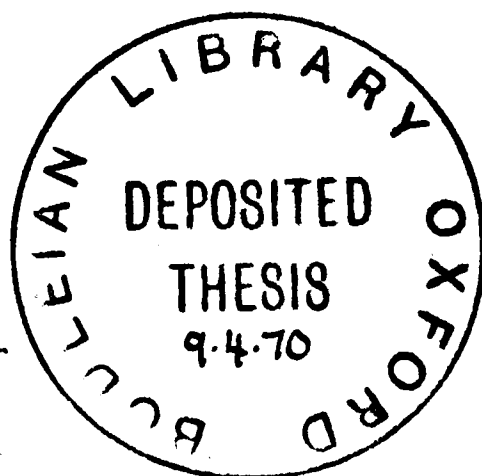


SOME ASPECTS OF THE CHEMISTRY
OF IRON SULPHUR COMPLEXES

A thesis submitted for the Degree
of Doctor of Philosophy

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The Queen's College, Oxford, 1969



It is a pleasure for the author to thank the many people who have helped him throughout this work. In particular he would like to thank Dr. H. A. O. Hill, his supervisor, for his tolerance and for guidance and encouragement over the past two years; Dr. C. E. Johnson, for his continued interest and help, and for many stimulating discussions; Dr. G. Lang, for carrying out calculations of some of the spectra, and for much helpful advice; Dr. M. S. Ridout and Dr. B. Window, for the loan of their computer programs and aid in using them; Mr. L. W. Becker and Mr. W. G. Murray, for their assistance in overcoming the domination of man by machines - Mr. Becker also kindly collected and processed some of the Mössbauer data; Mr. M. Clare, for the preparation of the sample of $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2\text{SbF}_6$; Mr. D. Chapple and Drs. Weiler and Strauss, for carrying out the microanalyses; A. E. R. E., Harwell, for the appointment during the tenure of which this research was carried out; his fiancée, for her encouragement and sympathy, and his tolerant colleagues in S.7, who retained their composure and good humour in the face of noxious sulphurous odours.

ABSTRACT

A Mössbauer Effect study of a number of complexes of iron with sulphur containing ligands has been carried out, in order to further the understanding of iron-sulphur chemistry and hence eventually provide suitable model complexes for the study of the non-haem iron proteins. The complexes investigated have been considered in three main sections, some dialkyldithiocarbamate complexes, some complexes that have been proposed as models for the non-haem iron proteins, and some complexes of some 2-substituted pyridines.

The iron(III) N,N dialkyldithiocarbamates exhibit anomalous magnetic properties which have been ascribed by other workers to a high-spin, low-spin equilibrium. All the iron(III) N,N dialkyldithiocarbamates that we have studied showed a single Mössbauer spectrum at all temperatures, so that the rate of exchange between the high-spin and low-spin states must be greater than $1.5 \times 10^{+7} \text{ sec}^{-1}$. The isomer shifts observed were large for low-spin ferric ions and suggest that the metal s-electrons are screened from the nucleus by electrons donated from the ligands. The isomer shifts and quadrupole splittings for all the complexes, except the high-spin iron(III) pyrrolidylthiocarbamate, exhibited anomalous dependences on temperature due to the existence of

the spin equilibrium. Iron(III) pyrrolidylthiocarbamate exhibited long electron spin relaxation times at 4.2°K. The other compounds, which are low-spin at low temperatures, also showed relaxation effects, though with shorter times. The magnetic hyperfine interactions in the Mössbauer spectrum of iron(III) N,N dimethylthiocarbamate gave information on the nature of the ground state of the complex, which was found to consist of almost equal amounts of d_{xz} and d_{yz} holes, with slightly less of d_{xy} . Mössbauer Effect and epr measurements on samples of this complex diluted in cobalt(III) N,N dimethylthiocarbamate confirmed this result. Estimates for the orbital separations were obtained as $\Delta d_{xz}, d_{yz} = 1.2 \text{ cm}^{-1}$ and $\Delta d_{yz}, d_{xy} = 91 \text{ cm}^{-1}$.

The dependence of the Mössbauer spectrum of iron(III) pyrrolidylthiocarbamate upon temperature and magnetic field has been interpreted in terms of a model with a large negative zero field splitting of the 6S state. The magnitude of the zero field splitting (4D) has been estimated as -9.3°K.

Bis(N,N diethylthiocarbamato)iron(III) chloride and bis(N,N diisopropylthiocarbamato)iron(III) chloride exhibited similar Mössbauer spectra to iron(III) pyrrolidylthiocarbamate at low temperatures. We have confirmed that the former compound is ferromagnetic, while the diisopropyl derivative is paramagnetic with the Kramer's doublet $| \pm 3/2 \rangle$ lying lowest.

Another complex of iron with dialkylthiocarbamate ligands that has been studied is the formally iron(I) complex, nitrosyliron

bis(N,N diethyldithiocarbamate). A high isomer shift was again observed. The quadrupole splitting showed little dependence on temperature and the application of an external magnetic field showed the sign of the major component of the electric field gradient to be positive. Magnetic hyperfine interactions are observed in large external magnetic fields at low temperatures. The variation of the effective field at the nucleus with H/T followed the Brillouin function for $S = 1/2$, and the value of the saturation hyperfine field was found to be $-110 \pm 5 \text{ kG}$. The orbital ground state of the iron atom could not be deduced from the sign of the quadrupole splitting, due to large contributions from the lattice and bonding electrons. From the magnetic hyperfine interactions it was deduced to be d_{z^2} .

The model complexes $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ which contain an Fe-S-S- linkage, as well as the related complex $\text{Fe}(\text{DTT})_3$ have been studied. (TTD = thio-p-toluyldisulphide, DTT = dithio-p-toluate) The isomer shifts have been interpreted in terms of the relative ability of the TTD and DTT ligands to delocalise electrons from the metal. The sign of the major component of the electric field gradient has been found to be negative for $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ but positive for $\text{Fe}(\text{DTT})_3$. The Mössbauer results have been used in conjunction with epr measurements to obtain information on the ground state of the complexes containing TTD ligands. The ground state is deduced to be a d_{xy} hole in both cases, but the agreement between the Mössbauer and epr data is not very satisfying.

Mössbauer Effect measurements on the model $\text{Fe}(\text{sacsac})_2\text{Cl}_4$, where sacsac is dithioacetylacetonate, have shown that the complex contains tetrahedral FeCl_4^{2-} ions, and does not have the structure originally proposed in which the iron is coordinated by the dithioacetylacetonate groups. The related complex $(\text{Ph}_2\text{C}_2\text{HS}_2)_2\text{FeCl}_4$ contains FeCl_4^{2-} ions in two different environments at high temperatures.

Tristetraphenylphosphonium trisdicyano-1,2-dithiolene iron was proposed as a model complex on the basis of its epr spectrum, which is qualitatively similar to that of the non-haem iron proteins. Mössbauer Effect investigations have been made on this complex and are reported here. The temperature dependence of the line widths and the relative line intensities has been interpreted in terms of the relative magnitudes of the spin-lattice and spin-spin relaxation times. An attempt to correlate the temperature dependence of the quadrupole splitting with that of the magnetic moment was only partially successful. Measurements in externally applied magnetic fields showed the sign of the major component of the electric field gradient to be negative; lattice contributions to the electric field gradient are not important in determining its sign. The ground state of the complex was deduced to be a d_{xy} hole well separated from higher states, from both the Mössbauer and epr measurements.

The complex $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2\text{SbF}_6$ has been investigated, and is proposed as a model complex for the non-haem iron proteins, on the basis of similarities in its structure and epr spectrum. The Mössbauer

Effect measurements have shown that the single unpaired electron is equally shared by the two iron atoms, which results in an anomalously small value for the hyperfine field at the iron nuclei. The epr spectrum has been interpreted in terms of a model in which a high-spin ferric ion and a high-spin ferrous ion are antiferromagnetically coupled to give a total spin S of $1/2$. Estimates of the relative energies of some of the orbitals of the ferrous ion have been made.

A number of complexes of iron with 2-substituted pyridine ligands have been prepared and studied. The preparation of complexes of thiopicolinic acid anilide, thiopicolinamide, pyridine-2-aldehyde thiosemicarbazone, 2-mercaptomethylpyridine, o-aminobenzenethiol and 2,2'-dipicolylidisedisulphide are reported. A number of these complexes are described and characterised for the first time. With one exception all the complexes contain ferrous ion; oxidation of the ligand usually occurred when the preparation of ferric complexes was attempted. The Mössbauer parameters of these complexes are reported and discussed. The values of the isomer shifts of the low-spin ferrous complexes of thiopicolinic acid anilide, thiopicolinamide and pyridine-2-aldehyde thiosemicarbazone are interpreted in terms of the relative σ -donor powers of the ligands. The complexes of o-aminobenzenethiol and 2-mercaptomethylpyridine were found to contain high-spin ferrous ions. The former complex was found to be antiferromagnetic at low temperatures, whilst at 77°K it exhibited the largest quadrupole splitting

yet reported for an iron compound, $4.06 \text{ mm. sec.}^{-1}$. The latter complex also showed a large quadrupole splitting at 77°K . The Mössbauer spectrum observed at low temperatures suggested the presence of some weak antiferromagnetism.

The single ferric complex of these ligands that was prepared, is a complex of 2,2'-dipicolyl disulphide and is the first complex of iron with a disulphide ligand to be reported. Further work is necessary before it is fully characterised.

Finally, the value of the information obtained from Mössbauer spectroscopy and epr in the elucidation of molecular and electronic structure is discussed. A correlation between the magnitude of the Fermi contact contribution to the hyperfine field is considered in the light of the data obtained during this work.

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CHAPTER ONE. INTRODUCTION.

1.1. Iron in biological systems. The non-haem iron proteins.

Iron is unique among the transition metals that are found in biological systems. It is generally present in higher concentrations than other trace elements due to its vital roles in electron transfer reactions and oxygen transport. Furthermore the extreme insolubility of iron at physiological pH and the variety of types of reaction involving iron have resulted in the evolution of numerous special coordination compounds.

The non-haem iron proteins constitute an important group of iron containing compounds that have a variety of roles in biological processes. They may be classified as follows⁽¹⁾:

I. Electron transferring non-haem iron proteins.

A. Labile sulphur proteins.

(i) Bacterial: Clostridial ferredoxin, Putidaredoxin,

Azobacter non-haem iron protein.

(ii) Plant: Chloroplast ferredoxin.

(iii) Animal: Adrenodoxin.

B. Non-labile sulphur proteins.

(i) Bacterial: Rubredoxin.

C. Flavoproteins: Succinic dehydrogenase, NADH dehydrogenase,

Xanthine oxidase.

II. Iron transferring non-haem iron proteins.

A. Bacterial: Ferrichrome.

B. Animal: Transferrin, Ferritin.

III. Oxygen transferring non-haem iron proteins.

A. Bacterial: Pyrocatechase.

B. Animal: Hemerythrin.

We are concerned with the compounds of group I, particularly with the ferredoxins.

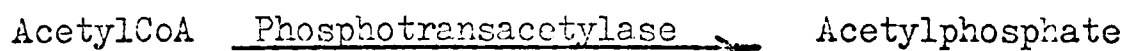
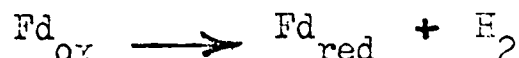
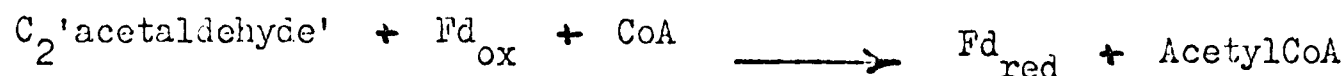
1.2. Ferredoxin.

The name ferredoxin is applied to all non-flavin, non-haem, iron containing proteins which function as electron carriers, show a redox potential on the 'hydrogen' side of pyridine nucleotides (-320mV), and which have the property of catalysing the photoreduction of TPN by isolated chloroplasts⁽²⁾.

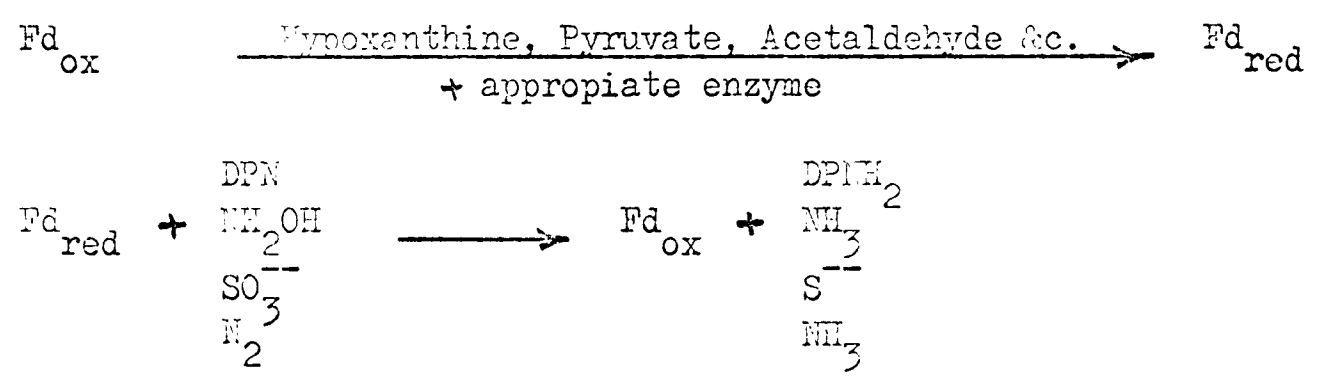
1.3. The function of ferredoxin.

The ferredoxins are involved in many important oxidation-reduction reactions in bacteria, plants and animals⁽¹⁾⁽³⁾⁽⁴⁾.

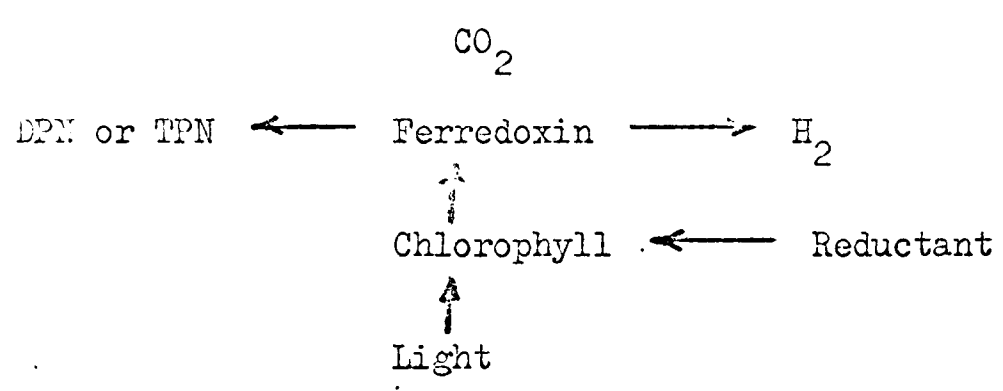
In anaerobic fermentative bacteria ferredoxin participates as an electron carrier in the breakdown of pyruvate to acetylCoA⁽⁵⁾:



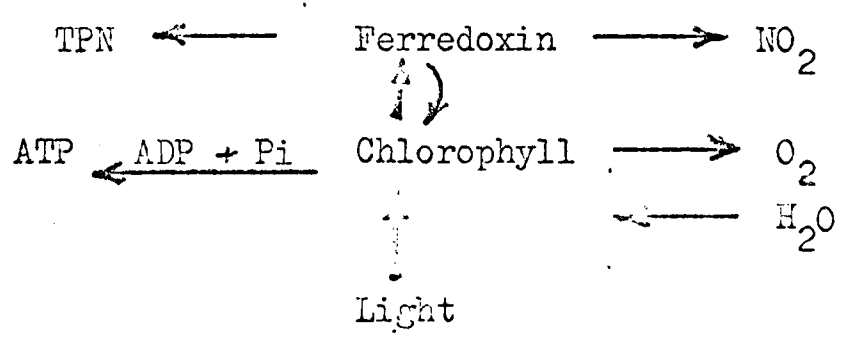
Anaerobic bacterial ferredoxin also participates in a number of other reactions⁽⁵⁾:



In photosynthetic bacteria, ferredoxin effects similar reduction reactions⁽⁴⁾. The reduction of ferredoxin is carried out by electrons supplied from photoactivated chlorophyll:



In green plants ferredoxin plays an important role in photosynthesis⁽⁷⁾. It acts as the first electron acceptor of photoactivated chlorophyll:



Green plants differ from photosynthetic bacteria in their ability to use water as an electron donor for the synthesis of starch and cell material.

