>
</tr>
<tr>
<td>323.0</td>
<td>37.30</td>
<td>12046</td>
</tr>
<tr>
<td>307.5</td>
<td>37.19</td>
<td>11434</td>
</tr>
<tr>
<td>294.1</td>
<td>36.92</td>
<td>10857</td>
</tr>
<tr>
<td>273.6</td>
<td>36.28</td>
<td>9925</td>
</tr>
<tr>
<td>253.5</td>
<td>35.08</td>
<td>8891</td>
</tr>
<tr>
<td>232.8</td>
<td>33.32</td>
<td>7756</td>
</tr>
<tr>
<td>212.8</td>
<td>30.80</td>
<td>6553</td>
</tr>
<tr>
<td>202.6</td>
<td>29.50</td>
<td>5976</td>
</tr>
</tbody>
</table>

$C_{H.S.} = 21640,$  
$C_{L.S.} = 2140$  
$\Delta H = 6.49 \text{ KJ mol}^{-1}$  
$\Delta S = 20.34 \text{ J. mol}^{-1} \text{K}^{-1}$
B) Dichloromethane

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>δ ppm</th>
<th>Tδ k. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>370.7</td>
<td>36.77</td>
<td>13629</td>
</tr>
<tr>
<td>361.2</td>
<td>37.03</td>
<td>13374</td>
</tr>
<tr>
<td>347.4</td>
<td>37.24</td>
<td>12936</td>
</tr>
<tr>
<td>332.8</td>
<td>37.38</td>
<td>12439</td>
</tr>
<tr>
<td>318.2</td>
<td>37.31</td>
<td>11871</td>
</tr>
<tr>
<td>303.6</td>
<td>37.10</td>
<td>11262</td>
</tr>
<tr>
<td>283.8</td>
<td>36.47</td>
<td>10349</td>
</tr>
<tr>
<td>263.6</td>
<td>35.53</td>
<td>9364</td>
</tr>
<tr>
<td>243.2</td>
<td>34.10</td>
<td>8292</td>
</tr>
<tr>
<td>222.8</td>
<td>32.32</td>
<td>7200</td>
</tr>
<tr>
<td>207.7</td>
<td>30.82</td>
<td>6400</td>
</tr>
<tr>
<td>187.4</td>
<td>28.32</td>
<td>5306</td>
</tr>
</tbody>
</table>

\[ C_{\text{H.S.}} = 24440, \quad C_{\text{L.S.}} = 2640 \]
\[ \Delta H = 6.28 \text{ kJ mol}^{-1} \]
\[ \Delta S = 17.13 \text{ J. mol}^{-1} \text{ k}^{-1} \]

As shown in Figure (1.11) the observed chemical shifts fit almost exactly the theoretically predicted curve and the thermodynamic parameters are in very good agreement with those obtained from the magnetic susceptibility study (cf. Tables 1.4 and 1.5). Due to high correlation found between the values of \( C_{\text{H.S.}} \) and \( C_{\text{L.S.}} \) and \( \Delta S \) and \( \Delta H \) it is necessary to cover as wide a temperature range as possible to produce meaningful results, which is why the dichloromethane results were extended beyond the boiling point of the solvent, to + 100°C.
In the analysis of the results it has been assumed that the paramagnetic shifts due to the high spin and low spin states will both follow a Curie \((T^{-1})\) dependence. This assumption is not strictly correct\(^{51}\) for the \(\text{^{2}T_2}\) ground state as shown by the work of La Mar, et al.,\(^{52}\) who concludes that to quantitatively interpret isotropic shifts in distorted complexes with \(T\) ground states, the Kurlard-McGarvey equations must be used.\(^{53}\) However, deviations of this type will be less important for the \(\text{^6A}_1\) high spin ground state. In this case, the pseudocontact contribution to the shift is small and the isotropic shift is almost entirely contact in character and does follow a \(T^{-1}\) dependence. As the shift due to the high spin state is about ten times larger than the shift due to the low spin state the general assumption of a Curie law dependence is reasonable.

The results presented in this Chapter, together with previous work,\(^{42,47}\) indicate that, in spite of difficulties often encountered with solubility and a limited temperature range, reliable thermodynamic parameters for systems showing spin-equilibria are much more easily derived from magnetic susceptibility measurements in solution rather than in the solid state.
C) EXPERIMENTAL

Magnetic susceptibilities were determined using an n.m.r. method,\(^1\) with 4\% (v/v) of hexamethyldisiloxane as the internal reference. The complete expression was applied, where \(\Delta f\) is the paramagnetic shift, \(f\) is the oscillator frequency, \(m\) is the mass of substance in 1 ml of solution, \(\chi_0\) is the mass susceptibility of the solvent, \(d_0\) is the density of the solvent and \(d_s\) that of the solution.

\[
\chi = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0 (d_0 - d_s)}{m}
\]

The paramagnetic shifts, \(\Delta f\), for Fe(S\(_2CN\)Pr\(_2\))\(_3\), in chloroform and dichloromethane solutions were obtained by the usual method with a Wilmad 517 split-tube. The shifts for all compounds in toluene solution were obtained by inserting into a standard n.m.r. tube a specially constructed sealed capillary tube (o.d. 3mm, length 100 mm) containing the deaerated solvent. The capillary was held in place by two PTFE spacers. This method was found to be more convenient than the conventional split-tube and also allowed for the solutions to be deaerated which makes the study of air unstable compounds possible by this method.

Density measurements of the solvent and solution were made at room temperature, -78.5\(^\circ\)C, in a solid CO\(_2\)-methanol bath (toluene and dichloromethane), -60\(^\circ\)C in a eutectic mixture of 27 mol \% benzene in chlorobenzene (chloroform), + 50\(^\circ\)C (chloroform) and + 80\(^\circ\)C (toluene). Density expressions of the form

\[
d_t = d_0 + at + bt^2
\]
were calculated (or for dichloromethane, $d_t = d_0 + at$), enabling the density at any temperature in the range studied to be calculated to the required accuracy. $d_0$ is the density at $0^\circ$C, $d_t$ the density at $t^\circ$C, $a$ and $b$ are constants. The density bottle consisted of a pyrex bulb (volume ca. 3.5 ml) attached to a 15 cm length of precision bore tubing (i.d. ca. 2 mm) to which a millimetre scale was subsequently fused. A correction was applied for the change in volume of the bottle with temperature. $\chi_0$, the mass susceptibilities of the solvents were calculated to be:

- **Benzene**: HMDS (96:4) $-0.729 \times 10^{-6}$
- **Chloroform**: HMDS (96:4) $-0.5171 \times 10^{-6}$
- **Dichloromethane**: HMDS (96:4) $-0.5670 \times 10^{-6}$
- **Acetone**: HMDS (96:4) $-0.6016 \times 10^{-6}$

using values of $\chi_M$ for the pure solvents quoted in reference 5.

Diamagnetic corrections were calculated from the observed susceptibility of NaS$_2$CNET$_2$\textsuperscript{54} and Pascals constants:\textsuperscript{55} Fe(S$_2$CNPr$_2$)$_3$, D.C. $= 348 \times 10^{-6}$; Fe(S$_2$CNPr$_2$Ph)$_3$, $390 \times 10^{-6}$; Fe(S$_2$CNBu$_2$)$_3$, $420 \times 10^{-6}$; Fe[S$_2$CN(CH$_2$Ph)$_2$)$_3$], $484 \times 10^{-6}$; Fe[S$_2$CN(CH$_2$)$_4$O]$_3$, $267 \times 10^{-6}$.

All n.m.r. spectra were measured at 60 MHz on a Perkin-Elmer R12 B spectrometer. Chemical shifts in dichloromethane at temperatures above the boiling point of the solvent were obtained by sealing the deoxygenated solution in a short 4 mm o.d. n.m.r. tube and placing this inside a standard n.m.r. tube, together with a little Voltalef 3S oil to prevent rattling. By this method chemical shifts were obtained at temperatures of up to $+100^\circ$C.
The variable temperature probe was calibrated with methanol and ethylene glycol using the calibrations determined by Van Geet.\textsuperscript{56,57}

For methanol

\[ t = 403.0 - 0.491|\Delta V| - 66.2 (\Delta V \times 10^{-2})^2 \]

where \( t \) is the temperature of the probe in °K and \( \Delta V \) is the chemical shift between CH\textsubscript{3} and OH groups in methanol. For ethylene glycol

\[ t = 466.0 - 1.694|\Delta V| \]

where \( \Delta V \) is the chemical shift between the CH\textsubscript{2} and OH groups of glycol. Results showed that the machine settings were accurate to within ± 1°C in the temperature range -80°C to +70°C and that above and below this range the accuracy was of the order of ± 2.5°C.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer using 1 cm I.R. quartz cells.

**Materials.**

Tris(N,N-diorganodithiocarbamato)Iron(III) complexes were prepared according to the procedure of A.H. White, et al.\textsuperscript{10} Freshly precipitated ferric hydroxide is stirred with an ethanolic solution of the appropriate secondary amine. An equimolar amount of carbon disulphide (to that of the amine) is then slowly added and a black precipitate begins to form almost immediately. After about 1 hr. the solid is filtered, extracted with chloroform and then reprecipitated with ethanol. In the case of tris(N-n-propyl-N-phenyldithiocarbamato)Iron(III), it was found that recrystallisation from a nearly saturated warm toluene solution was more successful than the chloroform-ethanol procedure. The solvent
was removed from the crystal lattice under reduced pressure either at room temperature or at ~ 80°C. The best conditions for the removal of solvent varied between the different complexes. Melting points and analytical data were used to ensure that the complexes were pure and solvent free before use. All relevant data is presented in Table 1.6.

The solvents, toluene (AR), chloroform (pure), dichloromethane (PURIS§) and acetone (AR) were supplied by Koch-Light Laboratories Ltd. and were used without further purification. Chloroform contained ~ 2% (v/v) of ethanol as a stabilizer. Hexamethyldisiloxane (silicone fluid DC 200/0.65 cs) was supplied by Hopkins and Williams Ltd. It was found to be preferable to tetramethylsilane as an internal reference because of its high boiling point.

\[\text{HMDS b.pt. 99.5°C}\]
\[\text{TMS b.pt. 26.5°C}\]
Table 1.6. Elemental Analysis\(^a\) and Melting Points for Tris(N,N-diorganodithiocarbamato)Fe(III) Complexes.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Drying Conditions</th>
<th>M. Pt. (°C)</th>
<th>Lit(^b) M. Pt. (°C)</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>N,N-di-n-propyl</td>
<td>R. T.</td>
<td>168-169</td>
<td>167-168</td>
<td>43.24</td>
</tr>
<tr>
<td>N,N-di-n-butyl</td>
<td>80(^\circ)C</td>
<td>149-150</td>
<td>146-151</td>
<td>48.44</td>
</tr>
<tr>
<td>N-n-propyl-N-phenyl</td>
<td>80(^\circ)C</td>
<td>209-211</td>
<td>212-214</td>
<td>52.80</td>
</tr>
<tr>
<td>N,N-dibenzyl</td>
<td>R. T.</td>
<td>210-212</td>
<td>212-214</td>
<td>61.85</td>
</tr>
<tr>
<td>Morpholyil</td>
<td>R. T.</td>
<td>-</td>
<td>-</td>
<td>33.54</td>
</tr>
</tbody>
</table>

\(^a\) Elemental Analyses were performed by the Microanalytical Laboratories of Imperial College.

\(^b\) Reference 10.
CHAPTER 2

VARIABLE TEMPERATURE MAGNETIC SUSCEPTIBILITY

MEASUREMENTS OF SPIN EQUILIBRIA

FOR

IRON(II) COMPLEXES WITH

2-(2'-PYRIDYL)BENZIMIDAZOLE.
A) 1) Spin-Equilibria in d^6 Complexes.

Figure (2.1).

**High spin and Low spin d^6 Complexes.**

\begin{align*}
\text{HIGH} \\
\Delta_0 \\
\text{Low}
\end{align*}

\[ \begin{array}{c}
\text{eg} \quad \{d_{x^2}, d_{x^2-y^2}\} \\
\text{t}_{2g} \quad \{d_{xy}, d_{xz}, d_{yz}\}
\end{array} \]

Electronic configuration \( t_{2g}^4 e_g^2 (T_2), S = 2 \)

Electronic configuration \( t_{2g}^6 \left(^1A_1\right), S = 0 \)

Figure (2.1) represents the d^6 configuration, e.g., Fe(II).

Both high spin and low spin ferrous complexes are known although quite strong ligand fields\(^5^8\) are required to form the spin-paired ground state. Examples are given in Table (2.1).
The same factors which influence the spin-equilibria in $d^5$ systems (see Chapter 1. A)(i)) apply equally in the case of $d^6$ equilibria. Several well documented examples of spin state equilibria can be found in Fe(II) chemistry. These include the compounds Fe phen$_2$ X$_2$ (where X = SCN and SeCN),$^{32}$ Fe[HB(Pz)$_9$]$^{47}$ and complexes with 2-pyridylmethylamine and related ligands.$^{33,62}$

Table 2.1. Magnetic Moments of $d^6$ Transition Metal Complexes.

<table>
<thead>
<tr>
<th>Spin State</th>
<th>S</th>
<th>$\mu_{S.O.}$ a</th>
<th>$\mu_{\text{eff}}$ a</th>
<th>Examples b,c</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>2</td>
<td>4.90</td>
<td>5.10-5.70</td>
<td>Fe(H$_2$O)$_6^{2+}$, Fe(Py)$_4$(SCN)$_2$</td>
</tr>
<tr>
<td>Low</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>Fe(phen)$_3^{2+}$, Fe phen$_2$(CN)$_2$</td>
</tr>
</tbody>
</table>

a reference 59  
b reference 60  
c reference 61

In the solid state, two different types of behaviour have been reported for Iron(II) spin-crossover systems.$^{63}$ Those which show a gradual changeover in the proportions of high and low spin states present, and those which change abruptly between the two ground states, within the space of a few degrees kelvin. The first type of behaviour is typified by the Fe[papth$_2$]$^{3+}$ cation$^{62}$ and the latter by [Fe phen$_2$(NCS)$_2$].$^{32,63}$

The magnetic behaviour of Fe phen$_2$(NCS)$_2$ is characterised by a precipitous drop in $\mu_{\text{eff}}$ at about 175°K (see Figure 2.2) this is associated with a phase-change in the solid brought about by the
constraints imposed on the lattice during the spin-changeover.

Figure (2.2). Temperature dependence of the Magnetic Moment of Fe phen$_2$(NCS)$_2$. $^{63}$

This has been confirmed by the observation of an anomaly in the heat capacity of the compound at the spin transition temperature. $^{64}$ Crystal structure data at temperatures above and below the spin transition point show the large changes in bond length that accompany such a transition. $^{65}$ As expected, this type of transition has not been found in the solution state as the rigid crystal lattice forces are not present. In all cases studied so far, a Boltzmann distribution holds for the spin-equilibrium complex in solution.

In the solid state, the most general attempt to fit experimental results to a theoretical function has been by Konig and Kremer $^{66}$ who, in a theoretical study of nineteen Fe(II)-N$_6$ complexes arrived
at the following expression for $\mu_{\text{eff}}^{\text{exp}}$:

$$
(\mu_{\text{eff}}^{\text{exp}})^2 = (1 - \alpha) \frac{A}{C \exp (\varepsilon/kt) + B} + a(\mu_{\text{eff}}^{\text{pure}})^2 + (\mu_{\text{eff}}^{\text{T.I.P.}})^2
$$

$\varepsilon$ is the energy separation between the centres of gravity of the ground states $^5T_2$ and $^1A_1$. $A$ and $B$ are sums of exponentials and $C$ is an adjustable parameter. It is also assumed that a fraction ($\alpha$) of molecules are permanently paramagnetic (supported by Mossbauer evidence) and the second order Zeeman effect contribution to the moment is taken into consideration too as $\mu_{\text{eff}}^{\text{T.I.P.}}$.