Adrenodoxin, a labile sulphur non-haem iron protein occurring in animals, has been implicated in adrenal steroid hydroxylation⁽¹⁾. It is believed to be one member of an electron transfer system which functions to produce active reduced oxygen which can be incorporated into the steroid molecule.

1.4. The structure of ferredoxin.

Some of the physical properties of some iron-sulphur proteins are illustrated by Table 1.1. The amino acid constituents of many ferredoxins have been established and the complete sequence has been determined in some cases⁽⁸⁾. The peptide chain of *Clostridium pasteurianum* ferredoxin has been synthesised⁽⁹⁾.

The ferredoxins contain 'inorganic' or labile sulphide which is present in equimolar amounts with iron and which is liberated as hydrogen sulphide on denaturation of the protein. It is now generally accepted that the labile sulphide is a special constituent of ferredoxin⁽¹⁰⁾ and is not of amino acid origin⁽¹¹⁾. The chemical bonding of the labile sulphide remains obscure however, although there is evidence that the iron and sulphur are associated⁽¹²⁾.

The nature of the iron in ferredoxin has provoked much discussion and experiment. Mössbauer spectroscopic measurements

Table 1.1.

<u>Protein</u>	<u>M.W.</u>	<u>E₀(mV)</u>	<u>Fe atoms per mol.</u>	<u>Labile S atoms/mol.</u>	<u>Epr spectrum reduced</u>
Anaerobic bacteria					
Clostridial ferredoxin	6500	-420	7	7	$g_x=1.89$ $g_y=1.96$ $g_z=2.00$
Photosynthetic bacteria					
Chromatium	6000	-490	4	4	?
Green plants					
Spinach ferredoxin	11200	-432	2	2	$g_x=1.89$ $g_y=1.96$ $g_z=2.04$
Animals					
Adrenodoxin	10300	164	2	2	$g_x = g_y = 1.94$ $g_z=2.01$

Physical properties of some iron-sulphur proteins

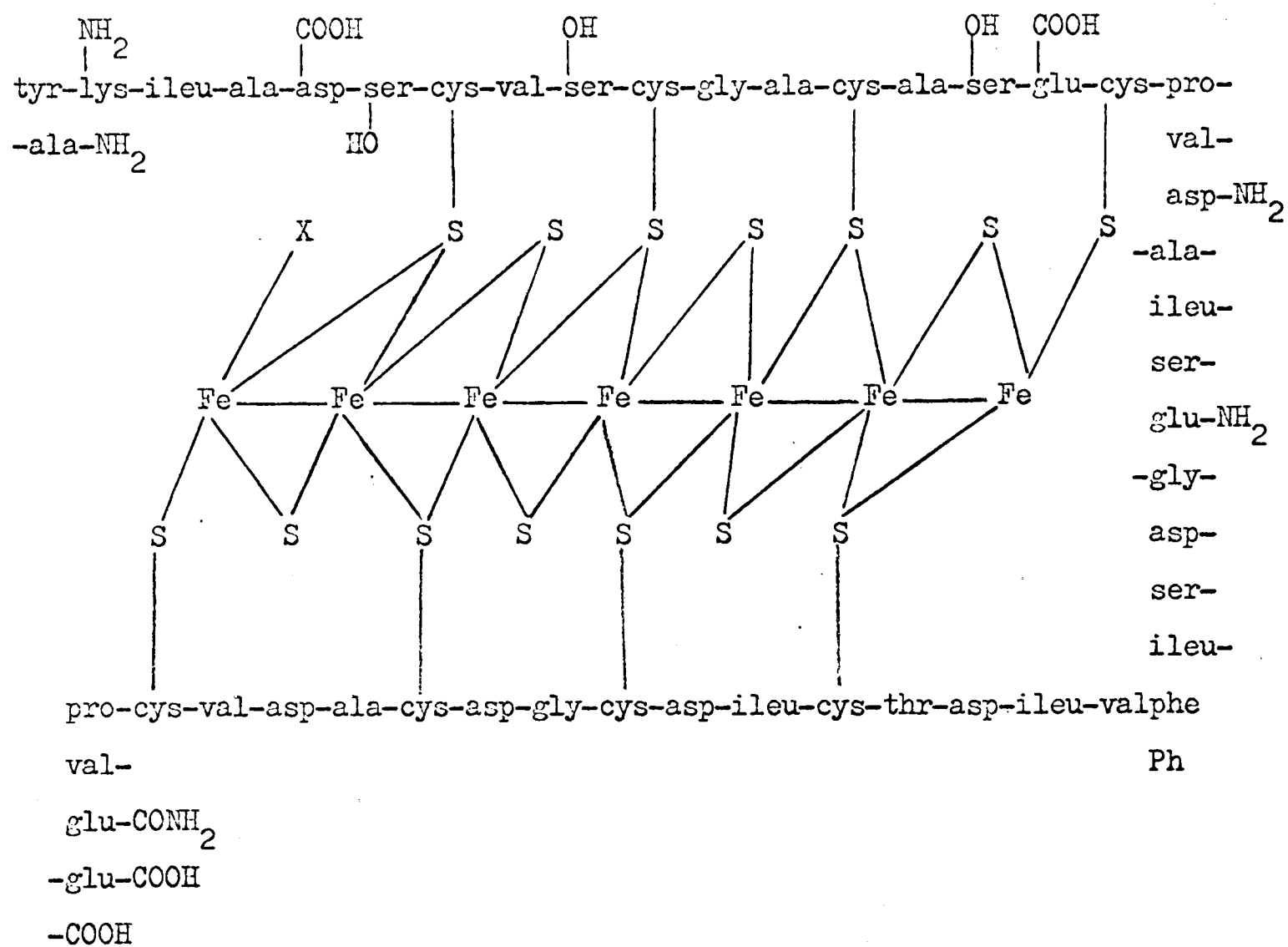
on ferredoxin from the green alga *Euglena* show that both iron atoms occupy identical sites. The iron atoms in the oxidised compound are in a diamagnetic state. On reduction the unpaired electron is shared equally by the two iron atoms and the Mössbauer spectrum observed at low temperatures and in external magnetic fields is characteristic of a low-spin ferric compound with a small hyperfine field⁽¹³⁾.

Mössbauer spectroscopy has proved a useful technique in the study of non-haem iron proteins. Electron paramagnetic resonance has also been applied widely but the results obtained pose difficulties in interpretation⁽¹³⁾⁽¹⁴⁾. The epr parameters for some non-haem iron proteins are given in Table 1.1.

A model structure for *Clostridium pasteurianum* ferredoxin has been proposed⁽¹⁵⁾ (Fig.1.1.) but preliminary X-ray data is not in full agreement with this model⁽¹⁶⁾. Further details of the structure and active site of ferredoxin must await the results of full X-ray structural studies. The structure of Rubredoxin, a related non-haem iron protein containing one iron atom per molecule, has been partially solved. The structure has extremely unusual features. The iron atom is coordinated by sulphur atoms occupying four of the apices of a distorted octahedron, the remaining two positions are unoccupied.⁽¹⁷⁾

1.5. The object of the present work.

Detailed structures of the non-haem iron proteins are unknown and the oxidation states, stereochemistries and ligand

Figure 1.1 .

Proposed structure for Clostridium pasteurianum ferredoxin

atoms of the iron atoms are not known with certainty. This lack of information makes the interpretation of their physical properties difficult and hinders the understanding of their precise biological function. The situation is further complicated by the fact that the inorganic chemistry of iron in its complexes with sulphur ligands is by no means fully understood. Although there are some 400 references in the literature to complexes of iron with sulphur containing ligands, only a very small proportion of these describe the preparation or properties of well characterised compounds. Some indication of the variety of oxidation states, spin states and stereochemistries that iron can adopt in its complexes with sulphur ligands is illustrated by Table 1.2.

The chemistry of iron-sulphur complexes is evidently complex and the application of information from the inorganic chemistry of these complexes to the study of the properties of the iron-sulphur proteins is of limited value. Our aim has been to study thoroughly some simple complexes of iron with sulphur ligands in order to further the understanding of iron sulphur chemistry and hence eventually hope to provide suitable model compounds for the study of the non-haem iron proteins.

1.6. The present work.

The complexes we have studied cover a wide variety of oxidation states and spin states. The principal physical techniques

Table 1.2.

<u>Formal oxidation</u> <u>state</u>	<u>Stereochemistry</u> <u>and/or coordination</u> <u>number</u>	<u>Spin state</u>	<u>Complex</u>
Fe(I)	6-coordinate	$S = 0$	$(\text{Fe}(\text{CO})_3\text{SMe})_2$
Fe(I)	5-coordinate square pyramidal	$S = 1/2$	$((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2\text{FeNO}$
Fe(II)	'tetrahedral'	$S = 0$	$(\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2$
Fe(II)	5-coordinate	?	$(\text{R}_2\text{NCS}_2)_2\text{Fe}$
Fe(II)	approx. cubic	$S = 0$	FeS_2 (pyrites)
Fe(II)	6-coordinate probably tetragonal	$S = 2$	$(\text{cysteine})_2\text{Fe}(\text{CO})_2$
?Fe(III)	'tetrahedral'	$S = 1/2$	$(\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2^+$
Fe(III)	octahedral	$S = 1/2$	$(\text{C}_2\text{H}_5\text{OCS}_2)_3\text{Fe}$
Fe(III)	5-coordinate ? square pyramidal	$S = 1/2$	$(\text{Fe}(\text{CN})_4\text{C}_4(\text{CF}_3)_4)^{2-}$
Fe(III)	5-coordinate square pyramidal	$S = 3/2$	$((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2\text{FeCl}$
Fe(III)	tetrahedral	$S = 5/2$	KFeS_2
Fe(III)	6-coordinate ? trigonal	$S = 5/2$	$((\text{CH}_2)_4\text{NCS}_2)_3\text{Fe}$
Fe(IV)	6-coordinate	$S = 1$	$(\text{FeS}_6\text{C}_6(\text{CN})_6)^{2-}$

Some complexes of iron with sulphur containing ligands

used have been Mössbauer spectroscopy and electron paramagnetic resonance spectroscopy (epr). The former technique has developed over the last decade or so into a useful tool for physical and chemical studies⁽¹⁸⁻²³⁾ and yields valuable information on how the properties of the Mössbauer nuclei are influenced by its environment. The results obtained are often complementary to those obtained by the more widely known technique of epr. The value of epr in the study of paramagnetic transition metal complexes has been appreciated for some considerable time. Useful information on a variety of materials has been obtained from epr measurements⁽²⁴⁻²⁷⁾. The theory and experimental methods of these physical techniques is presented in Chapter Two.

The results obtained from our study of iron-sulphur complexes have been presented in three parts. Firstly, a detailed Mössbauer Effect investigation of some complexes of iron with dialkyldithiocarbamate ligands has been carried out. The results and discussion of the iron dialkyldithiocarbamate complexes are presented in Chapter Three.

Chapter Four contains an account of investigations of the properties of a number of complexes which have been proposed as model systems for the non-haem iron proteins.

Some complexes of iron with 2-substituted pyridine ligands are dealt with in Chapter Five. The 2-substituent has been varied to give a wide range of sulphur donor atom, the pyridine

nitrogen atom remaining constant as the other ligating atom of the bidentate ligand. A number of novel complexes have been prepared. The preparations, characterisations and results from physical measurements are presented and discussed.

Chapter Six summarises the important results and emphasises the nature of the valuable information obtainable from Mössbauer spectroscopy especially when used as a complementary technique to epr spectroscopy. The value of the work in meeting our original objective is assessed.

CHAPTER TWO. PHYSICAL METHODS.

PART ONE. Theoretical considerations.

2.1. Mössbauer spectroscopy.

Mössbauer spectroscopy is the study of the recoil free absorption of gamma rays between nuclear ground and excited states. The recoil free emission and resonant absorption of gamma rays was discovered in 1957⁽²⁸⁾ since when the technique has been widely applied by scientists of many disciplines in a variety of investigations ranging from the detection of the gravitational red shift⁽²⁹⁾ to detailed studies of biochemicals⁽³⁰⁾.

The Mössbauer Effect.

When an isolated atom emits a gamma ray the total momentum of the system remains constant. The atom undergoes recoil, the recoil momentum being equal to the momentum of the gamma ray. For an emitted gamma ray:

$$E_0 - E_\gamma = \frac{E_\gamma^2}{2Mc^2} \quad (1)$$

where E_0 is the energy of the excited state of the decaying nucleus, E_γ is the energy of the gamma ray, M is the mass of the atom and c is the velocity of light. For an absorbed gamma ray:

$$E_0 + E_\gamma = \frac{E_\gamma^2}{2Mc^2} \quad (2)$$

If the atom is tightly bound in the lattice so that the recoil energy is less than the characteristic energy of the lattice vibrations, transfer of the recoil energy to the lattice is not possible and a fraction of essentially recoilless emissions or absorptions result.

If the absorber is in a chemically different environment to the emitter the energy separation between the ground and excited states will be different. The energy of the gamma rays can be modulated by moving the emitter at a velocity v' relative to the source. E_γ is altered by the Doppler Effect by an amount $E_0 v'/c$. By adjusting the velocity of the source the Doppler shift in the energy of the gamma rays can be varied until absorption occurs. The Mössbauer spectrum is thus obtained as a plot of gamma ray counts as a function of source velocity.

2.2. The line width

The energy of the gamma ray is very precisely defined, a fact of great importance in physical experiments. The value of the Mössbauer Effect as a chemical technique is found in the narrow line-widths of the transitions. The linewidth is smaller than the values of the magnetic dipole and electric quadrupole interactions of the nuclei with their environments. Thus the Mössbauer Effect provides a sensitive probe for the investigation of these interactions.

The minimum line width that can be observed is that of the emitting state. Broadening of the line can occur in a number of

ways of which two are important:

i) Broadening due to a magnetic field at the nucleus that is insufficiently strong for the appearance of magnetic hyperfine interactions⁽³¹⁾.

ii) Broadening due to a scatter of isomer shifts or quadrupole splittings. Thus Wertheim found that the Mössbauer spectrum of ^{57}Fe in stainless steel gave a broadened line due to the wide range of nearest environments in the alloy⁽³²⁾.

Non-fundamental sources of broadening which can be reduced by careful experimentation include the use of thick absorbers, the presence of mechanical vibrations and instrumental effects due to a finite solid angle between the source and the absorber.

2.3. The intensity.

The intensity of the Mössbauer Effect depends on the Debye-Waller factors of the source and absorber. The Debye-Waller factor expresses the fraction of gamma ray transitions that take place without recoil and is given by:

$$f = \exp\left(-\left(\frac{4\pi^2 \langle x^2 \rangle}{\lambda^2}\right)\right) \quad (3)$$

where $\langle x^2 \rangle$ is the mean square amplitude of the vibration in the direction of the emission of the gamma ray averaged over an interval equal to the lifetime of the excited nuclear level, and λ is the wavelength of the scattered radiation. Using a Debye approximation it

can be shown that:

$$f = \exp \left[\frac{-E_r}{k\theta_D} \left\{ \frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right\} \right] \quad \text{where } T \ll \theta_D \quad (4)$$

E_r is the recoil energy and θ_D is the characteristic Debye temperature defined by $h\nu_{\max} = k\theta_D$.

For a given source the intensity is a measure of the strength of binding of the absorber nucleus. Intensity measurements have been used to estimate the proportions of absorber nuclei in different lattice sites⁽³³⁾.

It is evident from eq. (4) that the Mössbauer Effect is limited to low energy ($<150\text{keV}$) gamma rays. Other considerations for the facile study of Mössbauer spectroscopy include the natural abundance of the absorber isotope, the half life of the source and the width of the absorption lines.

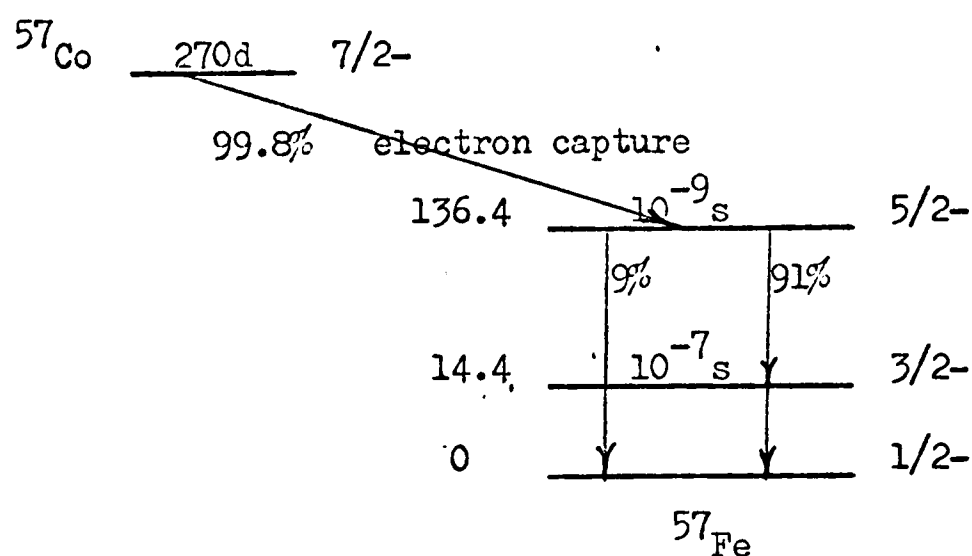
2.4. ^{57}Fe

Mössbauer Effect studies are possible for all nuclei having a low energy excited state and a small internal conversion coefficient. To date the Mössbauer Effect has been observed for over 70 isotopes. Of these ^{57}Fe is by far the most widely investigated. It is a convenient isotope to study since the line width is narrow, the source used, ^{57}Co , is quite easily prepared and has a convenient half life of 270 days. Furthermore, the natural abundance of ^{57}Fe although only 2% is sufficiently high for many compounds to be studied without resorting

to isotopic enrichment and the Debye-Waller factor for ^{57}Fe in its alloys and compounds is often high enough for measurements at high temperatures ($>300^\circ\text{K}$) to be made without difficulty.

The decay scheme for $^{57}\text{Co} \longrightarrow ^{57}\text{Fe}$ is shown in Fig. 2.1. ^{57}Co decays by electron capture through a highly excited state which decays in 91% of the cases to the first excited state of ^{57}Fe . This level has a nuclear spin of $3/2$. It decays to the ground state of nuclear spin $1/2$ with the emission of a 14.4 keV gamma ray.

Figure 2.1.



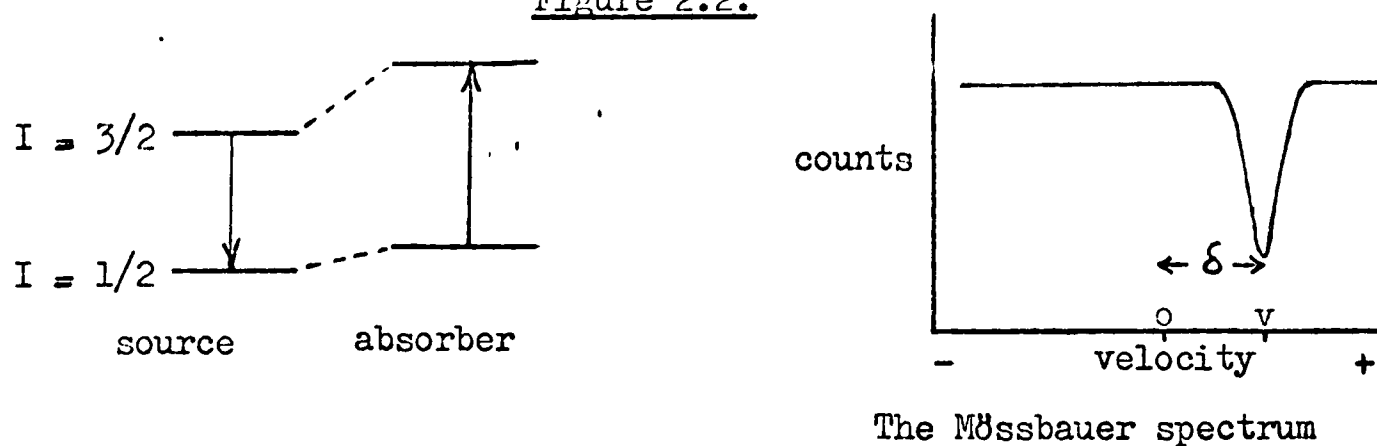
Decay scheme for $^{57}\text{Co} \longrightarrow ^{57}\text{Fe}$

The recoilless absorption of the 14.4 keV gamma ray by the ^{57}Fe nuclei of the absorber results in the Mössbauer spectrum, the parameters of which will now be considered.

2.5. The isomer shift.

If a Mössbauer experiment involves a single line source and absorber, resonance will not in general occur at zero velocity. The nucleus has a finite volume which interacts with the electron density at the nucleus. As the ground and excited states of the nucleus have different radii the interactions are different for the two states. The difference between the energies of the transition for the source and absorber is the isomer shift. The resonance condition is restored by moving the source relative to the absorber so that the energy of the gamma ray is shifted by an amount $E\gamma v/c$, and absorption is then observed at some velocity v (Fig. 2.2). For the ^{57}Fe 14.4 keV gamma ray a velocity of 1 mm. sec.⁻¹ corresponds to an energy of 4.8×10^{-8} eV or 0.0038 cm.^{-1}

Figure 2.2.



Isomer shift

If Z is the nuclear charge, R_e and R_g are the radii of the excited and ground states respectively and $\psi(0)_s$ and $\psi(0)_a$ are the

electronic wave functions at the origins of the source and absorber nuclei respectively, then the isomer shift is given by⁽³⁴⁾:

$$\delta = \frac{2\pi}{5} Ze^2 r^2 (R_e^2 - R_g^2) \left\{ |\psi(0)_a|^2 - |\psi(0)_s|^2 \right\} \quad (5)$$

The isomer shift is therefore proportional to the difference in electron density between the source and absorber nuclei. Since only s-electrons have a finite probability of being at the nucleus, the isomer shift is a measure of the s-electron density at the nucleus of the absorber with respect to the source.

For ^{57}Fe the first excited state is of smaller radius than the ground state, $((R_e - R_g)/R_g = -1.4 \times 10^{-3} \text{ }^{(35)})$, so that an increase in isomer shift corresponds to a decrease in s-electron density at the nucleus of the absorber.

The isomer shift is proportional to the sum of the contributions to the s-electron density at the nucleus from the 1s, 2s, 3s and 4s electrons. The contributions from the 1s and 2s electrons are large but constant, whereas the contributions from the 3s and 4s electrons are small but variable. The 3d shell is penetrated by the 3s and 4s shells and consequently the 3s and 4s electrons will be screened from the nucleus by the 3d electrons. The isomer shift will therefore depend on the oxidation state of the iron atom, contributions of 4s bonding and indirect contributions from 3d bonding⁽³⁶⁾.

The isomer shift can be used to establish the electron

configuration in conjunction with a correlation plot of the Walker, Wertheim and Jaccarino type⁽³⁷⁾, but such assignments are rarely unambiguous.

Erickson⁽³⁸⁾ has reviewed many of the theories advanced to account for the isomer shift systematics of iron compounds. Extended agreement between data and theory is not found, mainly because the theory has been forced to a limit where its approximations become invalid. The limited success of empirical correlations of isomer shift with for example, electronegativity or with the spectrochemical or nephelauxetic series, is probably due to the fact that isomer shifts depend on electron density distributions whereas the other quantities depend on electronic energy level differences. There is usually no simple relationship between these two quantities.

However, isomer shifts can and do provide useful information. In conjunction with other data an assignment of coordination number, spin and oxidation state can often be made. Furthermore, in a series of related compounds, variations in isomer shifts can enable at least qualitative discussions of the bonding to be made in terms of s- electron loss or gain.

All the isomer shifts we have measured are quoted with respect to a metallic iron absorber as standard. Data quoted from other sources have been adjusted where necessary to conform with our standard.

2.6. The temperature dependence of the shift.

The measured isomer shift contains a temperature dependent contribution resulting from the second order Doppler Effect due to lattice vibrations. The second order Doppler shift is given by⁽³⁹⁾:

$$\delta_T = \frac{C}{E_\gamma} \frac{dE_\gamma}{dT} = -\frac{1}{2Mc} \int_0^T C_L dT \quad (6)$$

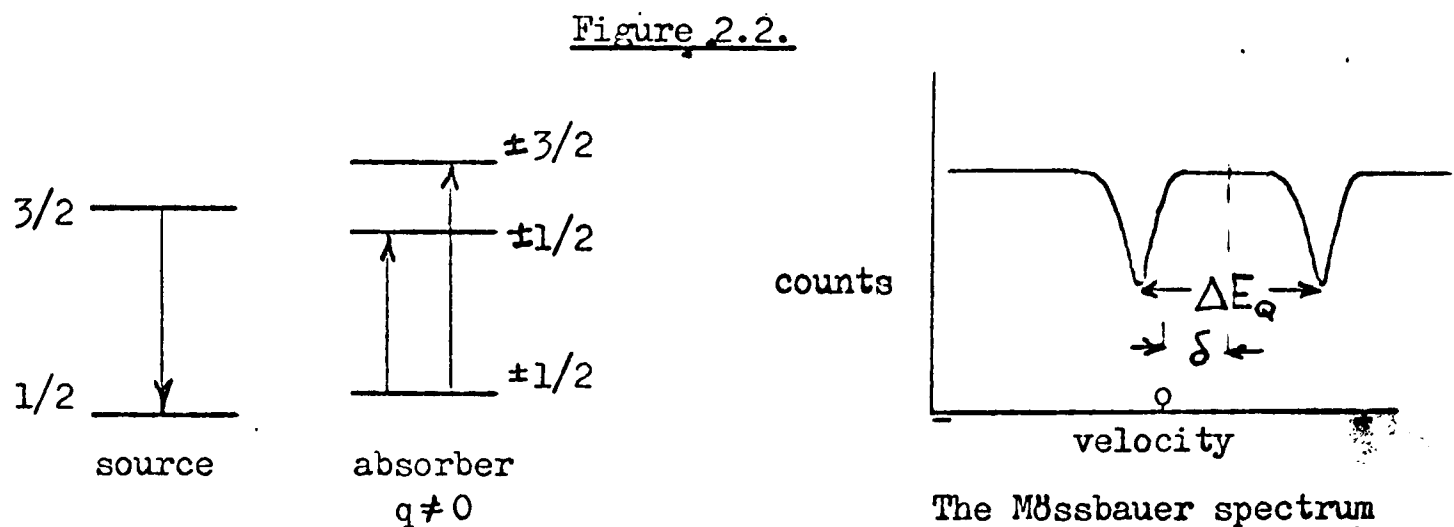
where E_γ is the energy of the gamma ray transition, C_L is the lattice specific heat and M is the atomic mass.

The second order Doppler Effect shifts the centre of absorption for a typical ferric compound by about $0.2 \text{ mm. sec.}^{-1}$ between 300°K and 0°K . The shift is towards higher velocity. All substances do not have the same temperature dependence of the shift. It is important to take account of this fact when shifts are compared. Isomer shifts should be compared at high temperatures, of the order of $0.6 \theta_D$, when the temperature dependent contribution becomes the same for all substances.

2.7. The quadrupole splitting.

A nucleus with spin $I \gg 1$ possesses a quadrupole moment, Q . Interaction of the nuclear quadrupole moment with an electric field gradient resulting from an anisotropic electrostatic environment, causes the $(2I + 1)$ degeneracy of the nuclear levels to be partially lifted. The first excited state of ^{57}Fe has a nuclear spin $I = 3/2$. Interaction with an electric field gradient splits the excited state into two levels. Transitions from the ground state to either of these levels

is now possible, giving a two line spectrum (Fig.2.2)



The quadrupole splitting

The quadrupole moment is a measure of the distortion of the nuclear volume from spherical symmetry and is defined⁽⁴⁰⁾:

$$eQ = \int \rho r^2 (3\cos^2\theta - 1) dv. \quad (7)$$

where ρ is the charge density in a volume element dv inside the nucleus at a distance r from the centre and at an angle θ between the radial coordinate and nuclear spin axes.

The electric field gradient is a tensor quantity but can be reduced to diagonal form in the proper coordinate system and be completely specified by the two independent components V_{zz} , the second derivative of the electrostatic potential V in the z direction, and η an asymmetry parameter defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$. For axial symmetry $V_{zz} = eq$, so that the sign of the major component of the electric field

gradient tensor is opposite to that of the actual gradient of the electrostatic field.

The interaction energy between the quadrupole moment and the electric field gradient is described by the Hamiltonian⁽⁴⁰⁾:

$$\mathcal{H}_Q = \frac{e^2 Q q}{2I(I-1)} (3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)) \quad (8)$$

where I is the nuclear spin and I_x , I_y and I_z are its resolved components along the x , y and z axes. The energy levels are given by:

$$E_Q = \pm \frac{1}{4} e^2 Q q \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (9)$$

The quadrupole splitting is then:

$$\Delta E_Q = 2E_Q = \pm \frac{1}{2} e^2 Q q \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (10)$$

When the coupling $e^2 Q q$ is positive the $I = \pm 3/2$ states have the higher energy, as in Fig.2.2. When it is negative the $I = \pm 1/2$ states have the higher energy.

The magnitude of the electric field gradient, and hence of the quadrupole splitting, is governed by a number of factors.⁽⁴¹⁾

The principal component, q , of the electric field gradient is given by:

$$q = q_l + q_v + q_c \quad (11)$$

where q_l , q_v and q_c are the contributions from the lattice, the valence electrons and the core electrons respectively. q_l is given by:

$$eq_l = \sum_i Z_i \frac{(3\cos^2\theta - 1)}{r_i^3} \quad (12)$$

where r and θ are polar coordinates and $Z_i e$ is the charge on the i th ion.

q_v is given by:

$$q_v = \sum_v \frac{\langle \psi | (3\cos^2\theta - 1) | \psi \rangle}{r^3} \quad (13)$$

where ψ is the wave function of the particular orbital. The magnitude of q_v depends on the expectation value of $(3\cos^2\theta - 1)$. Values of $\langle r^{-3} \rangle_{q_v}$ and η_v are given in Table 2.1. for some orbital wave functions.

Table 2.1.

	$\langle r^{-3} \rangle_{q_v}$	$ \eta_v $
d_z^2	-4/7	0
$d_x^2 - y^2, d_{xy}$	+4/7	0
d_{xz}, d_{yz}	-2/7	3
p_x, p_y	+2/5	3
p_z	-4/5	0

The value of the electric field gradient at the atomic site can be calculated from q_l and q_v . The electric field gradient at the nuclear site however, is greatly modified by the atoms own electrons whose wave functions are distorted by interaction with the external and internal electric field gradient and as a result create electric field gradients of their own which are proportional to q_l and q_v ⁽⁴²⁾.