The calculated functions are dependent on $\delta, \zeta, T$ and $k$.

$\delta$ = axial ligand field splitting, $\zeta$ = spin orbit coupling constant and $k$ = Stevens orbital reduction factor. By the very nature of the solid state results only expressions containing a large number of parameters can be made to fit experimentally observed results.

ii) Iron(II) Complexes with [2-(2'-pyridyl)benzimidazole]

and Related Ligands.

Three ligands of this type have been used in the study of the Iron(II) spin-crossover phenomena. They are 2-(2'-pyridyl)-imidazole, PYI.
2-(2'‐pyridyl)imidazoline, PYIM

and, 2-(2'-pyridyl)benzimidazole, PYB

Fe(PYIM)$_3$(ClO$_4$)$_2$ exists as two magnetically different isomers.$^{67}$ Form A is dark blue and low-spin and is obtained from Iron(II) perchlorate and the ligand PYIM in ethanol. Form B is obtained from propan-2-ol solution and is purple in colour. The magnetic moment is high spin with a rapid decrease to low spin at about 120°K, behaviour similar to Fe$^{II}_{\text{phen}}$(NCS)$_2$ (see Figure (2.2)).

As these chelating ligands are not symmetrical both mer- and fac-octahedral complexes are possible$^{68}$ (see Figure (2.3)).
Figure (2.3). Mer- and Fac-Octahedral Symmetry.

Analysis of the cation Fe\(^{II}\)(PYI)\(^{++}\) in the solid state shows the presence of a spin equilibrium\(^{69}\) but the results can not be interpreted in terms of a simple Boltzmann distribution. A plot of \(\ln K - vs - 1/T\) with \(K\), the equilibrium constant, calculated from the relative concentrations of high- and low-spin forms is a curve.

The final complex Fe\(^{II}\)(PYB)\(^{++}\) has been studied with many accompanying anions.\(^{68,70,71,72}\) The Mössbauer spectra of Fe\(^{II}\)(PYB)\(^{-}\)(NO\(_3\))\(_2\)\(\cdot\)H\(_2\)O, Fe\(^{II}\)(PYB)\(_3\)(Br)\(_2\) and Fe\(^{II}\)(PYB)\(_3\)(Cl\(_\infty\))\(_2\)\(\cdot\)2H\(_2\)O show isomer shifts (\(\delta\)) and quadrupole splittings (\(\Delta E_Q\)) characteristic of \(S = 0\) Fe(II) and \(S = 2\) Fe(II), with intensities depending on temperature.\(^{70}\)

Solid state magnetic studies\(^{68,72}\) have led to a confused picture with the spin equilibrium depending on many external factors such as anion, method of preparation\(^{72}\) and number of moles of water of crystallisation.\(^{68,71}\)

For example Figure (2.4) shows the magnetic behaviour of Fe(PYB)\(_3\)(Cl\(_\infty\))\(_2\) and two forms of Fe(PYB)\(_3\)(BF\(_4\))\(_2\). The main aim of the solution state results obtained and represented in the next
Figure (2.4): Variation of magnetic moments with temperature for Fe(PY8)_3(BF_4)_2 (from ethanol) •; Fe(PY8)_3(BF_4)_2 (from acetone) ○; Fe(PY8)_3(ClO_4)_2 (from acetone) ×. In the solid state (reference 70).
section is to simplify and clarify the spin-equilibrium of the cation Fe(PYB)$^{++}$ and obtain thermodynamic parameters on the basis of a Boltzmann distribution between the two available ground states.

B) Results and Discussion.

The magnetic moments as a function of temperature for the perchlorate and the tetrafluoroborate of Fe$^{	ext{II}}$(PYB)$^{++}$ are given below. The solvent was acetone, 90%; water 5% (to increase the solubility of the complexes); and hexamethyldisiloxane 5%.

\[
\begin{array}{cccccc}
\text{Temp} & 56.9 & 46.9 & 31.8 & 16.8 & 1.2 \\
\chi_M^I & 10.44 & 10.15 & 10.51 & 10.05 & 9.60 \\
\mu_{\text{eff}} & 5.25 & 5.10 & 5.06 & 4.83 & 4.59 \\
\text{Temp} & -14.4 & -30.1 & -45.8 & -61.4 & -82.4 \\
\chi_M^I & 8.28 & 6.68 & 4.77 & 2.90 & 1.37 \\
\mu_{\text{eff}} & 4.14 & 3.60 & 2.95 & 2.22 & 1.45 \\
\end{array}
\]

\[
\begin{array}{cccccc}
\text{Temp} & 56.9 & 46.9 & 31.8 & 16.8 & 1.2 \\
\chi_M^I & 10.37 & 10.34 & 10.41 & 9.98 & 9.53 \\
\mu_{\text{eff}} & 5.23 & 5.14 & 5.04 & 4.81 & 4.57 \\
\end{array}
\]
It can be seen from these results that as the error in \( \mu_{\text{eff}} \) is about ± 0.03 B.M. the two sets of data are the same, within experimental error, at each temperature. Thus, the major difficulty in assessing the solid state data has immediately been overcome. The results can be represented as \( \mu_{\text{eff}} - vs - T \) for the complex Fe\(^{2+}\)(PYB)\(^{++]\) (Figure 2.5, Table 2.2) by averaging the values of \( \chi_M' \) at each temperature.

### Table 2.2. Magnetic Moments as a Function of Temperature for the Cation Fe\(^{II}\)(PYB)\(^{++]\).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>( \chi_M' \times 10^3 ) (cgs)</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
<th>( \mu_{\text{calculated}} ) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.9</td>
<td>10.405</td>
<td>5.24</td>
<td>5.23</td>
</tr>
<tr>
<td>46.9</td>
<td>10.246</td>
<td>5.12</td>
<td>5.16</td>
</tr>
<tr>
<td>31.8</td>
<td>10.462</td>
<td>5.05</td>
<td>5.02</td>
</tr>
<tr>
<td>16.8</td>
<td>10.016</td>
<td>4.82</td>
<td>4.82</td>
</tr>
<tr>
<td>1.2</td>
<td>9.567</td>
<td>4.58</td>
<td>4.53</td>
</tr>
<tr>
<td>-14.4</td>
<td>8.199</td>
<td>4.12</td>
<td>4.13</td>
</tr>
<tr>
<td>-30.1</td>
<td>6.738</td>
<td>3.62</td>
<td>3.60</td>
</tr>
<tr>
<td>-45.8</td>
<td>4.752</td>
<td>2.94</td>
<td>2.96</td>
</tr>
<tr>
<td>-61.4</td>
<td>2.945</td>
<td>2.23</td>
<td>2.27</td>
</tr>
<tr>
<td>-82.4</td>
<td>1.375</td>
<td>1.45</td>
<td>1.43</td>
</tr>
</tbody>
</table>

\( ^{a} \mu_{\text{calculated}} \) represents the theoretical value of \( \mu \) at the temperature \( T \) according to the theory given below.
Figure (2.5): Variation of Magnetic Moments with temperature for Fe$^{II}$ (PYB)$_3$ X$_2$ in Acetone/Water. X = ClO$_4$ or BF$_4$. The solid lines are calculated from eq. (9) page 36.
Figure (2.6): $\ln a$ vs. $1/T$ for $\text{Fe}^{II}(\text{PYB})_3 X_2$ in Acetone/Water.

\[
a = \frac{\mu^2 - \mu_{B}^2}{\mu_{A}^2 - \mu^2}
\]
The equilibrium between high spin $^5T_2$ and the low spin $^1A_1$ ground states can be treated as a simple Boltzmann distribution, similar to the ferric dithiocarbamate case described on pages 34-36.

So we have the equation:

$$\ln \left( \frac{(\mu^2 - \mu_{B}^2)}{(\mu_{A}^2 - \mu^2)} \right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (9)

In this case the spin equilibrium is $S = 2 \rightarrow S = 0$, so it is expected that the low spin complex will be diamagnetic. In fact some residual paramagnetism is found for the $^1A_1$ state, this temperature independent paramagnetism was taken to be $200 \times 10^{-6}$ cgs. units, so at any temperature $\mu_B$ can be calculated from

$$\mu_B = 2.8278 \times (200T \times 10^{-6})^{1/2}$$

Magnetic moments of $\sim 0.5$ B.M. are fairly typical of pseudo-octahedral Fe(II) complexes. $\mu_A$ was assigned a value which would give the best least mean squares fit for the experimental data to the equation (9).

The computer program used for the analysis of these results was a suitably modified version of that set out in Appendix 1.

As shown in Figure (2.6) the plot of $1/T$ against $\ln[\mu^2 - \mu_{B}^2/\mu_{A}^2 - \mu^2]$ is linear over a wide temperature range indicating close agreement between the experimental results and the theory. The thermodynamic parameters obtained for the equilibrium $^1A_1 \rightarrow ^5T_2$ in this work are $\Delta H, 18.02$ kJ mol$^{-1}$ and $\Delta S, 71.12$ J mol$^{-1}$ K$^{-1}$ with $\mu_A = 5.57$ B.M. These are in good agreement with the results of L. J. Wilson, et al., 73 who carried out a similar magnetic study.
of the compounds \([\text{Fe(PYB)}_3(\text{BPh}_4)_2 \cdot 3\text{H}_2\text{O}\) and \(\text{tris}[2-(2'-\text{pyridyl})\text{imidazole}]\) Iron(II) tetraphenylborate, a closely related spin-equilibrium species, during the course of this work. Their results for the two compounds are as follows:

\[
\begin{align*}
\text{Fe(PYI)}_3(\text{BPh}_4)_2 &; \quad \Delta H = 15.90 \quad \Delta S = 48.52 \text{ in acetone} \\
\Delta H & = 15.48 \quad \Delta S = 52.72 \text{ in CH}_3\text{CN/CH}_3\text{OH} \\
\text{Fe(PYB)}_3(\text{BPh}_4)_2 &; \quad \Delta H = 19.66 \quad \Delta S = 77.82 \text{ in acetone} \\
\Delta H & = 21.34 \quad \Delta S = 92.05 \text{ in CH}_3\text{CN/CH}_3\text{OH} \\
(\Delta H \text{ in kJ mol}^{-1} &; \quad \Delta S \text{ in J. mol}^{-1} \text{ k}^{-1}).
\end{align*}
\]

The assumptions are that \(\mu_A\) (high-spin) = 5.5 B.M. and \(\mu_B\) (low-spin) = 0.

Similar work has been carried out on three other ferrous compounds exhibiting a spin equilibrium. These are firstly the bis[hydrotris(1-pyrazolyl)borate]Iron(II) complex studied by Jesson \(\text{Fe(6-MePy)(Py)}_2\text{tren})^{2+} \) and [Fe(6-MePy)\(\text{Py)}_2\text{tren})^{2+} \) (\(\Delta H = 19.25\) and 11.88 kJ mol\(^{-1}\) in acetone, respectively). \(\text{Fe(6-MePy)(Py)}_2\text{tren})^{2+} \) (\(\Delta H = 16.32\) kJ mol\(^{-1}\) in acetone) and secondly the two related cations \(\text{Fe}^{2+}\) and \(\text{Fe(6-MePy)(Py)}_2\text{tren})^{2+} \) (\(\Delta H = 19.25\) and 11.88 kJ mol\(^{-1}\) in acetone, respectively). \(\text{Fe(6-MePy)(Py)}_2\text{tren})^{2+} \)

The values of \(\Delta H\) found for these ferrous systems are much larger than those obtained for the ferric dithiocarbamates (6-9 kJ mol\(^{-1}\)). And, indeed, the bond energy and bond length changes associated with the iron core of the molecules is more dramatic than in the case of the ferric system. This is illustrated by the complex \(\text{Fe(6-MePy)(Py)}_2\text{tren})^{2+} \), the average Fe-N bond distance is 0.12\(\text{A}\) shorter at 200\(^{\circ}\)K (\(\mu_{\text{eff}} \sim 2.3\) B.M.) than at 300\(^{\circ}\)K (high-spin \(\mu_{\text{eff}} \sim 5.0\) B.M.).
The ΔS term for the equilibrium $^1A_1 \rightleftharpoons ^5T_2$ includes an electronic entropy term due to changes in the spin multiplicity and state degeneracy. This is equal to $R \ln 15 - R \ln 1 = R \ln 15 = 22.52 \text{ J. mol}^{-1} \text{ K}^{-1}$. However, in effect this electronic term is lower than this as distortion from true octahedral symmetry of the cation (to $D_3$) leads to splitting of the $^5T_2$ ground state.

$^5T_2 \text{(oh)} \rightarrow ^5E + ^5A_1$

So the actual spin equilibrium is either

$^1A_1 \rightleftharpoons ^5E \quad \Delta S \text{ (electronic)} = R \ln 10 = 19.14 \text{ J. mol}^{-1} \text{ K}^{-1}$
or

$^1A_1 \rightleftharpoons ^5A_1 \quad \Delta S \text{ (electronic)} = R \ln 5 = 13.38 \text{ J. mol}^{-1} \text{ K}^{-1}$

For the analysis of the complex $[\text{Fe(HB(pz)}_3]^2^7$, the latter equilibrium was taken to be the true equilibrium because of the high degree of trigonal distortion known to exist in the compound.

Once again, comparison of the results represented in this Chapter and in reference 73, with previous solid state work, shows the benefit of a solution state analysis of a spin-equilibrium system. Despite handling difficulties (see Chapter 2 (c)), because of possible air oxidation of the solutions, reliable magnetic data and thermodynamic parameters have been obtained. Moreover, the anomalous solid state results (see Figure (2.4)) have been clarified to give a clear picture of the equilibrium in the cation Fe(PYB)$_3^{++}$. 

---
C) EXPERIMENTAL

Magnetic susceptibilities were determined in a solvent containing acetone 90%, water 5% and hexamethyldisiloxane 5%. The compounds would not dissolve in an acetone/hexamethyldisiloxane mixture unless water was present.

The complete expression was applied to calculate $\chi$, as in Chapter 1 D). Again, an internal capillary was made containing the deaerated solvent, and using conventional rubber septum - steel needle techniques the Iron(II) solution could be anaerobically transferred to the n.m.r. tube under a positive pressure of argon, thus preventing air oxidation of the solution. The construction of the commercially available split-tubes makes it very difficult to deaerate both the inside and outside compartments of the tube. If the solution chamber is deaerated the solvent chamber must also be deaerated or else the paramagnetism of the oxygen present will alter the measured shifts, $\Delta f$.

Density measurements were made on all solutions at room temperature and at $\text{-78.5}^\circ\text{C}$ as in Chapter 1 D).

$\chi_0$, the mass susceptibility of the solvent was calculated to be $-0.6125 \times 10^{-6}$ and the diamagnetic ligand corrections $\text{Fe(PYB)₃(ClO₄)₂}$, $427 \times 10^{-6}$; $\text{Fe(PYB)₃(BF₄)₂}$, $437 \times 10^{-6}$.

All n.m.r. spectra were measured at 90 MHz on a Perkin-Elmer R32 spectrometer. The variable temperature probe was calibrated with methanol$^{56}$ and at all temperatures studied the machine settings were found to be accurate to within $\pm 2.0^\circ\text{C}$. 
Materials

Tris[2-(2'-pyridyl)benzimidazole]Iron(II) perchlorate and tris[2-(2'-pyridyl)benzimidazole]Iron(II) tetrafluoroborate were prepared by Dr. A.A.S.C. Machado and were a gift from Dr. D.M.L. Goodgame. The compounds are hygroscopic, becoming darker in colour if allowed to stand in air. They were dried for several hours in vacuo before being analysed.

Fe(PXB)₃(ClO₄)₂, Found: C, 50.77; H, 3.25; N, 14.61%.

Calculated for C₃₆H₂₇N₉O₅Cl₂Fe: C, 51.45; H, 3.24; N, 15.00%.

Fe(PYB)₃(BF₄)₂, Found: C, 52.68; H, 3.29; N, 15.28%.

Calculated for C₃₆H₂₇N₉B₂F₈Fe: C, 53.04; H, 3.34; N, 15.47%.

Microanalysis performed by Imperial College Microanalytical Laboratories.
CHAPTER 3

MAGNETIC TITRATIONS AND SPIN EQUILIBRIA

FOR

IRON(III) PORPHINE COMPLEXES.
A) 1) **Ferric Porphines**

The porphyrins are a biologically important group of compounds with a definitive parent structure, that of porphin C\textsubscript{20}H\textsubscript{14}N\textsubscript{4}, which comprise four pyrrole rings connected by four methine bridges to form a large macrocycle.\textsuperscript{75} This structure was first proposed by Kuster in 1912\textsuperscript{76} and after great controversy finally proven by the total synthesis of protoheme in 1929 by Fischer.\textsuperscript{77}

Porphyrins readily form complexes with a wide range of metals in which one, or more commonly two, of the NH protons are lost. The metal therefore, coordinates to the two lone pairs of the pyrrolenine nitrogens and also replaces the two pyrrole hydrogens so that two more lone pairs are donated from the porphyrin to the metal. Up to date, well over fifty different metals are known to form porphyrin complexes. The most important of these metals are Mg, V, Mn, Fe, Co, Ni, Cu and Zn which are all inserted into porphyrins by nature.

Metal porphyrin complexes of major physiological importance include haemoglobin (Fe), chlorophyll (Mg) and cytochromes (Fe).

In this Chapter, the ferric porphyrin complexes used are based on the two structures shown in Figure (3.1), the naturally occurring heme-porphyrin, protoporphyrin IX, PPIX-H\textsubscript{2}, and the synthetic porphyrin-tetraphenylporphyrin, TPH\textsubscript{2}.

Adler, et al.,\textsuperscript{78} describes the synthesis of TPH\textsubscript{2}, a condensation reaction of pyrrole and benzaldehyde in propionic acid\textsuperscript{79} which has been used to produce over seventy substituted TPH\textsubscript{2} porphyrins. These are meso-substituted porphyrins, the phenyl or substituted
Figure (3.1). Structure of $\text{Fe(PPix)}_X$ and $\text{Fe(TPP)}_X$.

$\text{Fe(Protoporphyrin IX)}_X$

$\text{Fe(Tetraphenylporphyrin)}_X$
phenyl rings are attached to the porphin structure at carbons 5, 10, 15 and 20, the methine bridging carbons.

In contrast, the naturally occurring protoporphyrin IX system is pyrrole substituted, as are all the common natural porphyrins. For solution work it is found that the dimethylester of the porphyrin is much more soluble in organic solvents and so this has been prepared and used in all the reported work in this Chapter.

Several methods for the metallation of porphyrins are available. For this work the dimethylformamide method was used with anhydrous ferrous chloride as the metal source. DMF is a good solvent for the porphyrin and for the metal carrier and the high refluxing temperature helps to remove HCl which is evolved during the reaction.

Metal porphines are of great interest, not only because of the biological importance of the compounds, but also due to the great diversity in structural, magnetic and coordination properties. The ferric porphyrins in particular are very varied in character and can be grouped as follows:

a) High spin, 5-coordinate  
b) High spin, 6-coordinate  
c) Intermediate spin, 6-coordinate  
d) Intermediate spin, 5-coordinate  
e) Intermediate spin, 4-coordinate  
f) Low spin, 6-coordinate
The first group, a), are very common and include all ferric porphyrin halides, e.g., Fe(TPP)Br$^{82}$ and Fe(PPIX)Cl$^8$. The environment of the Iron atom in these compounds is square pyramidal as shown in Figure (3.2).

Figure (3.2) Configuration of 5-Coordinated High-Spin Ferric Porphyrins.

As shown in Figure (3.2) the Iron atom is displaced out of the porphyrin plane. This displacement (Fe-Ct) is quite large, being 0.49 Å in Fe(TPP)Br$^{82}$, 0.38 Å in Fe(TPP)Cl$^8$, and 0.455 Å in chlorohemin$^8$. The average Fe-N distance represents the radius of the "hole" in the porphyrin plane. This distance varies from 1.96 to 2.10 Å, depending on the porphyrin$^8$. Typical metal halide distances are Fe-Ct, 2.192 Å (in Fe(TPP)Cl) and Fe-Br 2.348 Å (in Fe(TPP)Br). Group b) are high-spin and six-coordinate and include the compounds Fe(TPP)(Ethanol)$^+$.BF$_4^-$ and Fe(TPP)(DMSO)$^+$.I$^-$. An X-ray crystal study$^8$ has shown that the high spin ferric ion is in the plane of the porphine macrocycle, which refutes
Figure (3.3)  d orbital splitting for the spin states encountered in ferric porphines.

\[ \begin{align*}
\text{low spin} & : S = 1/2 \\
\text{high spin} & : S = 5/2 \\
\text{mixed spin} & : S = 5/2, 3/2 \\
\text{intermediate spin} & : S = 3/2
\end{align*} \]

DECREASING AXIAL LIGAND FIELD STRENGTH
INCREASING TETRAGONAL DISTORTION (Z < X, Y)
the earlier theory that high spin ferric is too large to be
accommodated in the plane, and hence only low-spin ferric complexes
are of this type.

Whereas Fe(TPP)(EtOH)$_2$ is high spin, Fe(OEP)(EtOH)$_2$ is found
to be intermediate spin and hence a member of group c).$^{88,89}$

This shows the delicate balance that exists in metal porphyrin
chemistry with respect to axial ligand, porphyrin and spin state.

$\mu_{\text{eff}}$ of Fe(OEP)(EtOH)$_2$ is 4.5 B.M. This is thought to be a quantum
mechanical admixture of $S = 3/2$ and $S = 5/2$ spin states rather
than a true intermediate $S = 3/2$ state, although earlier
reports did suggest that the intermediate magnetic moment was due
to $S = 3/2$ with a large orbital contribution to the moment.

This complex neatly fits into the pattern of decreasing
axial ligand field strength and increasing tetragonal distortion
which are the conditions necessary to produce the $S = 3/2$ spin
state for a $d^5$ ion (strong equatorial bonding and very weak or zero
axial bonding). See Figure (3.3). Other complexes known to be
in a quantum mechanical mixed spin state are Fe(TPP)Cl$_2$, $^{91}$ and
Fe(OEP)Cl$_2$, $^{92}$ both are five-coordinate and belong to group d),
their magnetic moments are $\mu_{\text{eff}} = 5.0$ and 4.8 B.M. respectively.
The true $S = 3/2$ state would probably be achieved with the so
far unobtainable Fe(TPP)$^+$, with no axial ligand field whatsoever.
$d_{z^2}$ would then be close in energy to the $t_{2g}$ orbitals, while
d$_{x^2-y^2}$ would lie well above the other four orbitals and would be
unoccupied. (A situation similar to the $S = 1$ state of Fe(II) TPP).$^{93}$
Group f) are the low-spin six-coordinate complexes and there are many examples of the type Fe(P)L₂⁺ where P = any porphyrin and L = nitrogenous base. Fe(TPP)(Im)₂⁺ Cl⁻ is typical and a crystal structure of this compound has been performed.⁹⁴ (See Figure (3.4)).

Figure (3.4) Structure of a Six-Coordinate Low-Spin Ferric Porphyrin.

Because of the complexity and interesting nature of these systems, a great deal of work has been carried out on metal porphines and their complexation reactions. A résumé of the current literature is given in the next section, followed by the results obtained during this study of metal porphyrin-nitrogenous base complexation reactions by an n.m.r. magnetic titration method.
ii) Complexation Reactions with Nitrogenous Bases.

The reactions which occur between nitrogeneous bases (such as pyridine, imidazole and substituted pyridines and imidazoles) and metal porphines have been the subject of a great deal of study for many decades. Much of the early work was carried out in aqueous alkaline solutions, for example, see the work of Keilin\textsuperscript{95} and Barron.\textsuperscript{96}

The main problems encountered in this work are those of metal porphine dimerization (to the μ-oxo-dimer) and aggregation. Gallagher and Elliot\textsuperscript{97} report a monomeric imidazole parahaematin complex in 2 mN NaOH which if left standing will precipitate out an aggregated species of unknown composition.

One method of combating this problem was to use a solvent containing 44.5\% by weight of ethanol in water.\textsuperscript{98} Hemin was found to be stable as a monomer in this solvent at dilute concentrations and a study of the reaction between the monomer and imidazole showed that the equilibrium was

\[ M + 2\text{Im} \rightleftharpoons M\text{Im}_2 \]

M = hemin, there was no evidence for a mono-imidazole complex being formed.

Work in recent years has switched mainly to organic solvents and the reaction

\[ \text{MPL}_p + n \text{L} \rightleftharpoons K \text{MPL}_p(n + p) \]  \hspace{1cm} (13)

where MP = metal porphine

L = nitrogeneous base

p = 0 or 1, n = 1 or 2, and p + n ≤ 2
can be analysed to give values for the equilibrium constant.

Three methods in particular have been used:

i) Absorption Spectrophotometry

ii) Nuclear Magnetic Resonance, and

iii) Magnetic Titrations.

i) **Absorption Spectrophotometry.** - Spectrophotometric titrations have been used by a number of workers to obtain kinetic data for porphyrin equilibria.

The equilibrium (13) can take three forms:

\[
\begin{align*}
 p &= 0 \quad n = 1 \quad MP + L \xrightleftharpoons{K_{1}} MPL \\
 p &= 1 \quad n = 1 \quad MPL + L \xrightleftharpoons{K_{2}} MPL_2 \\
 p &= 0 \quad n = 2 \quad MP + 2L \xrightleftharpoons{K_{12}} MPL_2
\end{align*}
\]

Provided that only one of these equilibria is operative in a ligand addition study the equilibrium constant can be obtained as follows.

\[
k_i = \frac{[MPL_p + n]}{[MPL_p][L]^n}
\]

If \( A = \) Absorbance of partially ligated solution

\( A_{\infty} = \) Absorbance of totally ligated solution

\( A_0 = \) Absorbance of metal porphine alone

then

\[
\frac{[MPL_p + n]}{[MPL_p]} = \frac{(A - A_0/A_{\infty} - A_0)}{(A_{\infty} - A/A_{\infty} - A_0)} = \frac{A - A_o}{A_o - A}
\]
\[ [L]^n K_1 = \frac{(A - A_\infty)}{(A_\infty - A)} \]

\[ n \log [L] + \log K_1 = \log \left[ \frac{A - A_\infty}{A_\infty - A} \right] \]

This method was successfully employed by Goff and Morgan\textsuperscript{99} to study axial binding to amino acid substituted porphyrins. It can also be used when the equilibrium constant is not large enough to produce a totally ligated species in solution\textsuperscript{98} (i.e., \( A_\infty \) cannot be measured experimentally). In this case

\[ K_1 = \frac{A - A_\infty}{A_\infty - A} \cdot \frac{1}{[L]^n} \]

\[ A_\infty - A = \frac{A - A_\infty}{K_1} \cdot \frac{1}{[L]^n} \]

\[ A = A_\infty - \frac{A - A_\infty}{K_1} \cdot \frac{1}{[L]^n} \]

A plot of \( A \) vs \( (A - A_\infty)/[L]^n \)

gives \(-1/K_1\) (slope)

and \( A_\infty \) (intercept)

The most comprehensive study of nitrogeneous base complexation involving the spectrophotometric titration method has been by Walker et al.\textsuperscript{100} They report the overall equilibrium constant \( \beta_2 \) for a series of para-substituted tetraphenylporphine complexes of
haloiron(III) with pyridines and imidazoles in five different solvents. Their results are reported in Table 3.2. Where possible, a value for $K_1$ was also given. $K_1$, the formation constant for the mono-base complex is very much smaller than $K_2$, in n.m.r. and magnetic titration experiments, no trace of mono-complex is found and the results are always reported as an overall constant $\beta_2$. The actual mechanism of complexation has been described by Burdige and Sweigart for the example of Fe(TPP)Cl and propyl imidazole.

a) Addition of 1 mole of base.

$$\text{Fe(TPP)Cl} + \text{Pr lm} \xrightarrow{K_1} \text{Fe(TPP)(Pr lm)Cl}$$

(H.S.) (H.S.)

b) Dissociation to form an ion pair

$$\text{Fe(TPP)(Pr lm)Cl} \rightleftharpoons \text{Fe(TPP)(Pr lm)}^+\text{Cl}^-$$

c) Further addition of base

$$\text{Fe(TPP)(Pr lm)}^+\text{Cl}^- + \text{Pr lm} \xrightarrow{K_2} \text{Fe(TPP)(Pr lm)}^2\text{Cl}^-$$

(L.S.)

$K_2 \gg K_1$ the driving force behind the reaction being the formation of a low spin complex from a high spin complex. The rate of dissociation b) will depend on the anion, hence for $\beta_2$ I > Br > Cl.
ii) **Nuclear Magnetic Resonance.** - This technique is ideally illustrated by the work of La Mar, et al.\(^\text{102}\) They studied the reaction between substituted pyridines and imidazoles and ferric porphyrin halides by proton n.m.r. The equilibrium constants \(\beta_2\) for the reactions were computed from the relative areas of the high spin meta-H doublet and the low spin 1-CH\(_3\), 5-CH\(_3\), or 5-H imidazole peaks (as appropriate). For pyridines either the 4-H or 4-CH\(_3\) pyridine peaks were used. By correcting for the different number of protons in each resonance the proportion of high spin and low spin (bis substituted) ferric porphyrin can be calculated at different ligand concentrations. The results obtained by La Mar are reported in Table 3.2.

iii) **Magnetic Titrations.** - This versatile technique has until now been rarely used in metal porphyrin chemistry. The variation of magnetic moment with pH has been measured in some instances using the Evans method for magnetic susceptibilities. A ferri-haem undecapeptide was studied by Jehanli, Stotter and Wilson,\(^\text{103}\) the pH titration showed the conversion to an antiferromagnetic bridged dimer at high pH. See Figure (3.5).

**Figure (3.5).** pH Dependence of a Ferri-Haem Undecapeptide (Reference 103).
Only two previous reports of magnetic titrations as a method of studying ligand complexation reactions have been made. The first of these was a single titration of imidazole against Fe(TPP)Cl.\textsuperscript{104} The equilibrium constant $\beta_2$ was found to be extremely high, $\sim 5 \times 10^5$ and the resulting titration curve is in the form of two straight lines covering the regions $0-2$ and $> 2$ (referring to molar ratio of ligand to metal porphyrin). The plot is shown in Figure (3.6).

**Figure (3.6).** Magnetic Titration Curve for the Equilibrium

$$\text{Fe(TPP)Cl} + 2\text{Im} \rightarrow \text{Fe(TPP)}(\text{Im})_2^+ + \text{Cl}^-.$$

The second report was of the titration of hemin with cyanide, imidazole and the mixed ligand, in Me$_2$SO-d$_6$ solution.\textsuperscript{105,106} The difference in binding is clear, cyanide ligation is a two-step process ($K_1 = 1.9 \times 10^4$, $K_2 = 1.1 \times 10^3$ at 20°C, the mono-cyano complex being low spin) and imidazole ligation is one-step ($\beta_2 = 6 \times 10^4$ at 20°C, smaller than that reported by reference 104 because of the competition to imidazole binding by the solvent DMSO-d$_6$). The results are illustrated in Figure (3.7).
Whichever method is used to study the reaction, the effects of metal porphyrin aggregation must always be considered. Molecular weight measurements show that the degree of aggregation depends on the solvent and the concentration (Table 3.1).

Table (3.1). The Variation of the Molecular Weight of Fe(PPIX-DME)Cl with Concentration and Solvent.

<table>
<thead>
<tr>
<th>Fe(PPIX-DME)Cl</th>
<th>0.008 M</th>
<th>0.004 M</th>
<th>0.002 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2060</td>
<td>1990</td>
<td>1820</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1070</td>
<td>950</td>
<td>790</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>910</td>
<td>830</td>
<td>740</td>
</tr>
</tbody>
</table>
The molecular weight of the compound as a monomer is 680.