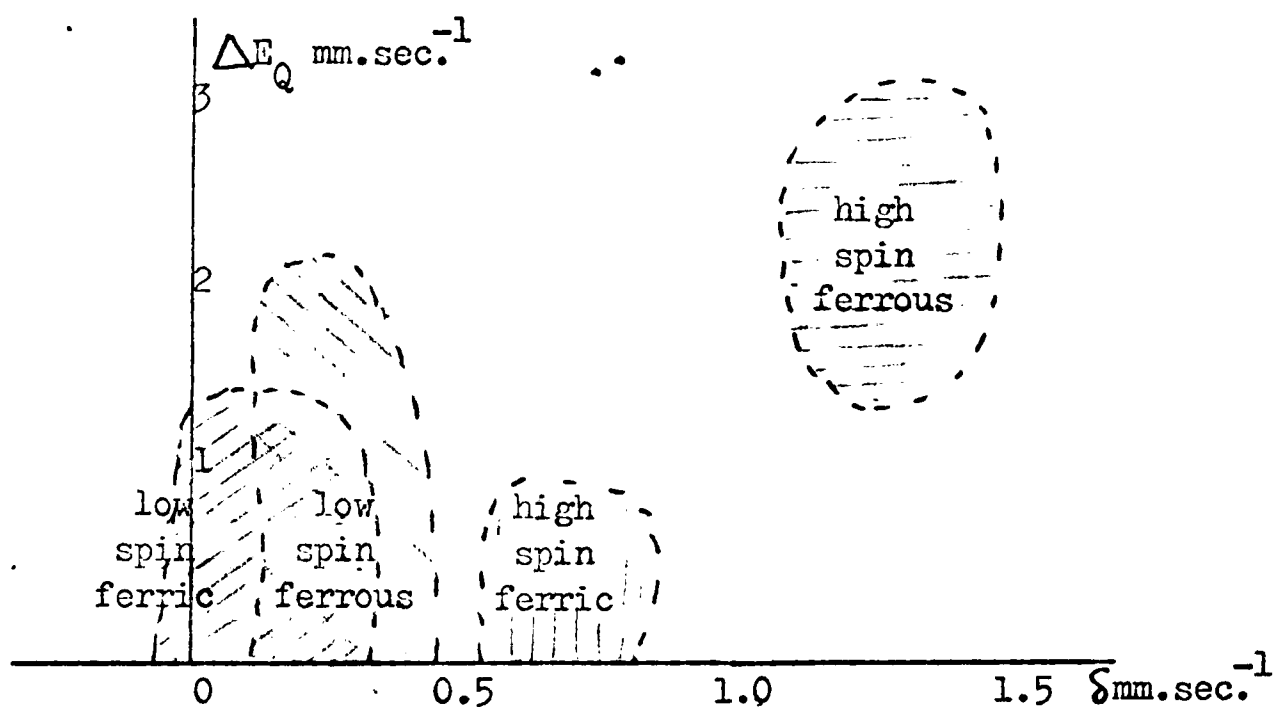
Eq. (11) then becomes:

$$q = (1 - R)q_v + (1 - \gamma_\infty)q_l \quad (14)$$

where R and γ_∞ are the Sternheimer shielding and antishielding factors. The magnitude of q then depends on the relative magnitudes of R and γ_∞ . For octahedral ferrous high-spin compounds q is dominated by the term in q_v . For high-spin ferric compounds, which have a 6S ground state, q_v is zero and the lattice contribution to the electric field gradient is dominant. In low-spin ferrous compounds with the configuration t_{2g}^6 there will be no contribution to q_v although now the effects of covalency may become important. Anisotropic σ and π bonding will give rise to a smaller $\langle r^{-3} \rangle$ for some 3d orbitals than for others. The resulting distortion of the 3d electron distribution will give rise to a large electric field gradient. In low-spin ferric compounds the term in q_v is important but contributions to the electric field gradient from the lattice and from bonding electrons will be significant and may dominate.

The factors contributing to the values of isomer shifts and quadrupole splittings for different iron compounds may enable the electronic configuration of the compound to be assigned. A plot of isomer shift vs. quadrupole splitting has been used for this purpose⁽⁴³⁾ and is illustrated in Fig. 2.3.

The temperature dependence of the quadrupole splitting may allow information to be obtained about the nature and population of orbital excited states close to the ground state.

Figure 2.3. $\delta/\Delta E_Q$ correlation diagram.

2.8. The sign of the quadrupole splitting.

If one of the lines of the quadrupole split pair can be assigned to a transition from the ground state ($m_I = \pm 1/2$) to either of the excited states ($m_I = \pm 3/2$ or $\pm 1/2$), the sign of the quadrupole splitting will be known and hence the sign of the major component of the electric field gradient tensor. A number of methods are available for determining this sign⁽⁴⁴⁾. In this work the sign of the quadrupole splitting has in all cases been established from an inspection of the magnetic hyperfine interactions in the Mössbauer spectrum and will therefore be considered in the section on magnetic hyperfine interactions.

One method that can be used to determine the sign of the quadrupole splitting is of interest however. This is the convenient experimental method of single crystal measurements. The ratio of the intensities of the two lines of the quadrupole split pair depends on the angle between the gamma ray direction and the field gradient axis. If a source of unpolarised gamma radiation is used and a single crystal, in which the major axis of the electric field gradient at each atom is identically aligned, is the absorber, then for the two transitions the probabilities and angular dependencies are⁽⁴⁵⁾:

<u>Transition</u>	<u>Probability</u>	<u>Angular dependence</u>
$\pm 3/2 \rightarrow \pm 1/2$	1	$3/2(1 + \cos^2 \theta)$
$\pm 1/2 \rightarrow \pm 1/2$	1	$(1 + 3/2 \sin^2 \theta)$

where θ is the angle from the axis of symmetry. Thus when $\theta = 0^\circ$ the ratio is 3:1 and when $\theta = 90^\circ$ it is 3:5. The assignment of the two transitions is thus straightforward.

For a powdered specimen the ratio of the two lines should be 1:1. A ratio of 1:1 is often not observed and this may be due to a number of reasons:

- i) The powder may not be perfectly randomly oriented.
- ii) Magnetic effects may be present.
- iii) The recoil free fraction may have an angular dependence if the atom is bound more strongly in one direction than in the other. This effect - the so-called Gol'danskii Effect - produces a

temperature dependent anisotropy of line intensities, the anisotropy becoming less marked as the temperature is lowered⁽⁴⁶⁾. Although often proposed to explain anisotropic line intensities, the Gol'danskii Effect has rarely been shown to be the unequivocal cause of this⁽⁴⁷⁾.

2.9. Magnetic hyperfine interactions.

The third important interaction that provides valuable information in a Mössbauer spectroscopic experiment is that resulting from the Zeeman splitting of the nuclear levels in a magnetic field. The Hamiltonian describing the magnetic hyperfine interactions between the nucleus and its electrons is:

$$\begin{aligned} \mathcal{H} &= - \underline{\mu} \cdot \underline{H} \\ &= -g_n \mu_n \underline{I} \cdot \underline{H} \end{aligned} \quad (15)$$

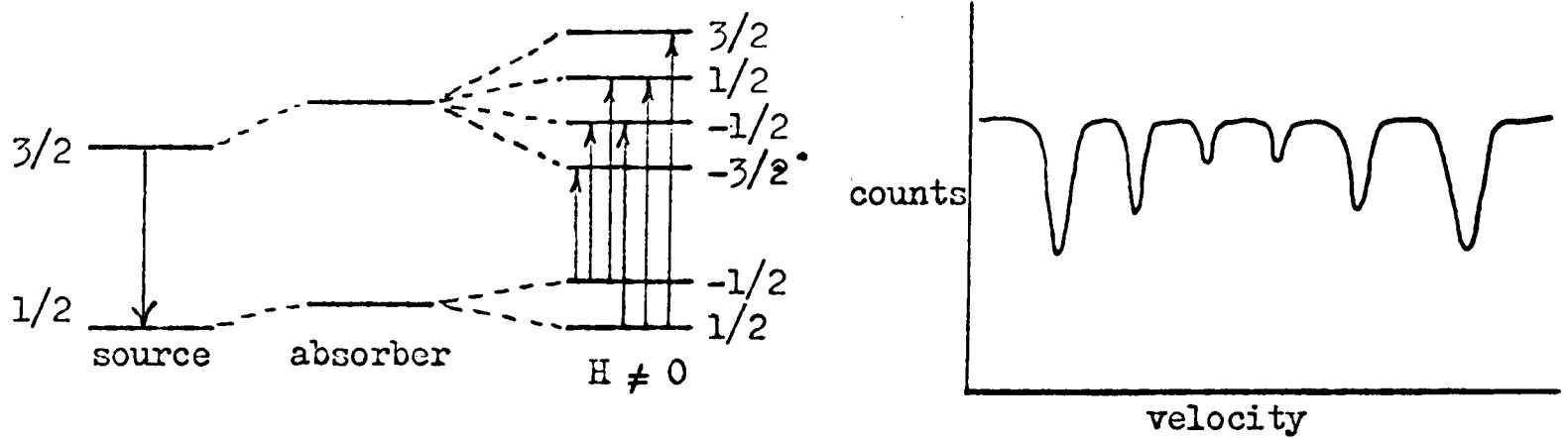
where μ is the magnetic moment of the nucleus, H is the magnetic field at the nucleus, μ_n is the nuclear magneton and g_n is the nuclear gyromagnetic ratio. For a nucleus of spin quantum number I , the energy levels are given by:

$$E_m = - \frac{\mu H m_I}{I} = -g_n \mu_n \frac{H m_I}{I} \quad (16)$$

where $m_I = I, I - 1, \dots, -I$.

For ^{57}Fe the ground state, $I = 1/2$, splits into two and the first excited state, $I = 3/2$, splits into four levels. For magnetic dipole transitions the selection rules are $\Delta m = 0, -1$ so that six transitions are observed. (Fig. 2.4.)

Figure 2.4.



The Mössbauer spectrum

Magnetic hyperfine interactions.

The intensities of the transitions depend on the angle θ between the gamma ray direction and the axis of magnetisation and are given by⁽⁴⁸⁾:

<u>Transition</u>	<u>Relative Intensity</u>
$\left. \begin{array}{l} 3/2 \rightarrow 1/2 \\ -3/2 \rightarrow -1/2 \end{array} \right\}$	$9/4 (1 + \cos^2 \theta)$
$\left. \begin{array}{l} 1/2 \rightarrow 1/2 \\ -1/2 \rightarrow -1/2 \end{array} \right\}$	$3 \sin^2 \theta$
$\left. \begin{array}{l} -1/2 \rightarrow 1/2 \\ 1/2 \rightarrow -1/2 \end{array} \right\}$	$3/4 (1 + \cos^2 \theta)$

Thus when $\theta = 0^\circ$ the ratios of the six lines are 3:0:1:1:0:3, and when $\theta = 90^\circ$ the ratios are 3:4:1:1:4:3. When θ is averaged over a sphere the intensities become 3:2:1:1:2:3.

The splitting of the nuclear levels depends on the size of the magnetic field but is independent of its origin. The hyperfine

field can be considered to be the sum of three contributions⁽⁴⁹⁾:

$$H_n = H_l + H_d + H_s \quad (17)$$

H_l is the contribution from the interaction between the nucleus and the orbital magnetic moment of the electrons:

$$H_l = 2\beta(g-2) \langle r^{-3} \rangle_{3d} S \quad (18)$$

where β is the Bohr magneton, g is the electron gyromagnetic ratio, r is the radial coordinate of the 3d electron and S is the spin. H_d is the contribution from the dipolar field arising from the dipolar interaction of the nucleus with the moment of the electron spin:

$$H_d = 2\beta \langle 3\cos^2\theta - 1 \rangle_{3d} \langle r^{-3} \rangle_{3d} S \quad (19)$$

where θ is the angular coordinate of the 3d electron. H_s is the contribution due to the Fermi contact interaction. This is the interaction between the nuclear and electron spins and is usually the major contribution. It may be expressed by:

$$H_s = -\frac{8\pi}{3}\beta \sum \left\{ |\psi_{\uparrow}^s(0)|^2 - |\psi_{\downarrow}^s(0)|^2 \right\} \quad (20)$$

where $|\psi_{\uparrow}^s(0)|^2$ and $|\psi_{\downarrow}^s(0)|^2$ are the s-electron spin densities at the nucleus for s-electrons with up and down spin respectively. Differences in spin up and spin down charge densities can appear even in filled s-shells if the atom contains a partially filled magnetic shell⁽⁵⁰⁾.

Interactions of the outer electrons with the core electrons will depend on the electron spin. The Fermi contact interaction field from one s-electron in iron is hundreds of megagauss so that even a small

difference in fields of opposite sign created by the action of s-electron pairs in internal shells can account for the appearance of fields of hundreds of kilogauss.

Thus large magnetic fields are present at the nucleus as a result of electronic interactions. The nuclear spin will couple with this field. If the electron spin relaxation time is much shorter than the Larmor frequency of the nucleus, then the time averaged value of the internal magnetic field at the nucleus will be zero.

However, in antiferromagnetic or ferromagnetic compounds where the electronic structures of all the atoms are spatially aligned, magnetic hyperfine interactions will be observed. Magnetic hyperfine interactions can also be observed in paramagnetic compounds. The application of an external magnetic field to a paramagnetic sample with fast relaxation rates can facilitate the observation of magnetic hyperfine interactions. The external magnetic field will tend to align the electron spins in a preferred orientation so that the time averaged value of the internal field is no longer zero. For these cases the effective magnetic field at the nucleus is proportional to the magnetisation.

Magnetic hyperfine interactions will also be observed in paramagnetic compounds when the electron spin relaxation time is long compared to the Larmor frequency of the nucleus. A well resolved spectrum may be observed by applying a magnetic field large enough to decouple the electron and nuclear spins. In this case the effective field at the nucleus

is not proportional to the magnetisation.

2.10. Combined magnetic and electric quadrupole interactions.

When an electric quadrupole interaction is present as well as magnetic hyperfine interactions, the position of the hyperfine energy levels depends on the ratio of the magnetic to the electric interaction energies, the symmetry of the electric field gradient and the angle between the principal axis of the electric field gradient tensor and the direction of the magnetic field. The splitting of the excited state is given by:

$$\mathcal{H}_{\text{ex}} = g_e \beta_n H_z + \mathcal{H}_Q \quad (I = 3/2) \quad (21)$$

and that of the ground state by:

$$\mathcal{H}_g = g_g \beta_n H_z \quad (I = 1/2) \quad (22)$$

where g_e and g_g are the nuclear g factors of the excited and ground states respectively. If z is the direction of the magnetic field and a principal axis of the electric field gradient also lies along the z direction, the energies of the hyperfine levels can be determined. They are given by⁽⁵¹⁾:

$$E_e = \begin{cases} \frac{1}{2} g_e \beta_n H \pm \frac{1}{4} e^2 Qq \left[\left(1 + \frac{g_e \beta_n H}{\frac{1}{4} e^2 Qq} \right)^2 + \frac{2}{3} \right]^{\frac{1}{2}} \\ \frac{1}{2} g_e \beta_n H \pm \frac{1}{4} e^2 Qq \left[\left(1 - \frac{g_e \beta_n H}{\frac{1}{4} e^2 Qq} \right)^2 + \frac{2}{3} \right]^{\frac{1}{2}} \end{cases} \quad (23)$$

The ground state splits into two levels with energies:

$$E_g = \pm \frac{1}{2} g_g \beta_n H \quad (24)$$

If the energy separations of the excited state levels are E_1 , E_2 and E_3 and that of the ground state is G , (Fig. 2.5.), then :

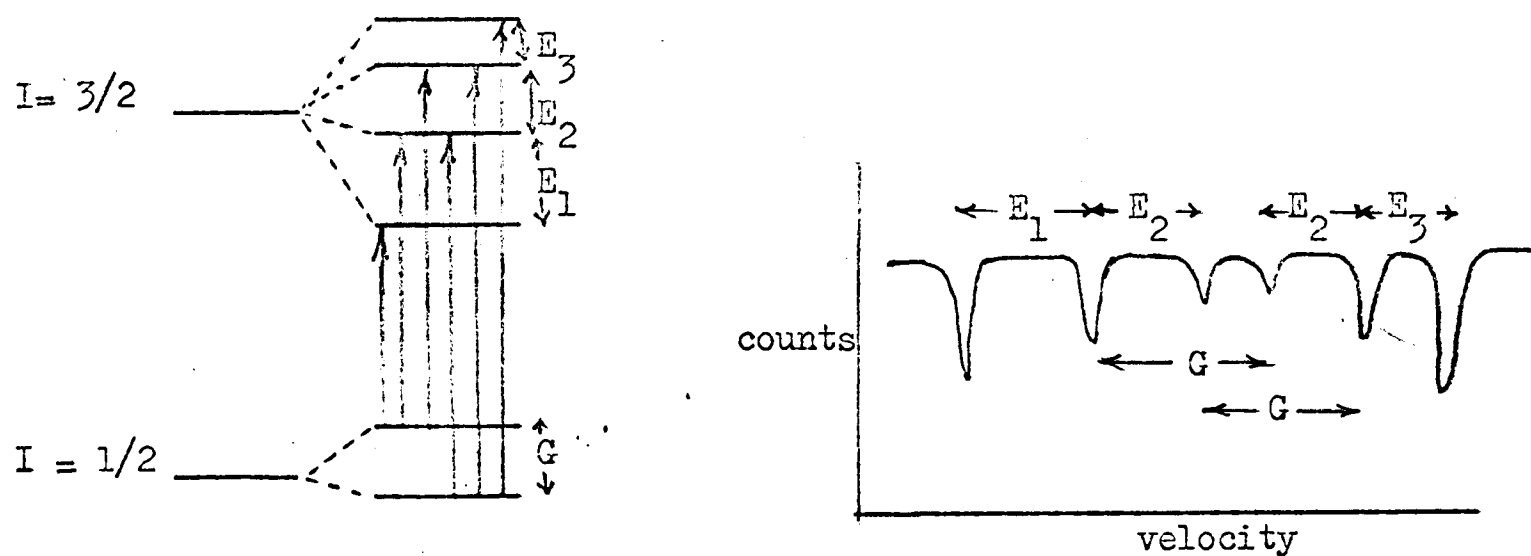
$$g_e/\beta_n H = \frac{1}{2}(E_1 + E_3) \quad (25)$$

$$G = g_g/\beta_n H \quad (26)$$

$$\frac{1}{2}e^2Qq = \frac{\frac{1}{4}(E_1 + E_2)^2 - (E_2 + E_3)^2}{E_1 + E_3} \quad (27)$$

$$\text{and } (\Delta E_Q)^2 = \frac{1}{2}((E_1 + E_2)^2 + (E_2 + E_3)^2) - (E_1 + E_3)^2 \quad (28)$$

Figure 2.5.