Some of the difference will be due to solvation, but clearly a solvent such as benzene is unsuitable for kinetic studies. The amount of aggregation in solution is also dependent on the anion, iodides aggregate more than bromides more than chlorides.

The following section presents the results of a series of magnetic titrations involving a variety of ferric porphyrins and ligating species. The results of the titrations are analysed to give the equilibrium constants $\beta_2$ which are compared with those of previous relevant work.

B) Magnetic Titrations of Ferric Porphines.

The experimental details of magnetic titrations are described in section D) of this Chapter. The results for each titration are given below.

1. Fe(PPIX-DME)Cl with 1-methylimidazole (35°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:3.2</th>
<th>1:6.4</th>
<th>1:9.5</th>
<th>1:15.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.92</td>
<td>4.30</td>
<td>3.01</td>
<td>2.63</td>
<td>2.38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:22.2</th>
<th>1:34.9</th>
<th>1:47.7</th>
<th>1:73.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.33</td>
<td>2.37</td>
<td>2.27</td>
<td>2.22</td>
</tr>
</tbody>
</table>
2. Fe(TPP)Cl with 1-Methylimidazole (35°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:3.2</th>
<th>1:6.4</th>
<th>1:9.5</th>
<th>1:12.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.94</td>
<td>5.24</td>
<td>4.22</td>
<td>3.54</td>
<td>3.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:15.9</th>
<th>1:23.8</th>
<th>1:31.8</th>
<th>1:44.5</th>
<th>1:69.9</th>
<th>1:95.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.86</td>
<td>2.66</td>
<td>2.51</td>
<td>2.46</td>
<td>2.46</td>
<td>2.43</td>
</tr>
</tbody>
</table>

3. Fe(TMPP)Cl with 1-Methylimidazole (35°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:3.2</th>
<th>1:6.4</th>
<th>1:9.6</th>
<th>1:12.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>6.05</td>
<td>5.33</td>
<td>4.18</td>
<td>3.44</td>
<td>3.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:16</th>
<th>1:24</th>
<th>1:32</th>
<th>1:44.8</th>
<th>1:70.4</th>
<th>1:96</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.85</td>
<td>2.63</td>
<td>2.56</td>
<td>2.49</td>
<td>2.46</td>
<td>2.47</td>
</tr>
</tbody>
</table>

4. Fe(TPP)Br with 1-Methylimidazole (35°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:0.6</th>
<th>1:1.3</th>
<th>1:1.9</th>
<th>1:2.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>6.11</td>
<td>5.71</td>
<td>5.01</td>
<td>4.39</td>
<td>3.81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:3.3</th>
<th>1:4.8</th>
<th>1:8</th>
<th>1:16</th>
<th>1:28.8</th>
<th>1:54.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>3.29</td>
<td>2.78</td>
<td>2.55</td>
<td>2.47</td>
<td>2.41</td>
<td>2.37</td>
</tr>
</tbody>
</table>
5. **Fe(Proto IX-DME)Br with 1-Methylimidazole (35°C).**

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:0.5</th>
<th>1:1</th>
<th>1:1.4</th>
<th>1:1.9</th>
<th>1:2.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.95</td>
<td>5.54</td>
<td>5.00</td>
<td>4.35</td>
<td>3.68</td>
<td>2.77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:4.8</th>
<th>1:7.9</th>
<th>1:15.9</th>
<th>1:28.5</th>
<th>1:53.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.40</td>
<td>2.27</td>
<td>2.27</td>
<td>2.26</td>
<td>2.22</td>
</tr>
</tbody>
</table>

6. **Fe(TMPP)Br with 1-Methylimidazole (35°C).**

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:0.6</th>
<th>1:1.3</th>
<th>1:1.9</th>
<th>1:2.5</th>
<th>1:3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>6.17</td>
<td>5.80</td>
<td>5.21</td>
<td>4.75</td>
<td>4.30</td>
<td>4.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:4.8</th>
<th>1:8.3</th>
<th>1:15.9</th>
<th>1:28.7</th>
<th>1:54.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>3.50</td>
<td>2.90</td>
<td>2.49</td>
<td>2.33</td>
<td>2.32</td>
</tr>
</tbody>
</table>

7. **Fe(TPP)Cl with 4-Dimethylaminopyridine (35°C).**

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:1.6</th>
<th>1:3.1</th>
<th>1:5.2</th>
<th>1:8.3</th>
<th>1:12.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.87</td>
<td>5.57</td>
<td>5.42</td>
<td>4.91</td>
<td>4.27</td>
<td>3.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:16.5</th>
<th>1:24.8</th>
<th>1:33.1</th>
<th>1:45.5</th>
<th>1:57.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>3.28</td>
<td>2.97</td>
<td>2.74</td>
<td>2.51</td>
<td>2.47</td>
</tr>
</tbody>
</table>
8. Fe(PPIX-DME)Cl with 4-Dimethylaminopyridine (35°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:1.6</th>
<th>1:3.1</th>
<th>1:5.2</th>
<th>1:8.3</th>
<th>1:12.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.91</td>
<td>5.58</td>
<td>5.02</td>
<td>4.23</td>
<td>3.54</td>
<td>3.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:16.5</th>
<th>1:24.8</th>
<th>1:33.1</th>
<th>1:45.5</th>
<th>1:57.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.87</td>
<td>2.60</td>
<td>2.56</td>
<td>2.50</td>
<td>2.40</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:3.1</th>
<th>1:6.2</th>
<th>1:9.7</th>
<th>1:14.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>5.91</td>
<td>4.53</td>
<td>3.33</td>
<td>2.77</td>
<td>2.56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:21.8</th>
<th>1:34.3</th>
<th>1:46.8</th>
<th>1:71.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.54</td>
<td>2.44</td>
<td>2.44</td>
<td>2.37</td>
</tr>
</tbody>
</table>

10. Fe(TPP)I with Pyridine (37.4°C).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:0</th>
<th>1:0.3</th>
<th>1:1</th>
<th>1:4.2</th>
<th>1:7.4</th>
<th>1:11.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>6.02</td>
<td>6.06</td>
<td>5.97</td>
<td>5.48</td>
<td>4.70</td>
<td>3.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>1:14.4</th>
<th>1:19.2</th>
<th>1:32</th>
<th>1:48</th>
<th>1:64</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.95</td>
<td>2.64</td>
<td>2.38</td>
<td>2.21</td>
<td>2.09</td>
</tr>
</tbody>
</table>

In each of the above tables the molar ratio is given as Molarity of metal porphine: molarity of base ligand. $\mu_{\text{eff}}$ is expressed in Bohr Magnetons.
The kinetics of this equilibrium are explained in Appendix 4. The results of all ten titrations have been fitted to an $A + 2L \rightleftharpoons A L_2$ equation and the equilibrium constant $\beta_2$ calculated by computer program (Appendix 3). The titrations have been represented graphically in Figures (3.8) to (3.17). A summary of the kinetic data obtained from these experiments and from those conducted by La Mar$^{102}$ (N.m.r. method) and Walker$^{100}$ (Absorption spectrophotometry method) is presented in Table 3.2.

The ten magnetic titrations performed during the course of this work encompass a wide variety of different porphyrins (with variations in macrocycle and axial ligand), ligands and temperatures. These particular combinations of the variable elements in the equilibrium were chosen for the purpose of illustrating several important points concerning the basic equilibrium process.

Firstly, let us consider the effect of temperature on the equilibrium. Figures (3.8 and 3.9) show the titration curves and give the equilibrium constants for the reaction between Fe(TPP)Cl and two mole equivalents of 1-Melm at the temperatures 35°C and 24.6°C. The figures show that a decrease of 10.4°C causes the equilibrium constant to rise to about 3.5 times its former value. Slightly larger values than this ($\sim 6 \times$ increase for 10°C) are indicated for Fe(TMPP)Cl (see Table 3.2) although this figure is more likely to be in error as the kinetic data at each temperature has been obtained by a different experimental method.

The importance of accurate temperature control in kinetic experiments of this type is once again underlined by the temperature dependence of this system. Such agreement as exists in the three sets of kinetic data shown in Table 3.2 for the three independent methods of obtaining $\beta_2$ are all the more encouraging for this fact.
FIGURE (3.8) MAGNETIC TITRATION OF Fe(TPP)Cl WITH 1-Melm (35°C)

Fe(TPP)Cl + 2 1-Melm ⇌ Fe(TPP)(1-Melm)²⁺ + Cl⁻

at 35°C

β₂ = 575 M⁻²

FIGURE (3.9) MAGNETIC TITRATION OF Fe(TPP)Cl WITH 1-Melm (24.6°C)

Fe(TPP)Cl + 2 1-Melm ⇌ Fe(TPP)(1-Melm)²⁺ + Cl⁻

at 24.6°C

β₂ = 2,050 M⁻²
Table 3.2. Kinetic Data for the Equilibrium Fe(P)X + 2L = Fe(P)L₂ + X⁻.

<table>
<thead>
<tr>
<th>Porphyrin Complex</th>
<th>Base Ligand</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>This work</th>
<th>N.M.R.⁹</th>
<th>Abs. Spec.⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(TPP)Cl</td>
<td>1m</td>
<td>Chloroform</td>
<td>25</td>
<td>-</td>
<td>&gt; 10⁶</td>
<td>1.58 x 10⁶</td>
</tr>
<tr>
<td></td>
<td>1-Melm</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.05 x 10³³</td>
<td>1.38 x 10³</td>
<td>1.5 x 10³</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>35</td>
<td>5.75 x 10²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TPP)Br</td>
<td>1-Melm</td>
<td>Chloroform</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>&gt; 2.5 x 10⁷</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>35</td>
<td>2.1 x 10⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TMPP)Cl</td>
<td>1-Melm</td>
<td>Chloroform</td>
<td>25</td>
<td>-</td>
<td>4 x 10³</td>
<td>3.6 x 10³</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>35</td>
<td>6.5 x 10²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TMPP)Br</td>
<td>1-Melm</td>
<td>Chloroform</td>
<td>35</td>
<td>6.7 x 10³⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TPP)I</td>
<td>Py</td>
<td>Chloroform</td>
<td>37.4</td>
<td>2.4 x 10²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1-Melm</td>
<td>&quot;</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>&gt; 1 x 10⁷</td>
</tr>
<tr>
<td>Fe(PPIX-DME)Cl</td>
<td>1-Melm</td>
<td>Chloroform</td>
<td>35</td>
<td>2.85 x 10³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(PPIX-DME)Br</td>
<td>1-Melm</td>
<td>Chloroform</td>
<td>35</td>
<td>9.79 x 10⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TPP)Cl</td>
<td>Me₂N-Py</td>
<td>Chloroform</td>
<td>35</td>
<td>2.6 x 10²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(PPIX-DME)Cl</td>
<td>Me₂N-Py</td>
<td>Chloroform</td>
<td>35</td>
<td>8.2 x 10²</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

⁹ Reference 102. ⁸ Reference 100. ³ At 24.6°C. ⁴ Uncertain value.
Another obvious but nonetheless very important factor in the equilibrium kinetics of this system has already been mentioned in the previous section. This is the correlation between $\beta_2$ and the anion axially coordinated to the metal porphyrin. As shown in the more detailed study of the equilibrium mechanism (Chapter 3, Section A (ii)), dissociation of the metal porphyrin complex to form an ion pair is one of the rate-determining stages of the equilibrium process. $\beta_2$ can be shown to increase dramatically with decreasing Fe-X bond strength. The enthalpy of formation of Fe(P)X is expected to increase by about 2.5 kJ for each halide ion, with $\Delta H_f^0$ most negative for $X = F$. Hence the order of $\Delta H_f^0$ is $F > Cl > Br > I$ (Fe-X bond energies were estimated from heats of formation of both gaseous and dissolved FeX$_3$).\(^{109}\)

So for $\beta_2$ we have the order $I > Br > Cl > F$; in fact Fe(TPP)F does not form a complex at all with 1-Melm.\(^{102}\) This order is illustrated further by Figures (3.11) and (3.14). Also, the fact that a titration could be performed using pyridine as a ligand at 37.4°C with Fe(TPP)I shows the great difference in reactivity between this complex and the equivalent chloride. At this temperature Fe(TPP)Cl does not give a totally bis-pyridine complex (i.e., the equilibrium does not approach completion) even in neat pyridine. (The magnetic moment of such a solution is $\sim 3.9$ B.M.). Even at -25°C La Mar\(^{102}\) reports the value of $\beta_2$ for

$$Fe(TPP)Cl + 2py \rightleftharpoons Fe(TPP)py_2^+ + Cl^-$$

to be only $9.3 \pm 0.9$ M\(^{-2}\).
It is interesting at this point to compare the ratio of $\beta_2$ for the bromide complex ($\beta_2^{Br}$) to that of the chloride complex ($\beta_2^{Cl}$) for the porphyrins used during these experiments. It is found that there is excellent agreement between $\beta_2^{Br}/\beta_2^{Cl}$ for the TPP and PPIX-DME systems. For TPP complexes $\beta_2^{Br}/\beta_2^{Cl} = 36.5$ and for PPIX-DME complexes $\beta_2^{Br}/\beta_2^{Cl} = 34.4$. This ratio does not hold, however, for the two complexes of tetra(p-methoxyphenyl)prophyrin for which $\beta_2^{Cl} = 6.5 \times 10^2 \text{ M}^{-2}$ and $\beta_2^{Br}$ is only $6.7 \times 10^3 \text{ M}^{-2}$, much lower than expected, although the value was shown to be consistent with further experiments. It is believed that this value is artificially low due to a further process occurring in the equilibrium system (perhaps aggregation which is known to be greater for bromides than chlorides and is possibly also increased by using tetra(p-methoxyphenyl)porphines rather than the TPP or PPIX-DME systems). The presence of significant amounts of a dimeric porphyrin complex would not only lower the value of $\beta_2$ obtained for the equilibrium but also cause the experimental results to no longer fit the simple $A + 2L \rightleftharpoons AL_2$ equilibrium pattern. This is observed for Fe(TMPP)Br with 1-Melm, a very poor computer fit to the simple theoretical values is obtained.

The effect of the porphyrin on the equilibrium is such that $\beta_2$ varies in the following manner; PPIX-DME >> TMPP > TPP. The electron-donating p-methoxy group would appear to stabilise the positive charge on the ferric ion and thus increase the rate of bis-complex formation. An electron withdrawing group such as Cl in the p-phenyl
**FIGURE (3.10) MAGNETIC TITRATION OF Fe(TPP)Br WITH 1-Melm (35°C)**

\[
\text{Fe(TPP)Br} + 2 \text{ 1-Melm} \rightleftharpoons \text{Fe(TPP)(1-Melm)}^2 + \text{Br}^- \\
\text{at 35°C}
\]

\[\beta_2 = 20,800 \text{ M}^{-2}\]

**FIGURE (3.11) MAGNETIC TITRATION OF Fe(PPIX-DME)Cl WITH 1-Melm (35°C)**

\[
\text{Fe(PPIX-DME)Cl} + 2 \text{ 1-Melm} \rightleftharpoons \text{Fe(PPIX-DME)(1-Melm)}^2 + \text{Cl}^- \\
\text{at 35°C}
\]

\[\beta_2 = 2,840 \text{ M}^{-2}\]
Figure 3.12: Magnetic Titrations of Fe(TPP)Cl with Me₂N-Py (35°C)

\[
Fe(TPP)Cl + 2Me₂N-Py \rightleftharpoons Fe(TPP)(Me₂N-Py)⁺ + Cl⁻
\]
at 35°C
\[\beta_2 = 260 \text{ M}^{-2}\]

Figure 3.13: Magnetic Titrations of Fe(PPIX-DPE)Cl with Me₂N-Py (35°C)

\[
Fe(PPIX-DPE)Cl + 2Me₂N-Py \rightleftharpoons Fe(PPIX-DPE)(Me₂N-Py)⁺ + Cl⁻
\]
at 35°C
\[\beta_2 = 820 \text{ M}^{-2}\]
**Figure (3.14) Magnetic Titration of Fe(PPIX-Dme)Br with 1-Helm (35°C)**

\[
\text{Fe(PPIX-Dme)Br} + 2 \text{Helm} \rightleftharpoons \text{Fe(PPIX-Dme)(Helm)}^+ + \text{Br}^-
\]

at 35°C

\[
\beta_2 = 97,900 \text{ M}^{-2}
\]

**Figure (3.15) Magnetic Titration of Fe(TMPP)Cl with 1-Helm (35°C)**

\[
\text{Fe(TMPP)Cl} + 2 \text{Helm} \rightleftharpoons \text{Fe(TMPP)(Helm)}^+ + \text{Cl}^-
\]

at 35°C

\[
\beta_2 = 650, \text{ M}^{-2}
\]
Figure (3.16) Magnetic Titration of Fe(TPP)I with Pyridine (37.4°C).

\[ \text{Fe(TPP)}I + 2 \text{Py} \rightleftharpoons \text{Fe(TPP)}\text{Py}_2^+ + \text{I}^- \]

at 37.4°C

\[ \beta_2 = 240 \text{ M}^{-2} \]

Figure (3.17) Magnetic Titration of Fe(TMPP)Br with 1-Niem (35°C).

\[ \text{Fe(TMPP)}\text{Br} + 2 \text{1-Niem} \rightleftharpoons \text{Fe(TMPP)(1-Niem)}_2^+ + \text{Br}^- \]

at 35°C

\[ \beta_2 = 6,960 \text{ M}^{-2} \]
positions would be expected to have the opposite, destabilising, effect and so give smaller $\beta_2$ values than TPP. This has been found to be the case in other work, e.g., reference 102. It is interesting to note that the electronic effects of the substituents present on the naturally occurring porphyrin lead to a rate constant considerably greater than that for either synthetic porphyrin. This much greater value of $\beta_2$ is noted for both pyridine and imidazole ligated complexes, compare Figures (3.8) and (3.11) and Figures (3.12) and (3.13).

The final variable is the basic ligand which is used as titrant. The data in Table 3.2 shows that the imidazoles clearly give much larger values of $\beta_2$ than the pyridines. This reflects the greater stability of the Fe$^{III}$ (P) imidazole complexes over the Fe$^{III}$ (P) pyridine complexes. This is thought to be due to $\pi$-bonding from the imidazole to the metal, which stabilises the high charge on the ferric ion complex. Within the groups of imidazoles and pyridines, we see from Table 3.2 that 4-dimethylaminopyridine coordinates much more strongly than pyridine itself, which is to be expected, and also that imidazole has a much larger $\beta_2$ than 1-Melm (about $10^3$ times greater). This large difference is at least partly due to hydrogen bonding (Figure 3.18), which stabilises N-H imidazole ferric porphyrin complexes over N-R imidazole ferric porphyrin complexes.
The magnetic titration results apart from providing kinetic data also provide magnetic moments for the species present at the beginning and at the end of the titration. These solution state magnetic moments for all ten magnetic titrations are shown in Table 3.3.

Table 3.3 shows that the ferric porphyrin chlorides have a value of \( \mu \) very close to the spin-only value of 5.92 B.M. with the bromides and iodides somewhat higher, in the range 5.94-6.17 B.M.

The bis 1-methylimidazole complexes were found to have the following magnetic moments in solution: Fe(PPIX-DME)(1-Melm)$_2^+$, 2.23 B.M., (average value of 1 and 4); Fe(TMPP)(1-Melm)$_2^+$, 2.39 B.M., (average value of 3 and 6); Fe(TPP)(1-Melm)$_2^+$, 2.40 B.M., (average value of 2, 5 and 9). The bis pyridine adduct of Fe(TPP)I appears to have a much lower magnetic moment in chloroform solution of \( \sim 1.9 \) B.M.
<table>
<thead>
<tr>
<th></th>
<th>Species Present at the Start of the Titration</th>
<th>μ (B.M.)</th>
<th>Species Present at the End of the Titration</th>
<th>μ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(PPIX-DME)Cl</td>
<td>5.92</td>
<td>Fe(PPIX-DME)(1-Melm)_2^+</td>
<td>2.21</td>
</tr>
<tr>
<td>2</td>
<td>Fe(TPP)Cl</td>
<td>5.94</td>
<td>Fe(TPP)(1-Melm)_2^+</td>
<td>2.43</td>
</tr>
<tr>
<td>3</td>
<td>Fe(TMPP)Cl</td>
<td>6.05</td>
<td>Fe(TMPP)(1-Melm)_2^+</td>
<td>2.46</td>
</tr>
<tr>
<td>4</td>
<td>Fe(PPIX-DME)Br</td>
<td>5.95</td>
<td>Fe(PPIX-DME)(1-Melm)_2^+</td>
<td>2.25</td>
</tr>
<tr>
<td>5</td>
<td>Fe(TPP)Br</td>
<td>6.11</td>
<td>Fe(TPP)(1-Melm)_2^+</td>
<td>2.39</td>
</tr>
<tr>
<td>6</td>
<td>Fe(TMPP)Br</td>
<td>6.17</td>
<td>Fe(TMPP)(1-Melm)_2^+</td>
<td>2.32</td>
</tr>
<tr>
<td>7</td>
<td>Fe(TPP)Cl</td>
<td>5.87</td>
<td>Fe(TPP)(Me_2N-Py)_2^+</td>
<td>2.40</td>
</tr>
<tr>
<td>8</td>
<td>Fe(PPIX-DME)Cl</td>
<td>5.91</td>
<td>Fe(PPIX-DME)(Me_2N-Py)_2^+</td>
<td>2.40</td>
</tr>
<tr>
<td>9</td>
<td>Fe(TPP)Cl</td>
<td>5.91</td>
<td>Fe(TPP)(1-Melm)_2^+</td>
<td>2.37</td>
</tr>
<tr>
<td>10</td>
<td>Fe(TPP)I</td>
<td>6.02</td>
<td>Fe(TPP)(Py)_2^+</td>
<td>1.90</td>
</tr>
</tbody>
</table>
The values for the magnetic moments of complexes obtained in this work agree well with those values previously obtained.\textsuperscript{112,113,114}

C) Spin Equilibria in Ferric Porphines.

The possibility of obtaining spin equilibrium data for a ferric porphyrin system similar to that obtained with the ferric dithiocarbamates was one of the major goals of this project. In the early seventies the spin state equilibrium theory was put forward by Hill and Moralle to account for their n.m.r. observations\textsuperscript{115,116} on bis-pyridinoiron(III) protoporphyrin IX complexes. Plots of the temperature dependence of the proton chemical shifts of several complexes including Fe(PPIX)(py)\textsubscript{2}Cl\textsuperscript{−}, Fe(PPIX)(4-CH\textsubscript{3}COpy)\textsubscript{2}Cl\textsuperscript{−} and Fe(PPIX)(3-Cl py)\textsubscript{2}Cl\textsuperscript{−} in CD\textsubscript{3}OD solution were found to be non-linear in nearly all cases at temperatures above 200\textdegree{}K. Line broadening was also observed and this began at about the same temperature. The formation of a high spin species as the temperature increases above 200\textdegree{}K would account for these observations. The rate of exchange between the spin states being much greater than the frequency shift difference of the protons in the high-spin and low-spin environments leads to a single broadened resonance being observed for each set of protons. The stoichiometry of the pyridine complex can be shown to be 2:1 by the n.m.r. spectra at temperatures up to about 290\textdegree{}K, depending on the pyridine being used.

Degani and Fiat\textsuperscript{117} also used n.m.r. spectra to study a hemin (Fe(PPIX)Cl)-pyridine-water system. Their results indicate that one pyridine and one water molecule are coordinated by hemin in solution from 5 to 20\% by weight of water in solution. No evidence
for a change in the 1:1 pyridine complex ratio with temperature was noted, but anomalous temperature dependent chemical shifts and relaxation times of the hemin protons again suggested a high spin to low spin equilibrium.

To study the spin equilibrium using the magnetic moments method of Chapters 1 and 2, it was necessary to make complexes of the type Fe(PPIX-DME)X where X is not a halide but an anionic group which can be readily replaced by pyridine. This is because over the temperature range necessary to study this phenomena by magnetic measurements in solution it is found that Fe(PPIX-DME)Cl or Fe(PPIX-DME)Br do not give bis pyridine complexes (at least not 100% bis pyridine complexes) as the equilibrium constants $\beta_2$ are too small. Anions such as $\text{CF}_3\text{SO}_3^-$, $\text{BF}_4^-$, $\text{PF}_6^-$ or $\text{CF}_3\text{SO}_3^-$ will be only very weakly bonded to the metal porphyrin, if at all. So they are very easily displaced by pyridine and the bis complex is stable at fairly low concentrations of pyridine and quite high temperatures. These compounds were not needed to observe the spin equilibrium at very low temperatures by the n.m.r. contact shift method previously discussed because this method is very much more sensitive to small amounts of the high spin complex than the magnetic method.

The two compounds eventually used in this experiment were Fe(PPIX-DME)(Py)(PF$_6^-$) and Fe(PPIX-DME)(Py)(ClO$_4^-$). Other workers have also attempted to synthesise similar complexes in the last few years. Ogoshi, et al., report on the perchlorate complex, Fe(ODE)ClO$_4^-$ and its adducts with pyridine and mono(4-substituted-pyridines). They found that the magnetic moments of these complexes in the solid state were in fact intermediate between
S = 5/2 and S = 1/2 spin states. Other compounds which have been recently characterised include Fe(TPP)\textsubscript{4}C\textsubscript{2}O\textsubscript{4} and Fe(TPP)(H\textsubscript{2}O)\textsubscript{2}C\textsubscript{2}O\textsubscript{4}\textsuperscript{−}, Fe(OEP)(1m)\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, \textsuperscript{118} Fe(OEP)(EtOH)\textsubscript{2}C\textsubscript{2}O\textsubscript{4}.EtOH\textsuperscript{88,89} and Fe(TPP)EtOH\textsubscript{2}.BE\textsubscript{4}\textsuperscript{−} \textsuperscript{86}.

The results, magnetic moment as a function of temperature for the four different solutions used in this experiment are given below.

1. Fe(PPIX-DME)(Py)\textsuperscript{+}PF\textsubscript{6} : 3% Pyridine Solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>61.9</th>
<th>49.9</th>
<th>37.8</th>
<th>25.8</th>
<th>13.8</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) eff</td>
<td>2.79</td>
<td>2.62</td>
<td>2.47</td>
<td>2.31</td>
<td>2.22</td>
<td>2.12</td>
</tr>
<tr>
<td>Temp</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-36.4</td>
<td>-48.9</td>
<td>-61.4</td>
<td></td>
</tr>
<tr>
<td>(\mu) eff</td>
<td>2.01</td>
<td>1.97</td>
<td>1.93</td>
<td>1.87</td>
<td>1.87</td>
<td></td>
</tr>
</tbody>
</table>

2. Fe(PPIX-DME)(Py)\textsuperscript{+}PF\textsubscript{6} : 6% Pyridine Solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>61.9</th>
<th>49.9</th>
<th>37.8</th>
<th>25.8</th>
<th>13.8</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) eff</td>
<td>2.77</td>
<td>2.56</td>
<td>2.42</td>
<td>2.26</td>
<td>2.18</td>
<td>2.11</td>
</tr>
<tr>
<td>Temp</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-34.3</td>
<td>-48.9</td>
<td>-61.4</td>
<td></td>
</tr>
<tr>
<td>(\mu) eff</td>
<td>2.07</td>
<td>1.91</td>
<td>1.95</td>
<td>1.87</td>
<td>1.86</td>
<td></td>
</tr>
</tbody>
</table>
3. Fe(PPIX-DME)(Py)$_2$ClO$_4^-$ : 3% Pyridine Solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>61.9</th>
<th>49.9</th>
<th>37.8</th>
<th>25.8</th>
<th>13.8</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.59</td>
<td>2.60</td>
<td>2.54</td>
<td>2.36</td>
<td>2.16</td>
<td>2.09</td>
</tr>
<tr>
<td>Temp</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-36.4</td>
<td>-48.9</td>
<td>-61.4</td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>1.82</td>
<td>1.86</td>
<td>1.84</td>
<td>1.77</td>
<td>1.77</td>
<td></td>
</tr>
</tbody>
</table>

(All temperatures are °C, $\mu_{\text{eff}}$ in B.M.).

These results are represented graphically in Figure (3.19).

It can be seen that within the bounds of accuracy of the experimental data all four curves are the same.

It is this equivalence which allows us to distinguish between a temperature dependent spin state equilibrium involving the species Fe(PPIX-DME)(Py)$_2)^+$ and the other possible explanation of these results, which is that as the temperature rises, the equilibrium

$$\text{Fe(PPIX-DME)X} + 2\text{py} \rightleftharpoons \text{Fe(PPIX-DME)(Py)$_2)^+$} + X^-$$

is being driven over to the left producing more of the high spin/intermediate spin Fe(PPIX-DME)X. If this were the true explanation, however, there would be a distinct difference between the results.

4. Fe(PPIX-DME)(Py)$_2$ClO$_4^-$ : 6% Pyridine Solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>61.9</th>
<th>49.9</th>
<th>37.8</th>
<th>25.8</th>
<th>13.8</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.72</td>
<td>2.67</td>
<td>2.53</td>
<td>2.35</td>
<td>2.25</td>
<td>2.08</td>
</tr>
<tr>
<td>Temp</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-36.4</td>
<td>-48.9</td>
<td>-61.4</td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>2.01</td>
<td>1.89</td>
<td>1.89</td>
<td>1.85</td>
<td>1.76</td>
<td></td>
</tr>
</tbody>
</table>
Figure (3.19): Spin Equilibrium of \( \text{Fe}(\text{PPIX-DME})(\text{Py})_2^+ X^- \) in chloroform.
obtained in 3% pyridine solution and those obtained in 6% pyridine solution. This is because clearly the balance of the above equilibrium would alter, at any given temperature, with pyridine concentration. As this is not observed, and as there is also no change when replacing the \( \text{CIO}_4^- \) anion with \( \text{PF}_6^- \) it can be taken as proof of the spin-state transition occurring in this system.

It is unfortunate that at these temperatures ( +60°C to -60°C) the equilibrium is such that the low-spin state is very much dominant. This means that the results are not analyzable in terms of \( \Delta H \) and \( \Delta S \) by the same method as the Iron(III) dithiocarbamate results, as the range covered is just not large enough to obtain meaningful results (1.8 B.M. – 2.8 B.M.).

Figure (3.20) shows the spin equilibrium of Fe(PPIX-DME)(Py)\(^+\) from 210-340°C, using values of \( \mu_{\text{eff}} \) calculated from all four sets of data.

The magnetic moment of Fe(PPIX-DME)(Py)\(^+\) when fully low spin appears to be 1.82 B.M. which is very much lower than the low spin values of other similar complexes, (Table 3.3). This does seem to agree, however, with a similarly small magnetic moment found for the only other bis pyridine complex studied, Fe(TPP)(Py)\(^+\), \( \mu_{\text{eff}} \approx 1.90 \) B.M.

During the course of this work, a similar report was published by Hill, et al.\(^\text{119} \) This work showed the presence of a spin equilibrium in several pyridine and imidazole complexes of Fe(OEP)\( \text{CIO}_4^- \) and Fe(OEP)\( \text{PF}_6^- \). Both chloroform solution and solid state results are reproduced overleaf.
Figure (3.20): Spin Equilibrium of $\text{Fe(PPix-DNB)}(\text{Py})_2^+$ in chloroform.
Figure (3.21) Temperature Dependence of the Effective Magnetic Moments, $\mu_{\text{eff}}$, of Hemichrome Salts; a) in Chloroform, b) in Solid State.