The Mössbauer spectrum

Combined magnetic and electric quadrupole interactions.

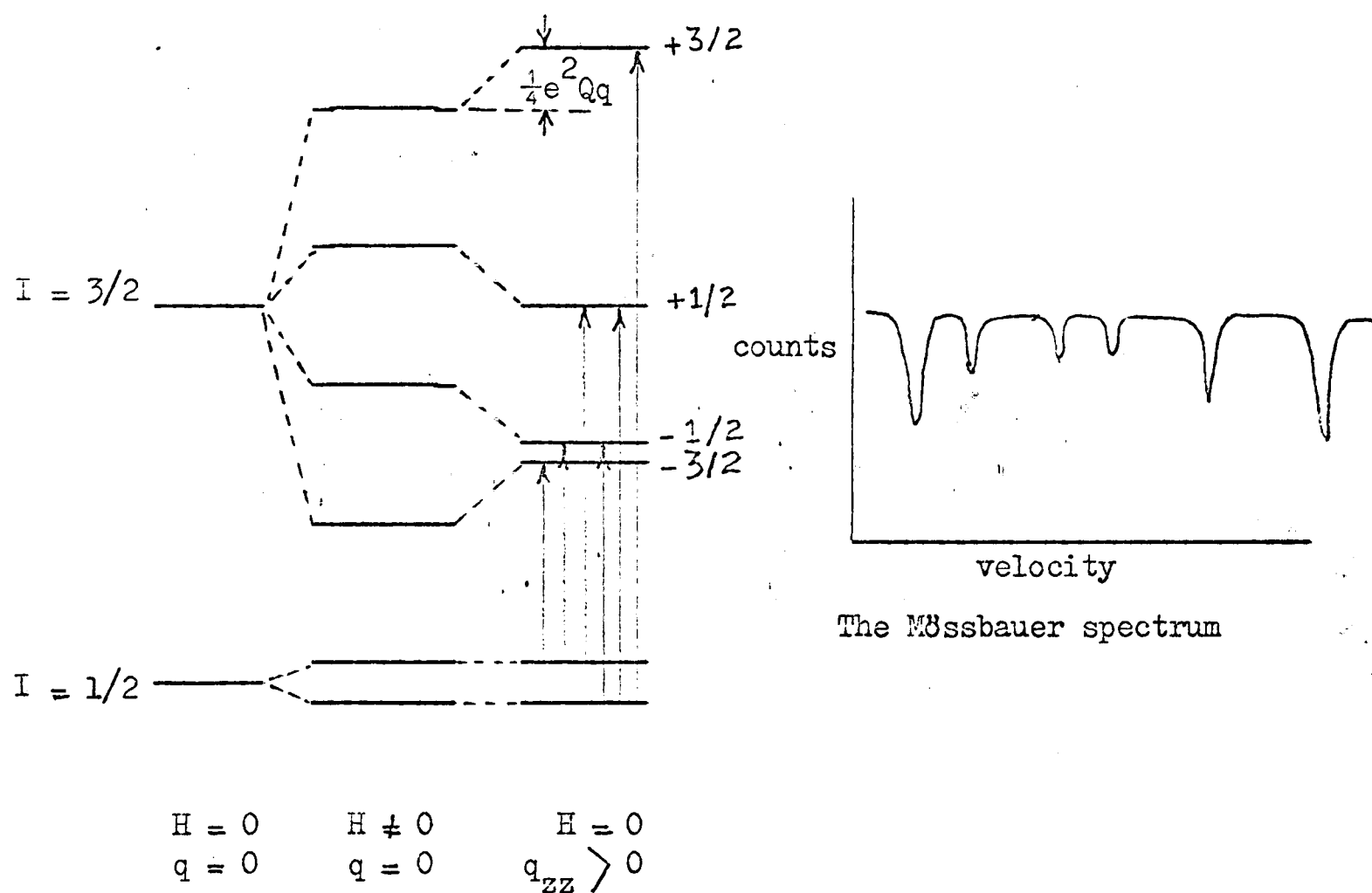
If the electric field gradient tensor is axially symmetric with its symmetry axis parallel to the magnetic field the

energy levels are given, from eq. (23) by:

$$E_e = -g_e \beta_n \frac{H m_I}{I} + (-1)^{|m_I|} + \frac{1}{2} \frac{e^2 Q q}{4} \quad (29)$$

All four magnetic sub-levels are displaced by the same amount. This is illustrated in Fig. 2.6 for the case where the major axis of the electric field gradient tensor is positive.

Figure 2.6.



Hyperfine splitting with V_{zz} parallel to H and > 0 .

For the case of an axially symmetric electric field gradient with a symmetry axis at an angle θ with respect to the magnetic

axis, when e^2Qq is much less than H , the energy levels are given by:

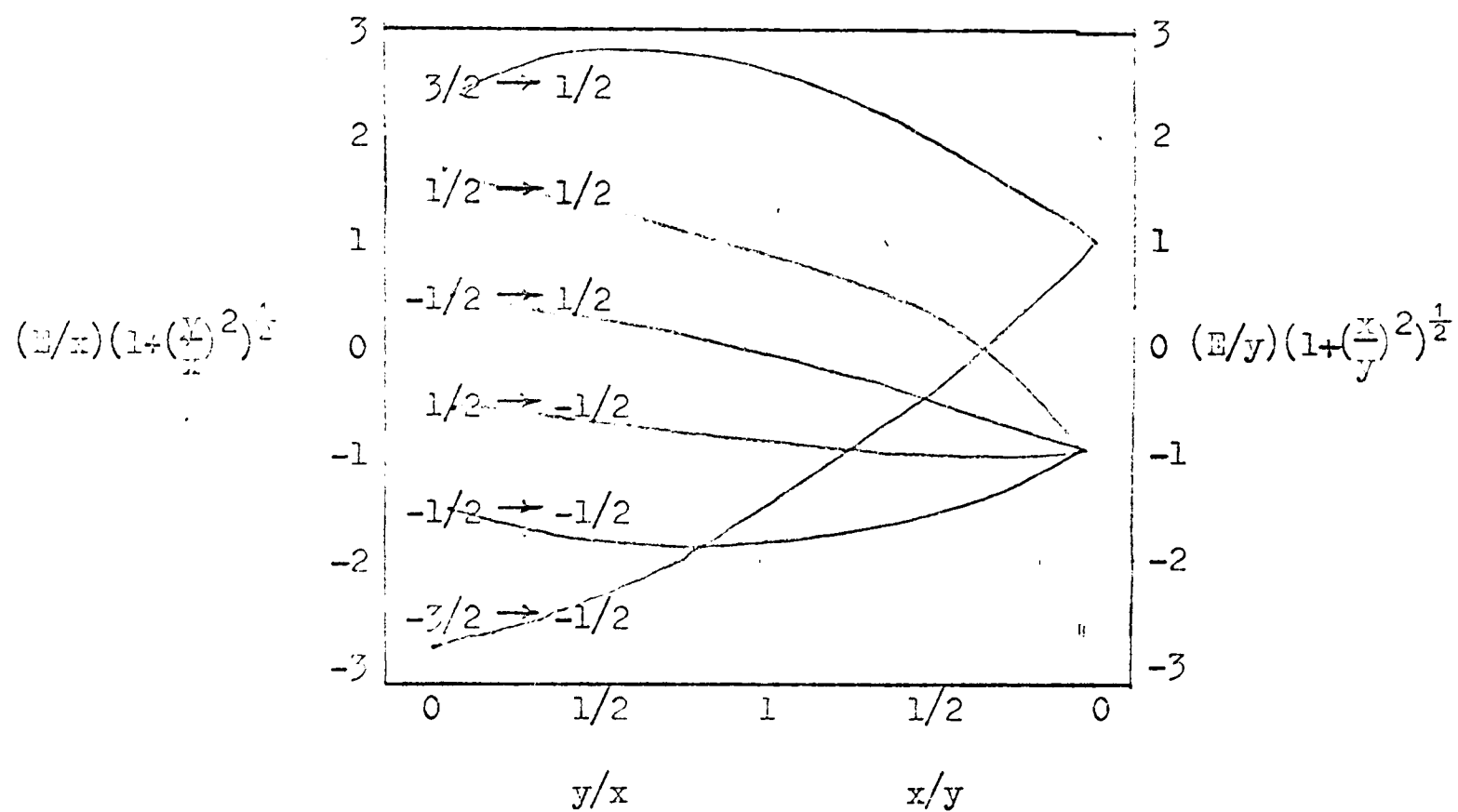
$$E_e = -g_e \beta_n H m_I + (-1)^{|m_I|} + \frac{1}{2} \frac{e^2 Q q}{4} \frac{3 \cos^2 \theta - 1}{2} \quad (30)$$

When the symmetry axis of the electric field gradient is perpendicular to the axis of magnetisation, the above equation (eq. (30)) becomes:

$$E_e = -g_e \beta_n H m_I + (-1)^{|m_I|} + \frac{1}{2} \frac{e^2 Q q}{8} \quad (31)$$

The quadrupole splitting observed in a perpendicular magnetic field will therefore be of opposite sign and half the magnitude of the splitting observed in zero field. For a powder specimen geometrical conditions favour the magnetic field to be perpendicular to the symmetry axis of the ligand field.

The relative separations of the absorption lines of the six line spectrum depend on the ratio of the magnetic field to the electric field gradient and have been evaluated for the Fe^{57} nucleus for the case where the symmetry axis of the electric field gradient is perpendicular to the axis of magnetisation⁽⁵²⁾. This is illustrated in Fig. 2.7.

Figure 2.7.

$$x = \frac{g_N \hbar}{2}, \quad y = \frac{e^2 Q q}{4}, \quad \frac{e q}{g_N} = -0.572$$

Separation of the six line spectrum for the ^{57}Fe nucleus at different magnetic field and electric field gradient ratios.

2.11. Electron paramagnetic resonance.

Epr is a powerful tool for the study of paramagnetic complexes. The method has been applied where possible to the investigation of the iron-sulphur complexes that we have prepared. Results from other sources are also discussed. A brief consideration of the principles and methods of epr spectroscopy is therefore given here.

2.12. Introduction.

When an isolated paramagnetic ion is placed in a magnetic field of strength H , its energy levels are split by the Zeeman Effect, and the energy of the resulting levels is given by:

$$E = g\beta H M_J \quad (32)$$

where g is the Lande g -factor defined by:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (33)$$

where L and S are the orbital and spin angular momentum quantum numbers, J is the total angular momentum quantum number and M_J is the component of J along the field acting on the ion. Transitions between M_J levels can be induced by subjecting the sample to electromagnetic radiation of the appropriate frequency. The resonance condition is:

$$h\nu = g\beta H \quad (34)$$

and the selection rule is $\Delta M_J = \pm 1$.

For a free electron $g = 2.0023$ and epr transitions at values of ν and H corresponding to values of g close to the free electron

value are commonly observed in organic free radical species. In transition metal compounds however, the situation is considerably modified as other perturbations apart from the first order Zeeman Effect are important in determining the number and energies of the electron spin states. The important interactions are those due to i) exchange interactions, ii) the ligand field and iii) hyperfine interactions due to nuclear spin.

i) Exchange interactions

Magnetic dipolar coupling and exchange effects between neighbouring paramagnetic species may dramatically alter the nature of the lowest electronic levels. The information obtained from the epr spectrum on the properties of discrete molecules is then of limited value. Hence epr measurements are carried out in dilute solution ($\sim 10^{-3}M$) or in diamagnetic solids doped with a small quantity of the paramagnet.

ii) The ligand field

When an atom is placed in a chemical environment the orbital motion of its electrons is strongly perturbed. Epr transitions are then observed at experimentally determined g-values such that:

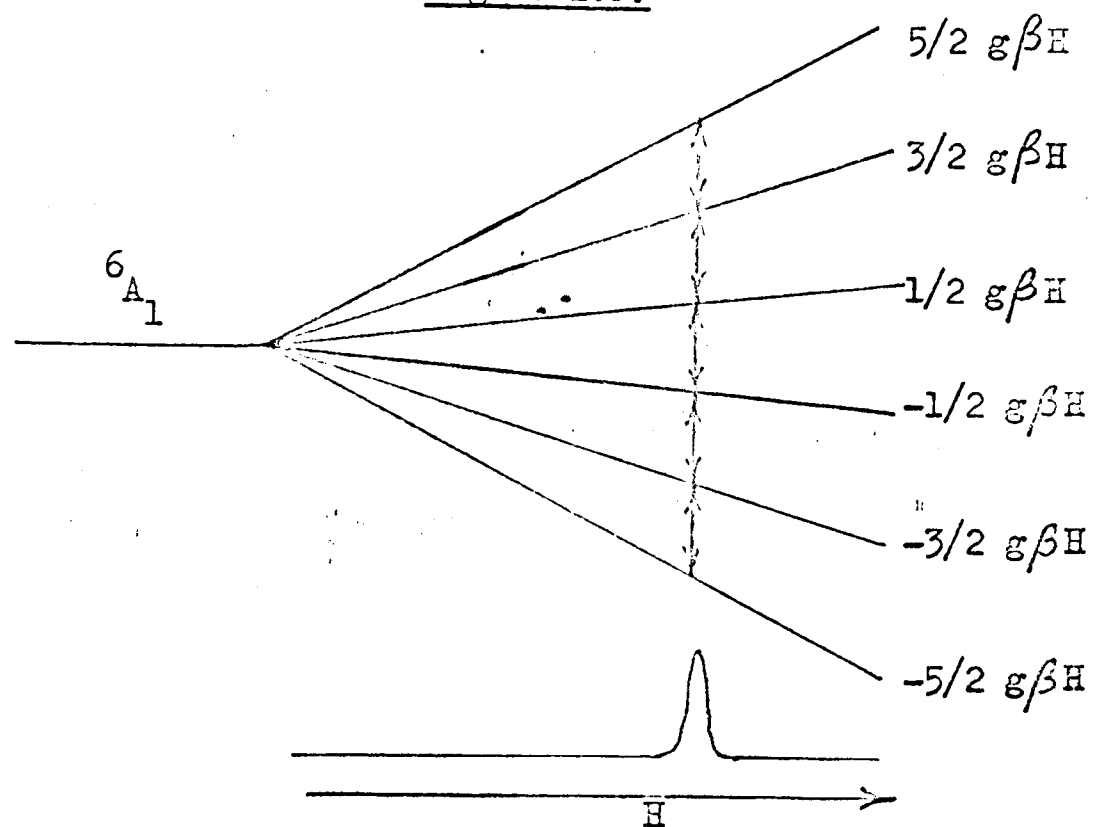
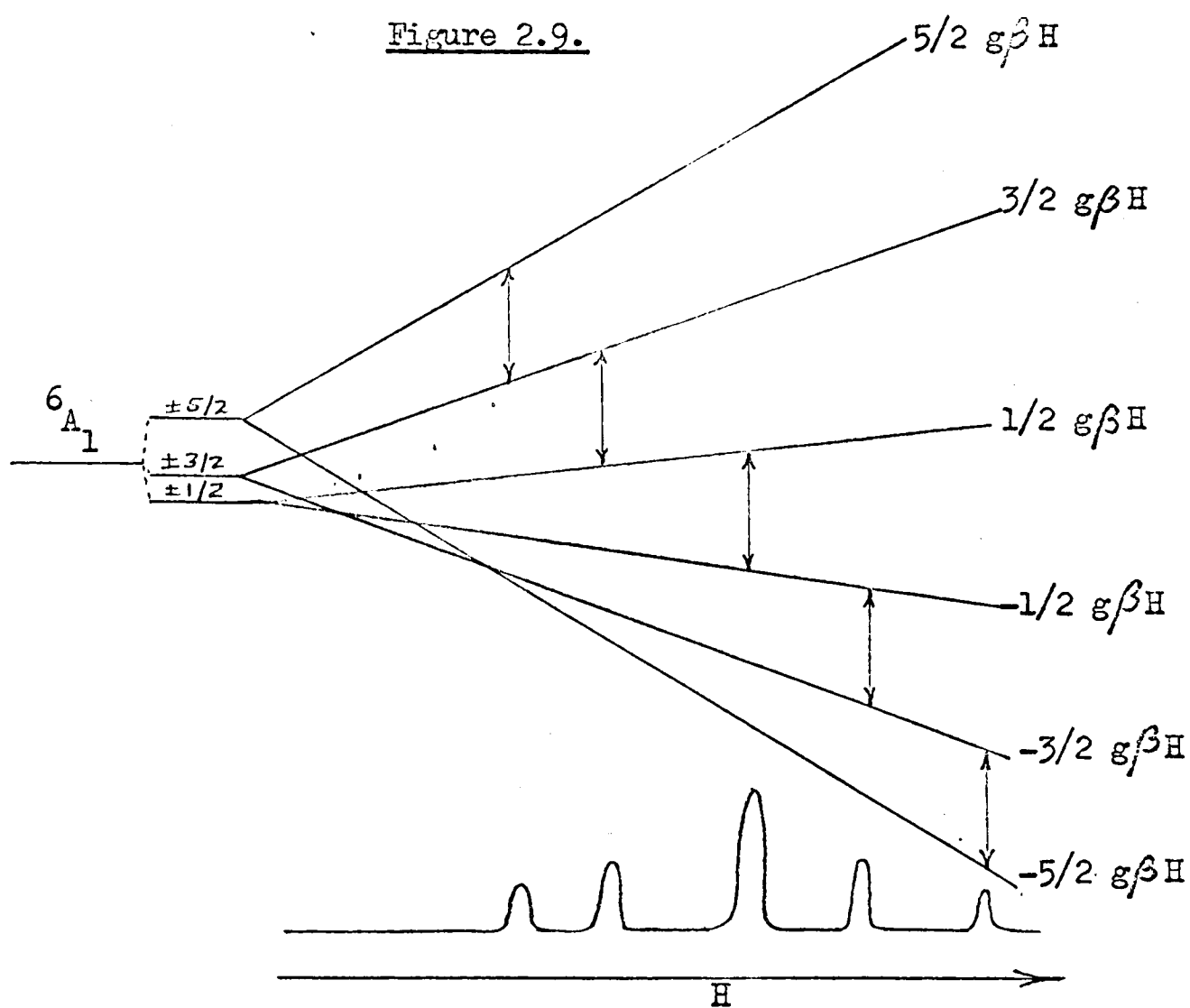
$$g = h\nu / \beta H \quad (35)$$

The orbital degeneracy of an isolated transition metal ion is partly lifted when the ion is placed in a ligand field. If the degeneracy were completely removed, the orbital angular momentum would be completely quenched and an isotropic g-value of 2 would always be observed. However, spin-orbit coupling opposes the quenching as it tends to sustain

the orbital angular momentum by coupling it with the spin angular momentum. The g-value then differs from 2 by an amount related to the spin-orbit coupling.

If the metal ion is in a field of non-cubic symmetry the g-value will also be anisotropic. The splitting of the M_J levels will vary with direction and the measured g-value will depend on the orientation of the complex with respect to the magnetic field.

A further consequence of ligand field components of low symmetry is that the degeneracy of the M_J levels may be lifted, even in the absence of a magnetic field. This zero field splitting is a consequence of a second order spin-orbit coupling perturbation. The first order spin-orbit coupling interaction, described above, leads to deviations of the g-value from the spin only value. The second order interaction changes the energies of the M_J levels. The situation is illustrated for the high spin ferric ion which has a 6A_1 ground state. In cubic symmetry, the degeneracy of the M_J levels is lifted. The energy levels diverge linearly with field strength. The five possible transitions occur at the same energy and a single line spectrum is observed (Fig. 2.8.). When a small axial field is present the degeneracy of the M_J levels is lifted. When the magnetic field is applied the energy levels no longer diverge linearly with increasing field and all five transitions may be detected (Fig. 2.9.).

Figure 2.8.Figure 2.9.Zero field splitting.

iii) Hyperfine splitting

If the metal ion which contains unpaired electrons also possesses a nuclear spin I , each M_J level is $(2I + 1)$ -fold degenerate with respect to the nuclear spin. In a magnetic field this degeneracy is removed and transitions can occur in the epr spectrum according to the selection rules $\Delta M_J = \pm 1$, $\Delta M_I = 0$. Hyperfine splitting may also arise from the interaction of unpaired electrons with the ligand nuclei, if the unpaired electron has a finite probability density at the ligand nucleus. A considerable amount of information about the unpaired electron distribution can be obtained from the hyperfine splitting.

2.13. The complementary nature of Mössbauer spectroscopy and epr.

The value and scope of the techniques of Mössbauer spectroscopy and epr spectroscopy may be realised by considering the expression used to describe the energy of the electron and nuclear interactions. The general Hamiltonian is given by⁽⁵³⁾:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{LF} + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_N + \mathcal{H}_Q + \mathcal{H}_H + \mathcal{H}_h \quad (36)$$

where $\mathcal{H}_0$ is that part of the Hamiltonian of the free ion that depends only on the configurational variables of the electrons and not on their spins; $\mathcal{H}_{LF}$ is the part describing the effect of the ligand field;

$\mathcal{H}_{LS}$ describes the magnetic interactions between the electron spins and the orbital moments; $\mathcal{H}_{SS}$ describes the mutual interaction between the magnetic moments due to electron spin; $\mathcal{H}_N$ describes the interaction between the magnetic moment of the nucleus and the magnetic field

resulting from the orbital and spin moments of the electrons; $\mathcal{H}_Q$ is the term describing the interaction between the electrons and the nuclear quadrupole moment; $\mathcal{H}_H$ describes the interaction of the electrons with an external field and $\mathcal{H}_h$ describes the direct interaction of the nuclear moment with the external field.

The isomer shift observed in the Mössbauer spectroscopic experiment depends on $\mathcal{H}_0$ essentially, although further perturbations, from $\mathcal{H}_{LF}$ and $\mathcal{H}_{LS}$ especially, may also be important. The quadrupole splitting parameter depends on $\mathcal{H}_Q$. The effective field observed at the Mössbauer nucleus due to the Fermi contact term depends on $\mathcal{H}_N$. In Mössbauer experiments conducted in applied magnetic fields $\mathcal{H}_H$ and $\mathcal{H}_h$ may become important.

The total Hamiltonian is in general very complex. For the interpretation of epr experiments Abragam and Pryce⁽⁵³⁾ developed a perturbation procedure for the calculation of the splittings within the ground state of the paramagnetic ion. The method employs the so-called spin-Hamiltonian which is the sum of those terms of the total Hamiltonian involving spin operators.

2.14. The spin-Hamiltonian.

The lowest energy levels between which transitions are observed in an epr experiment are usually well separated from all higher lying levels. The spin-Hamiltonian is a perturbing potential which when applied to the wave functions of the levels concerned yields their

energies. It provides a standard phenomenological way in which the epr spectrum can be described in terms of a small number of constants. Once values for the constants have been determined from experiment, calculations relating them back to the energy states of the ion are possible, although this may prove to be very difficult.

The spin-Hamiltonian for the case where the ground state is an orbital singlet is given by⁽⁵³⁾:

$$\mathcal{H}_S = \beta H_i g_{ij} S_j + S_i D_{ij} S_j + S_i A_{ij} I_j + I_i P_{ij} I_j + \gamma \beta_N H_i I_j \quad (37)$$

where g_{ij} , D_{ij} , A_{ij} and P_{ij} are components of the tensor quantities $\underline{g}$, $\underline{D}$, $\underline{A}$, and $\underline{P}$. g is the spectroscopic splitting factor determined from experiment according to eq. (35), and containing contributions from higher states as well as the spin only value. D_{ij} describes the zero field splitting of the ground state and arises from terms in $\mathcal{H}_{LS}$ and $\mathcal{H}_{SS}$ as well as $\mathcal{H}_{LF}$. A_{ij} characterises the magnetic interactions between the electrons and the nucleus and arises from $\mathcal{H}_N$ and P_{ij} describes the quadrupole interaction, $\mathcal{H}_Q$. The last term in eq. (37) is equivalent to $\mathcal{H}_h$ of the total Hamiltonian.

The value that S takes in the spin-Hamiltonian is that of a fictitious spin characterising the $(2S + 1)$ levels between epr transitions are observed. It may or may not equal the free ion spin.

The spin-Hamiltonian has been used in the interpretation of the magnetic hyperfine interactions of Mössbauer spectra⁽⁵⁴⁾ as well as

being widely applied to epr. In the consideration of the epr spectra of iron compounds the term $A\mathbf{S}\cdot\mathbf{I}$ may usually be neglected since hyperfine splitting is rarely observed in the epr spectrum of unenriched iron compounds. In a Mössbauer experiment, however, this term is important since it is the ^{57}Fe nucleus ($I_g = 1/2$, $I_e = 3/2$) that gives rise to the Mössbauer spectrum.

The application of the principles above to the cases that particularly concern us, namely the high-spin and low-spin ferric ions, will now be considered.

2.15. The high-spin ferric ion.

In a weak octahedral field the ground state of the ferric ion is 6A_1 . Higher order interactions than spin-orbit coupling and the crystal field, together with an axial field split the 6A_1 state into three Kramers doublets. The spin-Hamiltonian for a complex of orthorhombic or lower symmetry is⁽⁵⁵⁾:

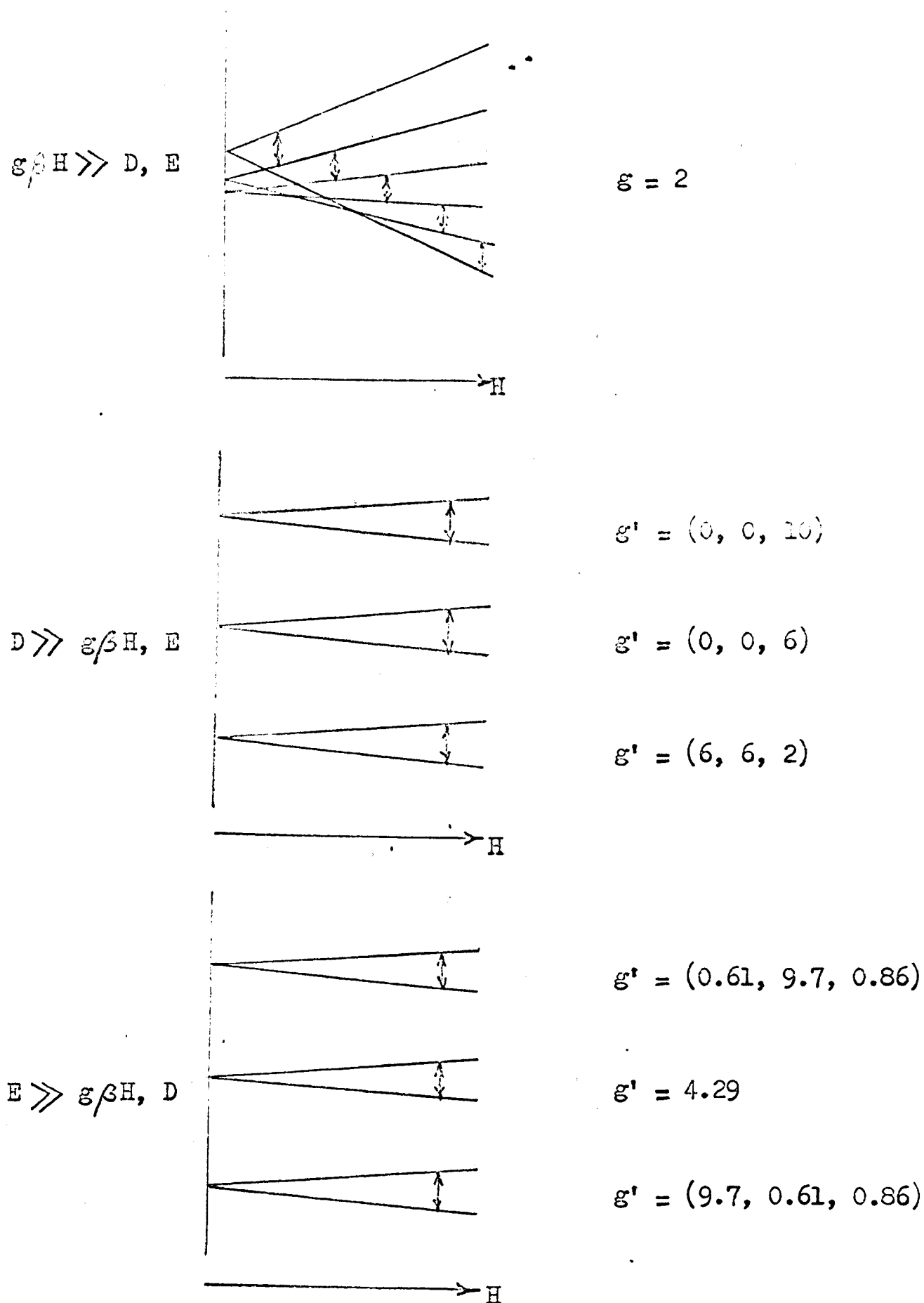
$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2) \quad (38)$$

where D is the axial fine structure term and E is the rhombic fine structure term.

Fig. 2.10 illustrates the situations when different terms in the Hamiltonian are dominant. If the Zeeman term, $g\beta\mathbf{H}$, is much larger than D and E the Hamiltonian becomes:

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} \quad (39)$$

The energy levels are $\pm 1/2 g\beta H$, $\pm 3/2 g\beta H$ and $\pm 5/2 g\beta H$ so that an

Figure 2.10.

Energy levels and apparent g -values when different terms are dominant

in the high-spin ferric ion spin-Hamiltonian.

isotropic g of 2 is observed⁽⁵⁶⁾. When D or E are much larger than the magnetic field energy it is possible to use a spin-Hamiltonian with fictitious spin S' of $1/2$ for the lowest doublet. When D is dominant and positive, $g_{\parallel} = 2$ and $g_{\perp} = 6$ ⁽⁵⁷⁾; when E is large, apparent g -values corresponding to an isotropic transition at $g = 4.29$ and to two anisotropic transitions with g -values ranging from 0.61 to 9.7 are observed⁽⁵⁸⁾.