(a) $\mu_{\text{eff}} / \text{B.m.}$

- $\times$, Fe(OEP)$(3\text{-CIPy})_2^+\text{ClO}_4^-$
- $\circ$, Fe(OEP)$(4\text{-NH}_2\text{Py})_2^+\text{ClO}_4^-$
- $\square$, Fe(OEP)$(\text{Py})_2^+\text{ClO}_4^-$
- $\blacksquare$, Fe(OEP)$(1\text{-Melm})_2^+\text{ClO}_4^-$

(b) $\mu_{\text{eff}} / \text{B.m.}$

- $\times$, Fe(OEP)$(3\text{-CIPy})_2^+\text{PF}_6^-$
- $\square$, Fe(OEP)$(\text{Py})_2^+\text{ PF}_6^-$
- $\triangle$, Fe(OEP)$(\text{Py})_2^+\text{PF}_6^-$
- $\circ$, Fe(OEP)$(4\text{-NH}_2\text{Py})_2^+\text{PF}_6^-$
- $\blacksquare$, Fe(OEP)$(1\text{-Melm})_2^+\text{PF}_6^-$. 
Interestingly, the solid state results of the compounds Fe(OEP)(Py)$_2$PF$_6$ and Fe(OEP)(Py)$_2$C/O$_4$ are strikingly different, whereas in solution they would be expected to be the same (see Chapter 2).

This work, together with the experimental results obtained for and reported in this thesis, show clearly that the Fe(P)(Py)$_2$ ion and related complexes are spin-transition compounds.

D) EXPERIMENTAL

Magnetic titrations were performed directly in the n.m.r. tube by an adaptation of the Evans' magnetic susceptibility method. Only about 3 mg of material was needed. The weighings were made on a Beckmann LM-500 microbalance and the material was transferred to the n.m.r. tube by washing through a small glass funnel with dichloromethane. The dichloromethane was then evaporated off under a stream of argon to leave an accurately known amount of dry compound in the tube.

The solvent for all of the titrations contained ethanol-free chloroform, 97% and hexamethyldisiloxane, 3%. 400 μls of solvent was added to the n.m.r. tube using a 500 μl syringe (Scientific Glass Engineering Pty. Ltd.).

* All percentages refer to volume percent (v/v).
A specially constructed sealed capillary was inserted into the tube for magnetic measurements. The capillary contained hexamethyldisiloxane, 53% and bromoform, 47%. The shift due to the paramagnetic metal complex cannot be measured directly under these circumstances as the chemical environments of capillary and solvent are different. A calibration was made of the chemical shift between capillary and solvent and the shift between capillary and solvent plus the maximum amount of titrant. It was found that the calibration shift increased linearly with increasing volume % of titrant. So the real shift due to the metal complex could be calculated from the measured shift (capillary vs solution) minus the calibration shift (capillary vs solvent). All spectra were recorded on a Perkin-Elmer R32 90 MHz spectrometer.

The titrant was added directly into the solution using a S.G.E. 5 µl syringe, either neat or in dilute solution as appropriate. The n.m.r. tube was then shaken and returned to the n.m.r. probe. An allowance for the change in concentration during the course of the titration was made. Volume changes in the solution occurred because of two reasons

i) Addition of titrant

ii) Evaporation of chloroform

µ was calculated using the simple formula

\[
\mu = 0.0618 \left( \frac{\Delta f T}{\tau M} \right)^{1/2}
\]

(see Introduction)
Spin equilibria were measured for two compounds in 3% and 6% pyridine solutions. The solvent also contained ½% of hexamethyldisiloxane and 96½% or 93½% of ethanol-free chloroform. The capillary method was again used to obtain the paramagnetic shift. The capillary contained propyl iodide (76%) and hexamethyldisiloxane (24%). This capillary is suitable for low temperature work as propyl iodide does not freeze until -98.7°C. A calibration is required of solvent against capillary at different temperatures in order to construct a calibration curve for the spin-equilibrium experiment.

The simple formula

$$\mu = 0.0618 \left( \frac{\Delta T}{T} \right)^{1/2}$$

was used to calculate \( \mu \) at each temperature. The molarity, M, must be corrected to take account of the change in concentration with temperature, any of the three methods described in the Introduction can be used.

The solvent for all magnetic titration and spin-equilibria studies in this section was chloroform. Before use, chloroform (Analar, Hopkin and Williams) was passed through a column packed with dry basic alumina (Hopkin and Williams) to remove the ethanol stabiliser.

Pyridine (Analar, B.D.H. Ltd.), 1-methylimidazole (Aldrich Ltd.) and dimethylaminopyridine (Aldrich Ltd.) were used as received, with no further purification.
The variable temperature probe was calibrated with methanol by the method of Van Geet.

**M A T E R I A L S**

**Tetraphenylporphyrin:** Was prepared by the method of Adler, et al.

The preparation involved a condensation reaction between freshly distilled pyrrole and benzaldehyde in a propionic acid medium. The purity of the product was checked by visible absorption spectroscopy (Appendix 5). TPP$_2$ is obtained as vivid purple crystals which were dried in vacuo at room temperature to remove any adsorbed acid.

**μ-oxo-bis[Iron(III)tetraphenylporphyrin]:** The μ-oxo dimer was prepared by gently refluxing TPP$_2$ (1 g) with FeCl$_2$ (0.51 g) in dimethylformamide (100 ml). The course of the reaction was followed by visible absorption spectroscopy. The complete disappearance of the characteristic four banded TPP$_2$ spectrum signifies that the reaction has gone to completion (See Appendix 5). The porphyrinic material was obtained by precipitation from the reaction mixture with water. After filtration and drying, the solid was dissolved in chloroform (150 ml) and a KOH solution (25% ; 115 ml) added and the two phase system stirred vigorously for about 1 hr. As the μ-oxo dimer is to be used as the basis for the preparation of all Fe$^{III}$-TPP complexes it was rigorously purified by dry column chromatography of the chloroform layer, followed by recrystallisation using a xylene-chloroform mixture or cyclohexane-chloroform. After drying for up to 15 hours in vacuo at 100°C, the material was characterised by its visible absorption spectrum (Appendix 5) and elemental analysis.
(Fe.TPP)\textsubscript{2}.0, calc. for C\textsubscript{88}H\textsubscript{56}N\textsubscript{8}O\textsubscript{2}Fe\textsubscript{2}: C, 78.11\%; H, 4.17\%; N, 8.28\%. Found: C, 77.79\%; H, 4.22\%; N, 8.17\%. Yield $\sim$ 0.74 g ($\sim$ 67\%).

**Iron(III) tetraphenylporphyrin chloride: (Fe.TPP)\textsubscript{2}.0**

(100 mg) was dissolved in methylene chloride (100 ml) and a steady stream of HCl was passed through the solution for about 30 seconds.\textsuperscript{122} The solvent was then removed on a rotary-evaporator and the chloro complex dried in vacuo. The complex was characterised by its visible absorption spectrum (Appendix 5) and by elemental analysis. Fe(TPP)Cl, calc. for C\textsubscript{44}H\textsubscript{28}N\textsubscript{4}FeCl: C, 75.07\%; H, 4.01\%; N, 7.96\%. Found: C, 75.00\%; H, 3.97\%; N, 7.89\%. Yield $\sim$ 100\%.

**Iron(III) tetraphenylporphyrin bromide: Was prepared by an adaptation of the method of Fischer\textsuperscript{123} for the purification of hemin.** Fe(TPP)Cl (200 mg) was dissolved in chloroform (10 ml) and the solution added slowly to a gently boiling mixture of glacial acetic acid (70 ml), saturated aqueous sodium bromide (1 ml) and concentrated hydrobromic acid (2 ml). After cooling the reaction mixture overnight, the porphyrinic material was filtered and washed with water, then isopentane and then dried in vacuo at 70°C for several hours. Fe(TPP)Br, calc. for C\textsubscript{44}H\textsubscript{28}N\textsubscript{4}FeBr: C, 70.61\%; H, 3.77\%; N, 7.49\%. Found: C, 70.95\%; H, 3.80\%; N, 7.48\%.
Iron(III) tetraphenylporphyrin Iodide: A solution of (Fe.TPP)$_2$.0 (125 mgs) in chloroform (50 ml) was treated with a one hundred fold excess of KI/H$_2$SO$_4$ (aq.) (3.1 g. KI in 25 ml dil. H$_2$SO$_4$). The aqueous layer was removed and the chloroform solution filtered and concentrated. Fe(TPP)I was precipitated by the addition of pentane.

The compound was then recrystallised from a warm CHCl$_3$/n-pentane mixture, filtered and washed with pentane and then dried in vacuo. Elemental analysis; Fe(TPP)I, calc. for C$_{44}$H$_{28}$N$_4$FeI: C, 66.44% ; H, 3.55% ; N, 7.04%. Found: C, 65.91% ; H, 3.56% ; N, 6.94%.

Tetra(p-methoxyphenyl)porphyrin: Was prepared by a method analogous to TPPH$_2$ using p-methoxy benzaldehyde as the starting material. TMPPH$_2$, calc. for C$_{48}$H$_{38}$N$_4$O$_4$: C, 78.45% ; H, 5.21% ; N, 7.62%. Found: C, 78.67% ; H, 5.28% ; N, 7.64%.

$\mu$-oxo-bis[Iron(III)(p-methoxyphenyl)porphyrin], Iron(III)-(p-methoxyphenyl)porphyrin chloride and Iron(III)(p-methoxyphenyl)porphyrin bromide:

All three compounds were prepared by procedures analogous to those employed in the preparation of the TPP complexes. The two halide complexes were characterised by elemental analysis. Fe(TMPP)Cl, calc. for C$_{48}$H$_{36}$N$_4$O$_4$FeCl: C, 69.96% ; H, 4.40% ; N, 6.80%. Found: C, 70.24% ; H, 4.63% ; N, 6.74%. Fe(TMPP)Br, calc. for C$_{48}$H$_{36}$N$_4$O$_4$FeBr: C, 66.37% ; H, 4.18% ; N, 6.45%. Found: C, 66.67% ; H, 4.12% ; N, 6.47%.
Iron(III) protoporphyrin IX chloride: Was supplied by B.D.H. Chemicals Ltd. and by Aldrich Chemical Co. Ltd. Elemental analysis (Aldrich Hemin), calc. for $C_{34}H_{32}O_{4}N_{4}FeCl$: C, 62.64%; H, 4.95%; N, 8.59%. Found: C, 62.05%; H, 4.94%; N, 8.29%.

Iron(III) protoporphyrin IX-dimethylester chloride: The diacid Fe(PPIX)Cl is unsuitable for solution state magnetic studied in organic solvents because of poor solubility. To overcome this problem the dimethylester was prepared. Esterification was achieved by the method of Kuster and Schlayer. A chloroform/pyridine solution of the hemin was refluxed gently for 2-3 minutes in methanol containing concentrated hydrochloric acid. The diester was filtered off after overnight cooling in an ice box and then recrystallised from chloroform and petroleum ether. The characteristic visible absorption spectrum of the diester was given in Appendix 5. Analysis, Fe(PPIX-DME)Cl, calc. for $C_{36}H_{36}N_{4}O_{4}FeCl$: C, 63.59%; H, 5.34%; N, 8.24%. Found: C, 63.30%; H, 5.26%; N, 8.21%.

Iron(III) protoporphyrin IX-dimethylester bromide: Was prepared by the same metathesis reaction as Fe(TPP)Br using Fe(PPIX-DME)Cl as the starting material. Analysis, Fe(PPIX-DME)Br, calc. for $C_{36}H_{36}N_{4}O_{4}FeBr$: C, 59.69%; H, 5.01%; N, 7.73%. Found: C, 58.89%; H, 4.87%; N, 7.62%.

μ-oxo-bis[Iron(III) protoporphyrin IX-dimethylester]: Was prepared by treating a chloroform solution of the chloride complex with aqueous KOH solution. Visible absorption spectra can be used to confirm the conversion of the chloride into the μ-oxo-dimer (See Appendix 5).
(Pyridine) Iron(III) protoporphyrin IX-dimethylester hexafluorophosphate:

This compound was prepared by a method analogous to the preparation of FeOEP(Py)$_2$PF$_6$. Elemental analysis of the product clearly indicates that the monopyridine complex is formed.

Hot concentrated aqueous ammonium hexafluorophosphate (10 mls) was added to a hot solution of Fe(PPIX-DME)Br (55 mgs) in a solvent containing a 1:10:8 ratio of pyridine, dichloromethane and methanol (9.5 mls). The solid formed was extracted into dichloromethane, filtered through phase separating paper to remove all traces of water and the dichloromethane was then removed to leave Fe(PPIX-DME)(Py)(PF$_6$).

Analysis, Fe(PPIX-DME)(Py)(PF$_6$), calc. for C$_{41}$H$_{41}$N$_5$O$_4$FePF$_6$:

C, 56.69%; H, 4.76%; N, 8.06%. Found: C, 56.08%; H, 4.87%; N, 7.98%.

Iron(III) protoporphyrin IX-dimethylester perchlorate-methanolate.

This preparation is based on a published procedure for the preparation of metal porphine perchlorates by refluxing the appropriate metal porphine chloride with AgClO$_4$ in benzene or THF. It was found that the use of TlClO$_4$ instead of AgClO$_4$ is a useful improvement to the method. TlClO$_4$ is not hygroscopic, thallium is less likely to attack the double bonds present in the porphyrin periphery (vinyl substituents are found on pyrrole carbons 3 and 8 in protoporphyrin IX) than silver, and thallium compounds are also
less photosensitive. TlClO₄ can be readily prepared from Tl₂CO₃ and aqueous HClO₄. The solution was heated to boiling, until all the carbon dioxide had evolved and (after filtration if necessary) the solution was allowed to cool in an ice-bath to precipitate TlClO₄ which was recrystallised from water.

The metal porphine perchlorate was then prepared by refluxing for 2 hrs, a methanol solution (~ 10 mls) of Fe(PPIX-DME)Br (107 mgs) and TlClO₄ (50 mg, 10% excess, dried in vacuum at 100°C for 30 minutes). The hot solution was filtered to remove the precipitated TlBr. After cooling, the solution was evaporated to dryness and the residue redissolved in dichloromethane, any insoluble material was removed by centrifuging. The dichloromethane solution was then concentrated and the porphyrinic material precipitated by the addition of cyclohexane. Yield 78 mg or 65% theoretical.

(Pyridine) Iron(III) protoporphyrin IX-dimethylester perchlorate: Fe(PPIX-DME)(CH₃OH)ClO₄, was dissolved in a small amount of pyridine, which was then slowly evaporated under a steady stream of argon. The resulting crystals were thoroughly dried in vacuum and characterised by elemental analysis. Fe(PPIX-DME)(Py)(ClO₄), calc. for C₄₁H₄₁N₅O₈FeCl : C, 59.83% ; H, 5.02% ; N, 8.51%. Found: C, 59.86% ; H, 5.06% ; N, 9.10%.

Iron(III) protoporphyrin IX-dimethylester trifluoromethane-sulphonate-methanolate.

Thallium trifluoromethanesulphonate was prepared by the reaction of Tl₂CO₃ and aqueous CF₃SO₃H. Fe(PPIX-DME)Br (200 mgs) and
TfCF$_3$SO$_3$ (100 mgs) were then refluxed in methanol (~18 ml) and the procedure described for the preparation of Fe(PPIX-DME)CF$_3$O$_4$. Methanolate was followed to give a compound which analysed as the bis-methanolate of Fe(PPIX-DME)CF$_3$SO$_3$.

Fe(PPIX-DME)(MeOH)$_2$CF$_3$SO$_3$, calc. for C$_{39}$H$_{44}$N$_4$O$_9$FeSF$_3$:
C, 54.61% ; H, 5.17% ; N, 6.53%. Found: C, 53.69% ; H, 4.34% ; N, 6.63%.

The low carbon analysis is not unusual for these compounds because of partial decomposition to fluoride complexes. The all analyses were performed by Imperial College Microanalytical Laboratories.
CONCLUSIONS

The work presented in this thesis shows the usefulness and great adaptability of the n.m.r. method for measuring magnetic susceptibility of paramagnetic compounds in dilute solution.

The spin equilibria studies of Chapters One and Two are proof that an equilibrium of this type is most successfully studied in the solution state, and many of the anomalous and irregular results of solid state work are clarified by going into solution.

The Iron(III)dithiocarbamates and the Iron(II) complexes with 2-(2'-pyridyl)benzimidazole are both relatively straightforward systems and the possibility for expanding this type of work in these areas is not great.

On the other hand, the vast scope of the metal porphine field provides ample opportunities for advancement and diversification of work using the basic tool of the n.m.r. method. For example it is possible to extend the magnetic titration method into several different areas. Firstly, to cover ferrous porphyrins; it is quite easy to reduce a ferric porphyrin in situ using a few drops of aqueous sodium dithionite solution. After addition of the reducing agent to the n.m.r. tube and shaking for a few minutes, the tube is centrifuged in order to bring the dithionite solution to the top of the chloroform solution - now containing a ferrous porphyrin. The aqueous layer at the top of the chloroform
protects against air leaking into the tube and causing oxidation, and is also away from the magnet of the n.m.r. and does not affect the signal homogeneity. Preliminary experiments have already been made using this technique.

Magnetic titrations could also be made directly with gases, e.g., O₂, and also using the intermediate spin complexes such as Fe(TPP)CO₄⁻ to provide more interesting results.

Follow up work with the metal porphine spin equilibrium compounds is another field for future work. Substituted pyridines could be used to give examples of a spin equilibrium with a wider range than the one studied so far. Alternatively, another solvent could be used so that the temperature of the Fe(PPIX-DME)(Py)²⁺ ion can be raised to well above 60°C. With a wider range of data, the computer program established for use with the Iron(III)dithiocarbamates could be used to calculate the thermodynamic parameters of the spin equilibrium for a metal porphyrin for the first time.
APPENDIX 1

Computer program Four for tabulating Temp (°C), \( \chi, \chi_M', \chi_M^{(e x p t)} \) and \( \mu_{(c a l c)} \) and evaluating the parameters \( \Delta H \) and \( \Delta S \) and \( \mu_{l o w ~ s p i n} \) for a \( ^2T_2 \rightleftharpoons ^6A_1 \) spin state equilibrium process. The program calculates the thermodynamic parameters by varying \( \mu_{l o w ~ s p i n} \) and obtaining the best fit by least mean squares for the experimental results to the straight line

\[
\frac{1}{T} = \ln \left( \frac{\mu^2 - \mu^2_{l o w ~ s p i n}}{35 - \mu^2} \right)
\]

This assumes a value of 35 for \( \mu^2_{h i g h ~ s p i n} \). The calculations of magnetic susceptibility and magnetic moments are made using the exact expression, the user is required to enter the following information:

1) Number of temperatures studied (JN);
2) The measured shift in Hertz at each temperature (DELFAT);
3) The temperature in °C (ATEMP);
4) The concentration at each temperature (CONC);
5) The density factor \( (d_o - d_s) \) at each temperature (DY).

The following constants must also be entered depending on the compound studied and the solvent used.

1) \( \chi_0(s o l v e n t) \) (SOLV);
2) Diamagnetic ligand correction (DIACOR); molecular weight of complex (WEIGHT).
The program will vary the value of $\mu_{\text{low spin}}$ from $\sqrt{3}$ to $\sqrt{7}$ in 400 steps. If it is thought likely the $\mu_{\text{low spin}}$ will fall outside this range, then the limits can easily be altered by replacing the appropriate fortran statement.

All programs were run at the Imperial College Computer Centre on either a CDC 6400 or a CYBER 174 machine.
**PROGRAM FOUR (INPUT, OUTPUT, TAPE 5 = INPUT, TAPE 6 = OUTPUT)**

***** T. A. JAMES *****

*****PROGRAM TO CALCULATE THERMODYNAMIC PARAMETERS FOR A SPIN EQUILIBRIUM COMPLEX IN SOLUTION *****

DIMENSION DELTAF(2),ATEMP(2),TINV(2),TTEMP(2),CONC(2),DY(20),
XG(20),XI(20),XA(20),AMU(20),X(20),SLOPE(500),CEPT(500),CORR(500),
JN = 12
Z = 0.0
MHW = 0.0
TOTTIN = 0.5
KOUNT = 0

READ IN VALUES OF TEMPERATURE, CONCENTRATION, SHIFT IN HERTZ AND DENSITY CORRECTION

READ(5,1001) (DELTAF(K), K = 1,JN )
1001 FORMAT (F6.3)
READ(5,1002) (ATEMP(K), K = 1,JN)
1002 FORMAT (F6.1)
READ(5,1003) (CONC(K), K = 1,JN)
1003 FORMAT (F3.6)
READ(5, 1004) (DY(K) , K = 1,JN)
1004 FORMAT (F8.5)

WEIGHT = 686.8345
DIACOR = 0.00038997
PI = 3.14159265

CALCULATES MAGNETIC SUSCEPTIBILITY AND MAGNETIC MOMENTS FOR EACH TEMPERATURE

DO 21: K = 1,JN
TTEMP(K) = ATEMP(K) + 273.16
XG(K) = (3.0 * DELTAF(K))/(2.0 * PI * 6000000.0 * CONC(K)) + SOLV +
SOLV * AMU(K) / CONC(K)
XM(K) = XG(K) * WEIGHT
XA(K) = XG(K) + DIACOR
AMU(K) = SQR((XG(K) * TTEMP(K)) * 2.878
21 CONTINUE

CALCULATES THERMODYNAMIC PARAMETERS BY VARYING μLOW SPIN AND OBTAINING BEST FIT BY LEAST MEAN SQUARES

DO 3001 K = 1,JN
TINV(K) = 1.0 / TTEMP(K)
TOTTIN = TOTTIN + TINV(K)
Z = TINV(K) * TINV(K) + Z
3001 CONTINUE

D = FLOAT(JN) * Z - TOTTIN * TOTTIN
DO 3002 I = 1,301
PCORF = 0.0
SUMX = 0.0
ALPS = 0.0
SOLW = 2.99 + FLOAT(I) * 0.01
IF(SOLW.LT.AMU(JN) * AMU(JN)) GO TO 9191
CORR(I) = 0.39999999
IF(CORR(I) .GT 0.9) GO TO 3002

9191 KOUNT = KOUNT + 1
DO 3003 K = 1,JN
X(K) = AMU(K) * AMU(K) - SOLW / (35.0 - AMU(K) * AMU(K))
SUMX = SUMX + X(K)
ALPS = X(K) * TINV(K) + ALPS
3003 CONTINUE

SLOPE(I) = (FLOAT(JN) * ALPS - TOTTIN * SUMX) / D
CEPT(I) = (SUMX / FLOAT(JN)) - (SLOPE(I) * TOTTIN / FLOAT(JN))
DO 3004 I = 1,JN
XYZ = SLOPE(I) * TINV(K) + CEPT(I) - X(K)
PCORF = PCORF + XYZ * XYZ
3004 CONTINUE

CORR(I) = PCORF
3002 CONTINUE

DO 752 I = 1,301
W = CORR(I)
IF(W .GT 0.0, 0) GO TO 1234
IF (W.GT.WIW) GO TO 7500

WH = W
WHW = 8.31434 * SLOPE(I)
WSW = 8.31434 * CEPT(I)

ROOT = SQRT(2.99 + FLOAT(I) * 0.01)
M = I

7500 CONTINUE

DO 6666 I = 1,301
IF (COR2(I).GT.0.9 ) GO TO 6666
SLOPE(I) = -8.31434 * SLOPE(I)
CEPT(I) = CEPT(I) * 8.31434

6666 CONTINUE

ATEMP0 = ATEMPO(I) + 20.0
T.MPO = ATEMP0 + 273.16
CBA = 1.0 + EXP(WSW / 8.31434 - WHW / (8.31434 * TEMPO))
UCALCO = SQRT(35.0 - ((35.0 - (2.99 + FLOAT(M) * 0.01)) / CBA))
ATEMP1 = ATEMPO(I) + 40.0
T.MP1 = ATEMP1 + 273.16
CBA = 1.0 + EXP(WSH / 8.31434 - WHW / (8.31434 * TEMPO1))
UCALC1 = SQRT(35.0 - ((35.0 - (2.99 + FLOAT(M) * 0.01)) / CBA))
ATEMP2 = ATEMPO(JN) - 20.0
T.MP2 = ATEMP2 + 273.16
CBA = 1.0 + EXP(WSH / 8.31434 - WHW / (8.31434 * TEMPO2))
UCALC2 = SQRT(35.0 - ((35.0 - (2.99 + FLOAT(M) * 0.01)) / CBA))
ATEMP3 = ATEMPO(JN) - 40.0
T.MP3 = ATEMP3 + 273.16

WD 5963 K = 1,301
ASC(K) = 1.0 + EXP(WSH / 8.31434 - WHW / (8.31434 * TEMPO(K)))
UCALC(K) = SQRT(35.0 - ((35.0 - (2.99 + FLOAT(M) * 0.01)) / ASC(K))

DO 6969 K = 1,301
XG(K) = XG(K) * 100900.0
XM(K) = XM(K) + 1.0
XS(K) = XS(K) * 1000.0
WRITE (6,3500) ATEMP1,UCALC1,ATEMP0,UCALCO


WRITE (6,3600) ATEMP2,UCALC2,ATEMP3,UCALC3


WRITE (6,2)01) WHW WHW

20:1 FORMAT (///4X,21H ENTHALPY CHANGE = F6.1,11H J PER MOLE //
21HX,TROPY CHANGE S = F5.2,18H J PLR MOLc PER K )

WRITE (6,2121) ROOT ,WIW

2121 FORMAT (///4X,53HOPTM ( VALUE FOR MAGNETIC MOMENT OF LOW SPIN FC
XRM = F5.3//40X,13HCORR.ATION = F12.8 )

STOP

END
APPENDIX 2

Computer program Three for tabulating TEMP (°K), $T\delta_{(EXPT)}$ and $T\delta_{(CALC)}$ and evaluating the parameters $\Delta H$, $\Delta S$, $C_{L.S.}$ and $C_{H.S.}$ for a $^2T_2 \rightleftharpoons ^6A_1$ spin equilibrium process. The program calculates the thermodynamic parameters by varying $C_{L.S.}$ and $C_{H.S.}$ in a grid system and obtaining the best fit by least mean squares for the experimental results to the straight line

$$\frac{1}{T} = \ln \left( \frac{C_{L.S.} - T\delta}{T\delta - C_{H.S.}} \right)$$

The experimental quantity, $\delta$, the paramagnetic shift is obtained as described in Chapter 1. The user is required to enter the following information:

1) Number of temperatures studied (JN);
2) The measured paramagnetic shift in ppm at each temperature (DELTAf);
3) The temperature in °K (TEMP);
4) Details of the grid to be studied in the form of ICH, middle value for $C_{H.S.}$; ICL middle value for $C_{L.S.}$; IVCH and IVCL, distances between successive points on the grid.

A large grid can be employed on the first run to cover all possible values of $C_{H.S.}$ and $C_{L.S.}$ The best fit values of $C_{H.S.}$ and $C_{L.S.}$ can then be used as new "middle values" for a second run with a much small grid step-size to produce results of the
required accuracy. The grid is $15 \times 15$ in the program as printed, but this can easily be altered by amending the appropriate statements.

All programs were run at the Imperial College Computer Centre on either a CDC 6400 or a CYBER 174 machine.
PROGRAM THREE (INPUT, OUTPUT, TAPE 5 = INPUT, TAPE 6 = OUTPUT)

*** T.A. JAMES CHEMISTRY DEPT. ***

***** PROGRAM TO CALCULATE THE CHEMICAL SHIFTS OF HIGH AND LOW SPIN SPECIES IN EQUILIBRIUM IN SOLUTION *****

DIMENSION Y (LTA(2)), TEMP(20), CT(20), TINV(20), X (20), XM (20), 20),
JN = 12

READ IN VALUES OF TEMPERATURE AND EXP. CHEMICAL SHIFT ALSO THE INITIAL ESTIMATES OF C HIGH SPIN AND C LOW SPIN

READ (5, 1003) ICH, ICL, IVCH, IVCL

READ (5,1001) (DELTA (K), K = 1, JN)

READ (5,1002) (TEMP(K), K = 1, JN)

6478 Z = 0.0

TOTTIN = 0.0

K = 1

1500 DT(K) = T(LTA(K) * TEMP(K)

TINV(K) = 1.0 / TEMP(K)

TOTTIN = TOTTIN + TINV(K)

Z = TINV(K) * TINV(K) + Z

K = K + 1

IF (K.LE.JN) GO TO 1500

DO 25 I = 1, JN

25 XH (I, J) = (FLCAT (J) * ALPS - TOTTIN * SUMX) / D

X3 (I, J) = (SUMX / FLOAT(JN)) - (XM (I, J) * TOTTIN / FLOAT(JN))

K = 1

5500 XYZ = X9 (I, J) * TTNV(K) + XB(I, J) - X (K)

PCORR = PCORR + XYZ * XYZ

K = K + 1

IF (K.LE.JN) GO TO 5500

COR'' (I, J) = FCORR

CONTINUE

CONTINUE

DO 6663 I = 1, JN

DO 7777 J = 1, JN

X9 (I, J) = -3.31434 * X'I (I, J)

X3 (I, J) = 8.31434 ¥ Xf3(I, J)

7777 CONTINUE

666E CONTINUE

CALCULATE OPTIMUM VALUES OF C HIGH SPIN AND C LOW SPIN BY L.M.S.