2.16. The low-spin ferric ion.

The epr spectra of low-spin d^5 ions have been treated theoretically by Stevens⁽⁵⁹⁾ and discussed by Griffith⁽⁶⁰⁾.

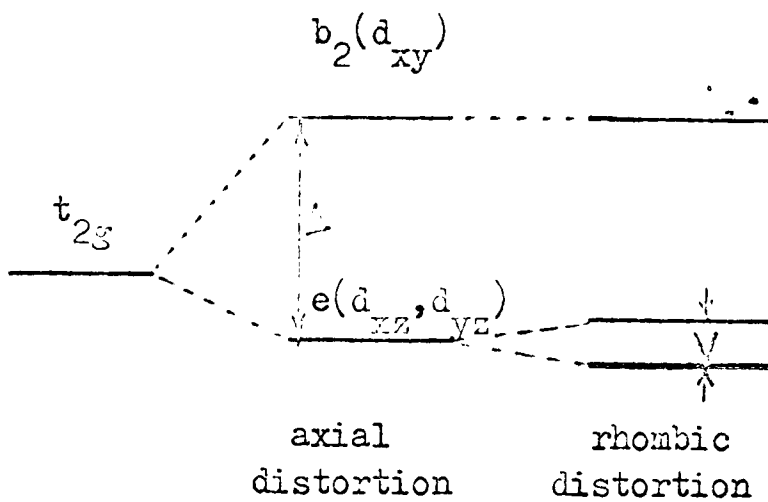
In strong crystal fields the ground state of the ferric ion is 2T_2 . The t_{2g}^5 configuration can be considered to be a hole in the closed t_{2g}^6 subshell. If the symmetry is cubic, this state is six-fold degenerate (orbital $\times$ spin). Under the influence of axial and rhombic distortions the degeneracy is lifted and the one hole real functions, ζ (xy), η (xz) and ξ (yz), have energies $\frac{1}{2}V$, $-\frac{1}{2}V$ and Δ respectively. (Fig. 2.11.)

A general form is assumed for the ground doublet:

$$\begin{aligned}\Psi &= A|1^+\rangle + B|\xi^-\rangle + C|-1^+\rangle \\ \Psi' &= A|-1^-\rangle - B|\xi^+\rangle + C|1^-\rangle\end{aligned}\tag{40}$$

where $+$ or $-$ represents spin up or down respectively and

$$\begin{aligned}|1\rangle &= -(\eta + i\xi)/\sqrt{2} \\ |-1\rangle &= (\eta - i\xi)/\sqrt{2}\end{aligned}$$

Figure 2.11.Energy level diagram for t_{2g} orbitals in one hole formalism.

$$\chi = (|2\rangle - |-2\rangle) / \sqrt{2} = i\zeta$$

The energy of each state and the coefficients of eq. (40) are found from the eigenvalues of the perturbation matrix which describes the coupling of the basis wave functions. The interaction with the magnetic field is represented by $\beta(g_x H_x + g_y H_y + g_z H_z)$ where:

$$g_x = 2(2AC - B^2 + kB(C - A))/2 \quad (41)$$

$$g_y = 2(2AC + B^2 + kB(C + A))/2 \quad (42)$$

$$g_z = 2(A^2 - B^2 + C^2 + k(A^2 - C^2)) \quad (43)$$

where k is an orbital reduction factor that takes account of covalency.

From the experimental g -values it may be possible to evaluate A, B, C and k and hence calculate the energy of the states. However, the process may be extremely complex and may have more than one solution. Good agreement has been found for epr measurements on

$K_3Fe(CN)_6$ diluted in $K_3Co(CN)_6$ ⁽⁶¹⁾, and more recently the method outlined above has been applied to a number of measurements on low-spin d^5 complexes of metals of the second and third transition series ⁽⁶²⁾.

PART TWO. Experimental methods.

Mössbauer spectroscopy.

Mössbauer spectra were recorded using the facilities at A.E.R.E., Harwell. A diagram of the apparatus is shown in Fig. 2.12.

2. 17. The source.

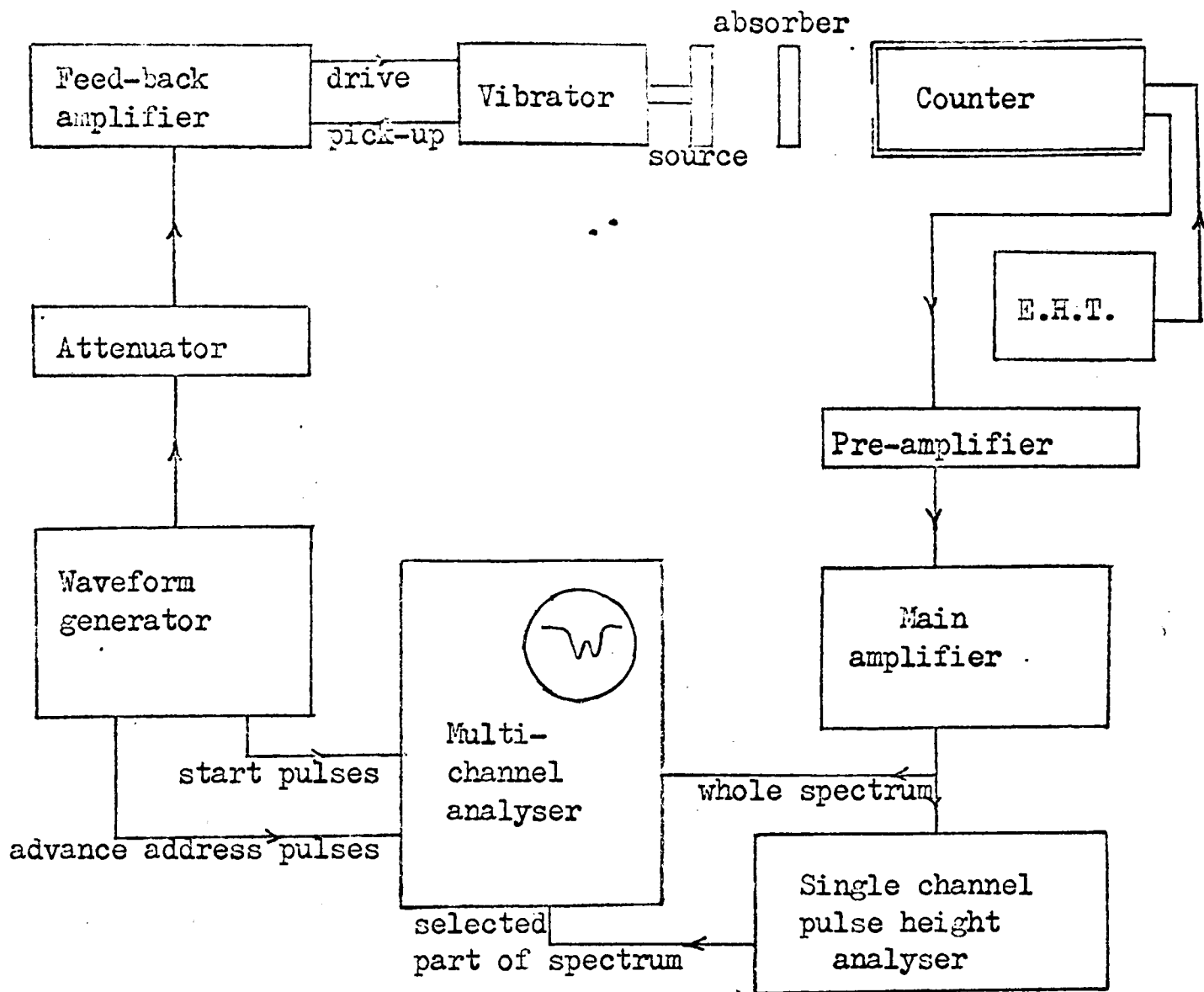
The sources used were ^{57}Co diffused into chromium or palladium foil. They were supplied by the Radiochemical Centre, Amersham. Source strengths ranged up to 100mc. Typical line widths of these sources were of the order of $0.24 \text{ mm. sec.}^{-1}$

2.18. Electronics.

The source was moved by a vibrator system described by Cranshaw⁽⁶³⁾. The motion of the source and a plot of source velocity vs. time is shown in Fig. 2.13.

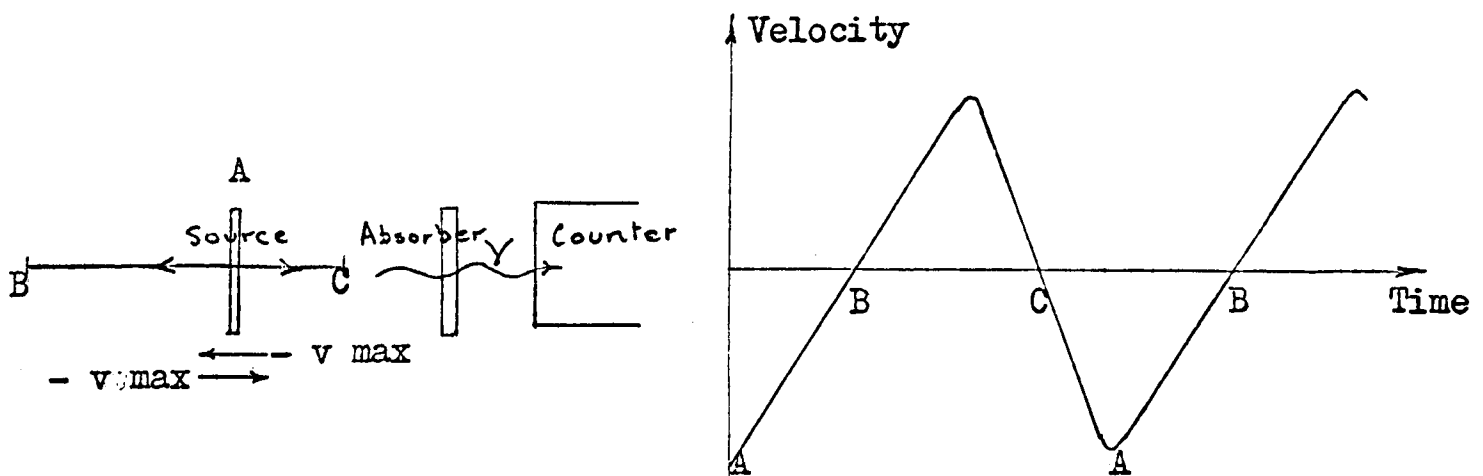
The gamma radiation from the source, after passing through the absorber entered an argon filled proportional counter. The pulses from the counter were amplified and stored in a multichannel analyser. A single channel pulse height analyser was used to set a 'window' on the 14.4keV gamma ray peak, thus ensuring that the spectrum observed was that due to the 14.4keV gamma rays.

The spectrum of counts vs. velocity was stored in 256 channels of the multichannel analyser. Each channel corresponded to 1/256th of the velocity sweep. Synchronism between the mechanical motion of the source and the rate at which the multichannel analyser stepped through



Block diagram of the Mössbauer spectrometer.

Figure 2.13.



The fly-back A $\rightarrow$ C $\rightarrow$ A occurs in half the time of the velocity sweep A $\rightarrow$ B $\rightarrow$ A.

The motion of the source.

its channels was maintained by a pulse from the waveform generator which triggered the analyser at the start of the velocity sweep.

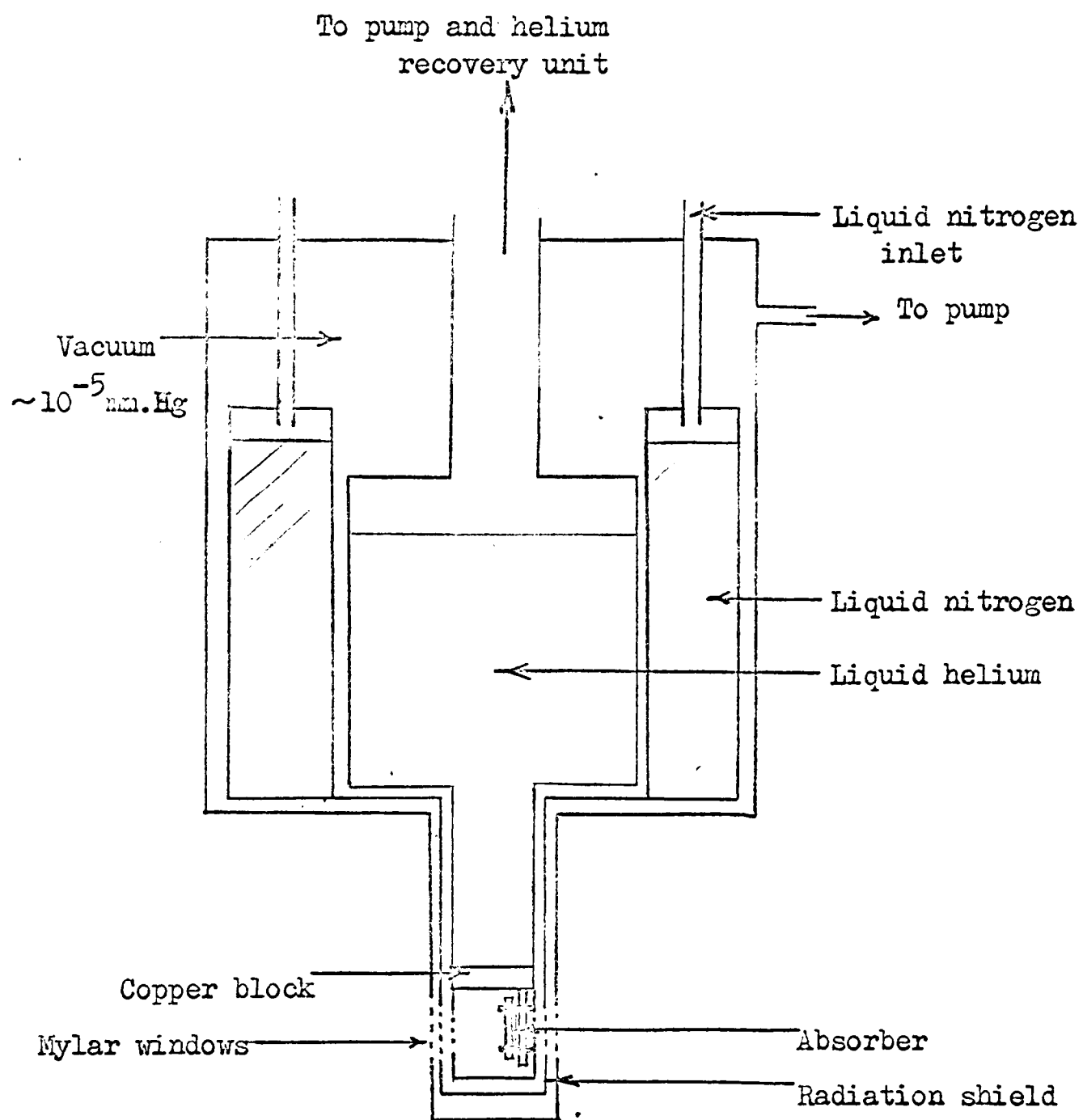
The spectrum was displayed on the oscilloscope screen. The data from the store was read out on to cards using an IBM card punch unit.

2.19. Dewars and magnets.

The samples were mounted between two pieces of aluminium foil which was fixed with grease over a small hole in 1/16" thick lead sheet. For room temperature measurements the cell was suspended over the end window of the counter. Source and counter were then aligned to give as high a count rate as possible while keeping a small solid angle between the source and the counter.

For measurements at 77°K and 195°K the sample holder was clamped into a brass fitting attached by a thick copper rod to the bottom of a Dewar. Refrigerants used were liquid nitrogen and acetone/dry ice. Pressures of 10^{-5} mm. Hg were maintained inside the Dewar, thus restricting evaporation of the refrigerant and reducing vibrations due to this. It was assumed that the sample was at the temperature of the refrigerant, having been allowed to cool for an hour or so before measurement of the spectrum was started.

The Dewar used for measurements at liquid helium temperatures is illustrated in Fig. 2.14. It was constructed to enable pumping on the liquid helium to be effected and temperatures as low as

Figure 2.14.The liquid helium Dewar for Mössbauer measurements.