ALSO CALCULATES THE ENTHALPY AND ENTROPY CHANGES FOR THE SPIN EQUILIBRIUM

DO 2577 I = 1,15

DO 3500 J = 1,15

ICHCOR = ICH + (A - I) * IVCH

ICLCOR = ICL + (A - J) * IVCL

PCORR = 0.0

SUMX = 0.0

ALPS = 0.0

K = 1

4500 X(K) = ALOG (FLOAT (ICLCOR) - DT(K)) / ( DT(K) - FLOAT(TICHCOR))

SUMX = SUMX + X(K)

ALPS = X(K) * TINV(K) + ALPS

K = K + 1

IF (K.LE.JN) GO TO 4500

XH (I, J) = (FLCAT(J) * ALPS - TOTTIN * SUMX) / D

X3 (I, J) = (SUMX / FLOAT(JN)) - (XM (I, J) * TOTTIN / FLOAT(JN))

K = 1

5500 XYZ = X9 (I, J) * TTNV(K) + XB(I, J) - X (K)

PCORR = PCORR + XYZ * XYZ

K = K + 1

IF (K.LE.JN) GO TO 5500

COR'' (I, J) = FCORR

CONTINUE

CONTINUE

DO 6663 I = 1, JN

DO 7777 J = 1, JN

X9 (I, J) = -3.31434 * X'I (I, J)

X3 (I, J) = 8.31434 ¥ Xf3(I, J)

7777 CONTINUE

666E CONTINUE

C

C 

C ****

C

***** POINT CUT THE ENTHALPY AND ENTROPY CHANGES FOR THE HIGH

C SPIN TO LOW SPIN EQUILIBRIUM AT THE POINT OF MAXIMUM

C CORRELATION. ALSO AT SELECTED OTHER POINTS AROUND THIS

C MAXIMUM VALUE. ****
NC = 0
IF (N, LT., 1, OR. N, GT., 15) GO TO 0877
WRITE (6, 7700) M

7700 FORMAT (//40X, *I = *,I2,* THIS IS A POINT AT THE EDGE OF THE GRID

0877 NC = NC + 1
IF (N, LT., 1, OR. N, GT., 15) GO TO 0880
WRITE (6, 8008) N

8008 FORMAT (//40X, *J = *,I2,* THIS IS A POINT AT THE EDGE OF THE GRID

0880 NC = NC + 1
IF (IVCH, LT., 40) GO TO 09123
IVCH = IVCH/5
IVCL = IVCL/5
ICH = ICHCOR
ICL = ICLCOR
GO TO 6478

09123 NC = NC + 1
WRITE (6, 0301) WHW, WSW

9001 FORMAT (//40X, 24H ENTHALPY CHANGE H = ,F6.1,13H J PER MOLE //
940X, 24H ENTROPY CHANGE S = ,F5.2,18H J PER MOLE PER K )

WRITE (6, 9002) ICHCOR, ICLCOR, WHW

9002 FORMAT (//40X, 35H CHEMICAL SHIFT OF HIGH SPIN FORM = ,I5 //
940X, 35H CHEMICAL SHIFT OF LOW SPIN FORM = ,I4 //) CORRELATION
N = I F 1.2, S

9876 FORMAT (//40X, 24H CORRELATION 8,8 = ,F12.8//40X, 6H H = ,F6.1 //
940X, 6H S = ,F5.2)

M = M + 2
N = N - 2
IF (M, LT., 1, OR. M, GT., 15) GO TO 2222
WRITE (6, 1232) COR1, XM(M,N), XB(M,N)

2222 N = N + 4
IF (N, LT., 1, OR. N, GT., 15) GO TO 3333
WRITE (6, 3672) COR1, XM(M,N), XB(M,N)

3333 M = M + 4
IF (M, LT., 1, OR. M, GT., 15) GO TO 4444
WRITE (6, 8670) COR1, XM(M,N), XB(M,N)

9870 FORMAT (//40X, 24H CORRELATION 1-2, J-2 = ,F12.8//40X, 6H H = ,F6
9.1//40X, 6H S = ,F5.2)

4444 N = N - 4
IF (N, LT., 1, OR. N, GT., 15) GO TO 5555
WRITE (6, 9339) COR1, XM(M,N), XB(M,N)

9868 FORMAT (//40X, 24H CORRELATION 1-2, J-2 = ,F12.8//40X, 6H H = ,F6
9.1//40X, 6H S = ,F5.2//)

5555 N = 0
DO 3993 K = 1, J11
ABC(K) = 1.0 + EXP(MCW / (8.31434 - TEMP(K))
ABC(K) = / . / ABC(K)
END

3993 CONTINUE
STOP
Computer program Five for tabulating the molar ratio, $\mu_{(EXPT)}$ and $\mu_{(CALC)}$, and evaluating the equilibrium constant for an equilibrium of the type $A + 2L \rightleftharpoons AL_2$. The tabulated results refering to specific points along the magnetic titration curve.

The method by which $\beta_2$ is calculated by the program is explained in Appendix 4. The user is required to enter the following information:

1) The number of titration points to be entered (JN);
2) The original concentration of the solution in moles/litre (CONC);
3) The original volume of solution in the n.m.r. tube in $\mu$l (VOL);
4) The operating temperature in $^\circ$K (TEMP);
5) The molecular weight of the titrant;
6) The values $\mu_{H.S.}^2$ and $\mu_{L.S.}^2$, the magnetic moments of the species $A$ and $AL_2$, respectively;
7) The new volume of solution after each addition of titrant (VOLUME (K)) in $\mu$l;
8) The total volume of titrant present in the n.m.r. tube after each addition (VOLBAS (K)) in $\mu$l and finally;
9) The chemical shift $\Delta f$ in Hertz (DELTAF (K)).
As the value of $\beta_2$ is to be varied it must also be decided at which value $\beta_2$ will begin ($\text{BETA} =$ ); what the step size will be ($\text{STEP} =$ ) and how many steps there will be ($\text{NUMBER} =$ ). Typical values for an equilibrium constant in the region 100-1,100 are given on the program overleaf.

All programs were run at the Imperial College Computer Centre on either a CDC 6400 or a CYBER 174 machine.
PROGRAM FIVE (INPUT, OUTPUT, TAPE 5 = INPUT, TAPE 6 = OUTPUT)

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DIMENSION A(50), E(50), X(50), VOLUME(50), VOLAS(50), DELTA(50), RATIO(50), U(50), UCAL(50), OIF(50), EST(50)

*** READS IN THE EXPERIMENTAL VALUES OBTAINED DURING THE TITRATION. VOLUME(K) = TOTAL VOLUME OF SOLUTION AND VOLAS(K) = TOTAL VOLUME OF ADDED BASE (LIGAND) AT ANY POINT OF THE TITRATION. DELTA(K) IS THE MEASURED SHIFT IN HERTZ. STARTING CONDITIONS ARE ALSO ENTERED. N = CONCENTRATION OF ORIGINAL SOLUTION Temp TEMPERATURE, OPERATING FREQUENCY ORIGINAL VOLUME, AND THE DENSITY AND MOLECULAR WEIGHT OF THE LIGAND. JN IS THE NUMBER OF EXPERIMENTAL POINTS. THE VALUES OF J HIGH SPIN AND U LOW SPIN (SQUARED) ARE ALSO NEEDED.

JN = 11
CONC = 0.009899
VOL = 400.0
F = 90.0
WEIGHT = 122.17
SPHISO = 39.06
SPLOISO = 5.76

READ (5, 2000) (VOLUME(K), K = 1, JN)

2000 FORMAT (F7.3)
READ (5, 3000) (VOLAS(K), K = 1, JN)

3000 FORMAT (F5.2)
READ (5, 4000) (DELTAF(K), K = 1, JN)

4000 FORMAT (F6.3)

*** CALCULATES EXPERIMENTAL MAGNETIC MOMENTS USING SIMPLE FORMULA AT EACH TITRATION POINT.

DO 4444 K = 1, JN
A(K) = CONC * VOL / VOLUME(K)
B(K) = (VOLAS(K) * F / VOLUME(K)) / WEIGHT
RATIO(K) = B(K) / (1.0 + B(K))
U(K) = SQRT(DR(K) / TEMP * A(K) + U.CAL) * 0.0618

4444 CONTINUE

*** MAIN SECTION OF PROGRAM SOLVES CUBIC EQUATION TO GIVE X FROM A, B, AND RATIO. ALSO VARIATES ETA TO FIND THE OPTIMUM VALUE OF THIS CONSTANT FOR THE BEST FIT OF EXPERIMENTAL RESULTS.

HOLD = 1.0
STEP = 0.1
NUMBER = 50
ETA = 1.0

1234 SUM = 0.0
DO 9999 K = 1, JN
IF (B(K) .LE. 1.0) GO TO 1515
P = -(A(K) + B(K))
Q = (A(K) * B(K) * ETA + + 0.0 * B(K) * ETA + 1.0 ) / (4.0 + BETA)
R = (A(K) * B(K) * ETA + 2.0) / (4.0)
ZM = (3.0 - P**2 / 4.0) / 3.0
ZN = (2.0 - * ETA + 9.0 * ETA + 27.0 * R) / 27.0
S = (ZM * ZN / 4.0) + (ZM**3 / 27.0)
IF (S .GE. 0.0) GO TO 7433
SA = SQRT((-ZM**3 / 27.0))
SB = (-ZM / 2.0) / SA
SC = ARCOS (SA) / 3.0
SD = SQRT((-ZM / 3.1) * 2.0)
P = 4.0
PC = COS(SC) + 2.094395102 / 3.0
PA = COS(SC) + 0.094395102 * SD - P / 3.0
PB = COS(SC) + 0.123456789 / 2.0

4444 CONTINUE

X(K) = PA
GO TO 6892

6892 IF (PA .GT. 0.00) 6892, 140, 153
PA = PHPA
PB = PB
PC = PC
PL = PL
X(K) = PA
GO TO 6892

140 IF (PA .GT. 0.00) 140, 153
PA = PA + 0.0001
PB = PB + 0.0001
PC = PC + 0.0001
PL = PL + 0.0001

153 IF (PA .LE. 0.00) 153, 140
PA = PA - 0.0001
PB = PB - 0.0001
PC = PC - 0.0001
PL = PL - 0.0001

X(K) = PA
GO TO 6892

6891 R = B(K) / 2.0

7439 XYZ = SORT (ZN * ZN / 4.0 + ZM**3 / 27.0)
AA1 = ( -ZN / 2.0 ) + XYZ
IF(AA1.GT.0.0) GO TO 0027
AA2 = -AA1
AA3 = ALOG(AA2)
AA4 = EXP(AA3/3.0)
AA = -AA4
GO TO 0037

0027
AA2 = ALOG(AA1)
AA = EXP(AA2 / 3.1)
GO TO 0037

0037
BE1 = ( -ZN/2.0 ) - XYZ
IF(BE1.GT.0.0) GO TO 0048
BE2 = -BE1
BE3 = ALOG(BE2)
BE4 = EXP(BE3 / 3.0)
BE = -BE4
GO TO 0053

0048
BE2 = ALOG(BE1)
BE = EXP(BE2 / 3.0)
GO TO 0058

0058
X(K) = (AA + EB) - P / 3.0
GO TO 1199

1515
X(K) = bb

1199
UCALC(K) = SQRT(((A(K) - X(K)) / A(K)) * SPHISQ + X(K) / A(K) + SPLOG SQ)
DIF(K) = (UCALC(K) ** 2 - U(K) ** 2) ** 2
SUM = SUM + DIF(K)
CONTINUE
IF(SUM.LT.HOLD) GO TO 212
ATE5 = BETA
HOLD = SUM
DO 5659 K = 1, JN
BEST(K) = UCALC(K)
5659 CONTINUE
CONTINUE
IF(NUMBER .EQ. 0) GO TO 9676
BETA = BETA + STEP
GO TO 1234

9876
WRITE (A, 2222) ATE5, HOLD
2222
FORMAT (///50X, 25HEQUILIBRIUM CONSTANT 3 = ,F8.1 ///50X, 14HCORRELATION = ,F8.4 ///50X, 11HOLAR FATI0, 5X, 7HUCALC), D0 1328 K = 1, JN
WRITE (A, 8321) RATIO(K), U(K), BEST(K)
8321
FORMAT ///50X, 441 ,F7.3, 6X, F5.3, 7X, F5.3)
1238 CONTINUE
STOP
END
APPENDIX 4: Kinetics of the \( A + L_2 \rightleftharpoons AL_2 \) Equilibrium.

Notation:  
\( A \) = metal porphine, FePX  
\( L \) = nitrogeneous base  
\( a \) = original metal porphine concentration  
\( b \) = original base concentration  
\( x \) = concentration of product \( AL_2 \)

\[
A + 2L \xrightleftharpoons[\beta_2]{a - x} AL_2 \\
\frac{b - 2x}{x}
\]

\[
\beta_2 = \frac{x}{(a - x)(b - 2x)^2}
\]

\[
\beta_2 = \frac{x}{(a - x)(b^2 - 4bx + 4x^2)}
\]

\[
\beta_2 = \frac{x}{ab^2 - (4ab + b^2)x + 4(a + b)x^2 - 4x^3}
\]

\[
0 = 4\beta_2x^3 - 4\beta_2(a + b)x^2 + [4ab\beta_2 + b^2\beta_2 + 1]x - \beta_2ab^2
\]

\[
0 = x^3 - (a + b)x^2 + \left[ \frac{b^2\beta_2 + 4ab\beta_2 + 1}{4\beta_2} \right] x - \frac{ab^2}{4}
\]

The above cubic equation can be solved to give a unique value of \( x \) at each point on the titration curve. (Given \( a \), \( b \) and \( \beta_2 \)).
As \( \mu^2 = \mu_{\text{H.S.}}^2 (X_{\text{H.S.}}) + \mu_{\text{L.S.}}^2 (X_{\text{L.S.}}) \)

where \( X_{\text{H.S.}} \) and \( X_{\text{L.S.}} \) represent the mole fractions of high- and low-spin forms present.

\[ \therefore \mu^2 = \mu_{\text{H.S.}}^2 (a - x) + \mu_{\text{L.S.}}^2 x \]

hence \( \mu \).

By solving the cubic expression for a given value of \( \beta_2 \) and then calculating \( \mu \) and comparing it to the experimental values of \( \mu \), it is possible to establish the values of \( \beta_2 \) which minimises the term \( \Sigma (\mu_{\text{calc.}}^2 - \mu_{\text{expt.}}^2)^2 \). This value of \( \beta_2 \) which gives the best fit to the experimental results is taken as the equilibrium constant for the equilibrium (1). This process is the basis of program Five (Appendix 3).

Absorption spectroscopy is a most useful technique in the preparation and characterisation of Iron porphine complexes. In some cases the degree of purity of the compound may also be ascertained. The absorption spectra of the series of ferric porphines prepared for Chapter 3 of this thesis are reported here. The spectra have been measured between 750 and 350 nm. The soret band typical of the conjugated \(\pi\) system of the porphyrin ring (at \(\approx 400\) nm) is shown on a different scale to the other absorption bands due to its intensity. Extinction coefficients are expressed in \(M^{-1} \text{ cm}^{-1}\) throughout.

a) Tetraphenylporphine, TPPH₂

TPPH₂ gives a typical porphyrin four-banded spectrum. The purity of the porphyrin with respect to the major impurity, the chlorin, can be judged by the ratio of the intensities of the bands at 645 nm and 590 nm. This ratio is 0.75 for TPPH₂ in \(\text{CH₂Cl}_2\). As the chlorin content increases, so does the ratio due to superimposition of the chlorin band at 651 nm \((e = 2.94 \times 10^4)\)

TPPH₂: 645 nm \((e = 5,900)\); 590 nm \((6,900)\); 549 nm \((9,300)\); 514 nm \((21,300)\); 412 nm \((360,000)\).
b) Iron(III) tetraphenylporphyrin chloride, Bromide and Iodide.
Fe(TPP)C100: 690 nm ($\varepsilon = 3,500$); 657 nm (3,200); 577 nm (4,000);
509 nm (13,500); 416 nm (105,700); 378 nm (62,800).
Fe(TPP)Br100: 689 nm ($\varepsilon = 3,000$); 667 nm (2,500); 581 nm (3,100);
511 nm (14,100); 416 nm (73,900); 390 nm (67,700).
Fe(TPP)I 100: 710 nm ($\varepsilon = 2,800$); 675 nm (2,300); 578 nm (3,400);
515 nm (12,150); 413 nm (80,000).

Although the spectra of these three compounds are fairly similar they can be distinguished by the amount of splitting (or lack of it, in the case of the iodide) of the Soret band, and also by change of wavelength of the absorption bands at $\sim 660$ nm and $\sim 510$ nm. These spectral changes are useful guides to product formation in metathesis reactions.

c) $\mu$-oxo-bis[Iron(III)tetraphenylporphyrin]
The μ-oxo-dimer gives an easily distinguishable two-banded spectrum:

\((\text{FeTPP})_2.0 : \text{611 nm (c = 2,650); 571 nm (5,600); 406 nm (62,100).}\)

(Extinction coefficients calculated for molarity of Iron atoms = 2 x molarity of compound, for direct comparison with the compounds \(\text{Fe(TPP)X).}\)

d) **Iron(III) protoporphyrin IX - dimethylester Chloride and Bromide.**

![](image)

The chloride and bromide of Iron(III) protoporphyrin IX-dimethylester can be distinguished by the ratio of intensities of the absorption bands I, II, and III. For the chloride this ratio is 1.00: 0.99: 0.49 and in the bromide 1.00: 0.91: 0.42.
Fe(PPIX-DME)Cl: 649 nm ($\epsilon = 3,900$); 544 nm (7,900); 516 nm (8,000); 384 nm (74,100).

Fe(PPIX-DME)Br: 645 nm ($\epsilon = 3,000$); 538 nm (7,000); 512½ nm (7,500); 389½ nm (68,700).

e) $\mu$-oxo-bis[Iron(III)protoporphyrin-IX-dimethylester].

(Fe PPIX-DME)$_2$.O: 573 nm with shoulder at 593 nm. This spectrum is easily distinguishable from that of Fe(PPIX-DME)Cl (see (d)).
REFERENCES

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76) W. Kuster, Hoppe-Seylers Z. Physiol. Chem., 1912, 82, 463.