1.1°K could thus be obtained. Temperatures were estimated by the use of pressure to temperature conversion tables.

A few measurements were made at temperatures just above that of liquid helium. For this a variable temperature device designed by Dr. B. Window was used. The sample was contained in a vacuum tight chamber which was immersed in liquid helium. A small heater coil enabled the sample to be warmed above the temperature of liquid helium. The temperature was measured by a copper-constantan thermocouple and could be held constant to within 0.5°.

Magnetic fields of up to 5kG could be applied to the samples in the nitrogen and helium Dewars by placing an electromagnet about the tailpiece of the Dewar. The magnetic field was perpendicular to the direction of the gamma ray beam. Larger magnetic fields were applied in a special Dewar containing a superconducting magnet. The absorber was immersed in liquid helium and surrounded by the magnet coils. The axis of the superconducting solenoid was perpendicular to the gamma ray direction. Fields of up to 30kG could be applied to samples in this apparatus.

2.20 The method of obtaining the parameters.

The Mössbauer parameters quoted in this thesis are with respect to iron metal as standard. The positions of the six lines of the iron spectrum have been accurately determined⁽⁶⁴⁾. The centre of the spectrum at room temperature is taken as zero velocity. This

standard has the advantages that it is readily available and reproducible, the quoted shifts are independent of the source used, since the same source is used for calibration, and the six line spectrum enables the linearity of the source motion to be checked.

The parameters were obtained by computation of the data. The data for the required spectrum were fed into an IBM 360/60 computer together with a calibration spectrum of metallic iron taken shortly before or after the required spectrum, on the same apparatus in as nearly as possible the same geometry. The positions of the lines of the iron spectrum was determined by the computer and hence the zero velocity point and scale of the spectrum was determined. A plot of the percentage effect vs. velocity was then carried out. This program was written by Dr. M. S. Ridout.

Other programs were used to obtain accurate values of peak positions. Approximate values of peak position, width and intensity were given. Line shapes were assumed to be Lorentzian and a least squares analysis was carried out for each line. Programs devised by Dr. B. Window and Dr. M. S. Ridout have been used for this analysis. The accuracy of the fitted parameters is estimated as $\pm 0.02 \text{ mm. sec.}^{-1}$

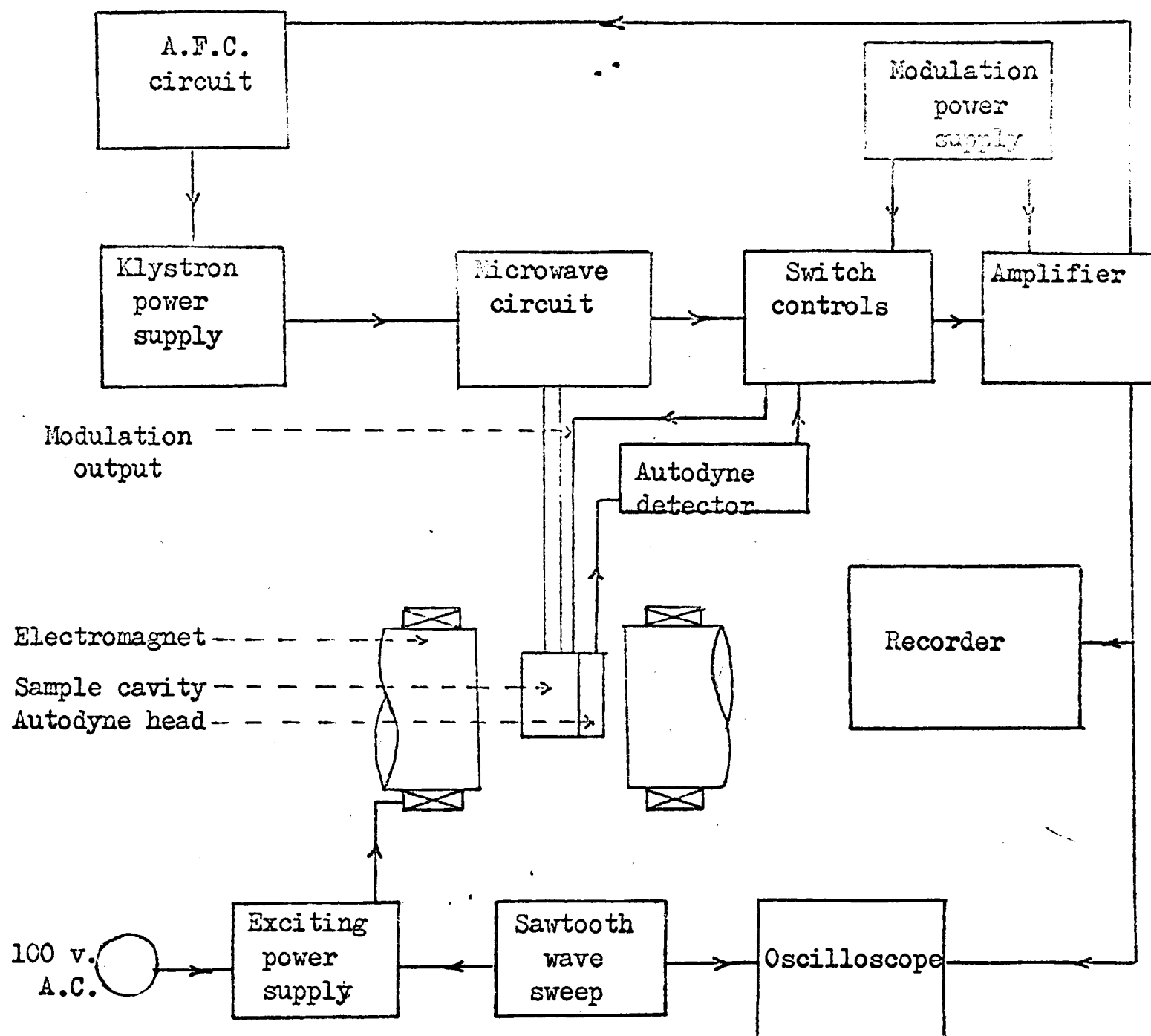
2.21. Electron paramagnetic resonance. Experimental details.

Epr spectra were recorded on a Japan Electronics Optics Laboratory JES-3BX spectrometer operating at a frequency of ~9200 Mcs. with 100 Mcs. modulation. A block diagram of the instrument is shown in Fig. 2.15.

The sample was placed in a silica tube which was placed between the poles of the electromagnet in the resonance cavity. The sample was then subjected to electromagnetic radiation of microwave frequency. The radiation originated from a klystron and was transferred to the cavity by means of a waveguide. The frequency of the radiation was constant. A magnetic field was applied perpendicular to the radiation direction and was varied by varying the electromagnet current. When the resonance condition was satisfied some of the radiation was absorbed. The absorption of the radiation was detected, amplified and recorded on chart paper. A plot of the first derivative of the absorption curve vs. the magnetic field strength was obtained.

The spectrum was calibrated by the use of a diphenylpicrylhydrazyl (DPPH) marker. DPPH resonates sharply at $g = 2.0036^{(65)}$. Splittings could be calibrated by the use of a nuclear magnetic resonance marker.

Spectra could be recorded at temperatures between 300°K and 100°K by cooling the sample using a variable temperature attachment. This device allowed a stream of cold nitrogen gas to be

Figure 2.14.Block diagram of the electron paramagnetic resonance spectrometer.

passed through the cavity containing the sample. The gas flow was generated by the evaporation of liquid nitrogen using an electric heater. The temperature was measured using a copper-constantan thermocouple.

Measurements at 4.2°K required the use of a special cavity which was incorporated into a liquid helium Dewar. These measurements were carried out at 80 cs. modulation.

Some epr measurements were also carried out on a Varian epr spectrometer at Imperial College London by kind permission of, and with the assistance of Dr. J.F. Gibson.

CHAPTER THREE. SOME COMPLEXES OF IRON WITH DIALKYLDITHIOCARBAMATE LIGANDS.

3.1. Introduction.

The dialkyldithiocarbamic acids, $RR'NCS_2H$, are unstable compounds⁽⁶⁶⁾, but they are stabilised by complex formation with many metals⁽⁶⁷⁾⁽⁶⁸⁾. Iron forms a number of different types of complex with these ligands covering a variety of oxidation states and spin states.

Ferrous salts react with the sodium salts of dialkyldithiocarbamic acids to give pale green complexes, $Fe(dtc)_2$. These have been shown to be five coordinate in the solid state⁽⁶⁹⁾ but little other work has been reported on these complexes.

The iron(III) N,N dialkyldithiocarbamates have been extensively studied due to their unusual magnetic properties. They have been assumed to have the structure shown in Figure 3.1, where coordination to the metal atom occurs via the sulphur atoms. Cobalt(III) N,N diethyldithiocarbamate, which is isomorphous with iron(III) N,N diethyldithiocarbamate⁽⁷⁰⁾, has a structure closely similar to that shown⁽⁷¹⁾. Iron(III) N,N di-n-butyldithiocarbamate, which has many anomalous properties and is not isomorphous with its cobalt(III) analogue has the unusually distorted structure shown in Figure 3.2⁽⁷²⁾.

One of the dialkyldithiocarbamate ligands of the iron(III) tris complexes can be replaced by a halide ion to give the

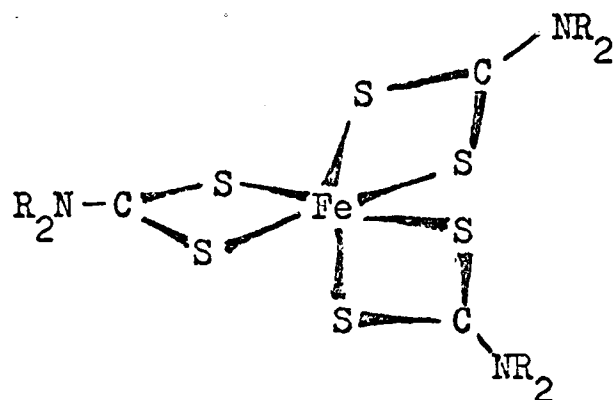
five coordinate bis(N,N dialkyldithiocarbamato)iron(III) halides⁽⁷³⁾ (Figure 3.3). These complexes have magnetic moments corresponding to a spin S of 3/2.

A related complex is nitrosyliron bis(N,N diethyldithiocarbamate), which has the structure shown in Figure 3.4⁽⁷⁴⁾. Infra red⁽⁷⁵⁾ and epr⁽⁷⁶⁾ measurements indicate that the formal oxidation state of the iron in this complex is one.

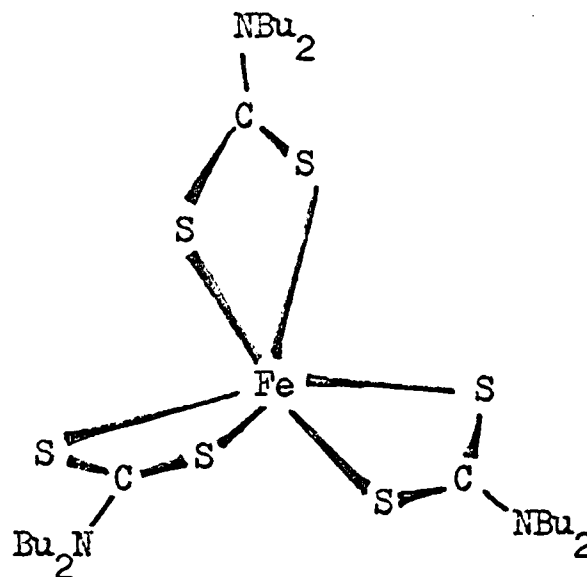
We have investigated the Mössbauer spectra of representative complexes of all the types described above, except the poorly characterised iron(II) complexes. The measurements provide information on the properties of iron in the several oxidation states, spin states and stereochemistries found in the dialkyldithiocarbamate complexes.

3.2. The iron(III) N,N dialkyldithiocarbamates.

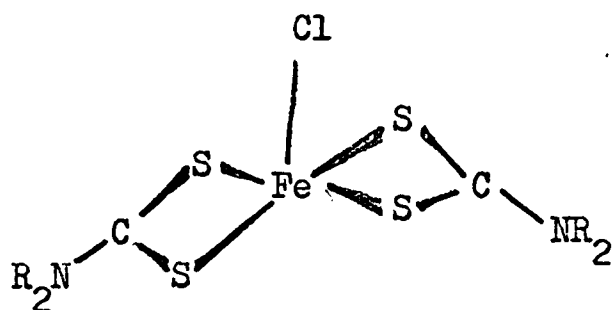
Cambi and his co-workers first observed that the magnetic moments of the iron(III) N,N dialkyldithiocarbamates had values intermediate between the values expected for typical high-spin or low-spin ferric complexes⁽⁷⁷⁾. The magnetic moment depended on the alkyl substituent and was also found to be temperature dependent⁽⁷⁸⁾. It was proposed that an equilibrium existed between 'isomeric forms of different magnetic properties'. White et al.⁽⁷⁹⁾ and Ewald et al.⁽⁸⁰⁾ verified Cambi's original results and showed that the anomalous behaviour was not due to any kind of intermolecular interaction. It was further shown that

Figure 3.1.

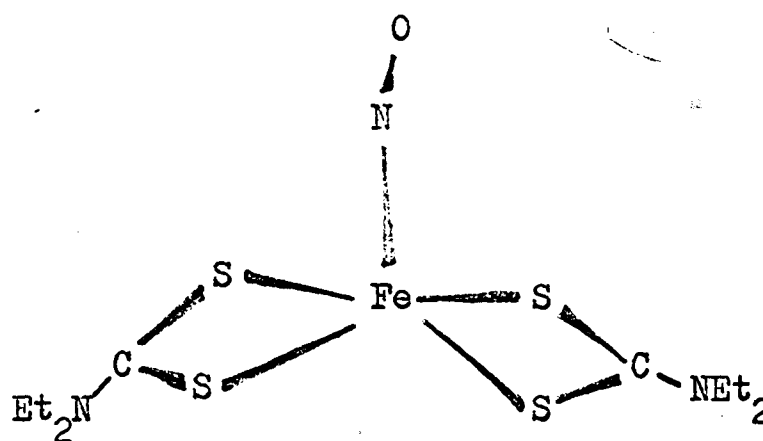
Assumed structure for the iron(III)
N,N dialkyldithiocarbamates.

Figure 3.2.

Structure of iron(III) N,N di-n-
butyldithiocarbamate.

Figure 3.3.

Structure of bis(N,N dialkyl-
dithiocarbamato)iron chlorides.

Figure 3.4.

Structure of nitrosyliron bis(N,N-
diethyldithiocarbamate).

the pressure dependence of the magnetic moments and the temperature dependence of the $d \leftrightarrow d$ transitions in the near infra red, were consistent with the concept of a high-spin, low-spin equilibrium.

A number of workers have investigated the Mössbauer spectra of the iron(III) N,N dialkyldithiocarbamates. The results obtained have not always been consistent and have been subject to a wide variety of interpretations. Wickmann and Trozzolo⁽⁸¹⁾ first reported measurements on these complexes, but later reported that the complexes they had studied were of the type $(R_2NCS_2)_2FeCl$ ⁽⁸²⁾.

Frank and Abeledo⁽⁸³⁾ reported room temperature Mössbauer spectra of a number of iron(III) N,N dialkyldithiocarbamates. Correlations between the isomer shifts, quadrupole splitting and magnetic moments were made but were limited by lack of data at lower temperatures.

Vainstein et al.⁽⁸⁴⁾ carried out measurements over a wider temperature range. The quadrupole splittings observed in the dimethyl and diethyl derivatives were ascribed to a non-equivalence of the iron-sulphur bonds. The temperature dependence of the quadrupole splitting was interpreted in terms of an equilibrium between two or three isomers. As the temperature decreased the equilibrium was presumed to shift towards that isomer having a spin intermediate between 1/2 and 5/2.

Golding and Whitfield⁽⁸⁵⁾ measured the Mössbauer spectra of some iron(III) N-phenyl, N-alkyldithiocarbamates over a limited temperature range. The values of the quadrupole splittings that they

observed were explained in terms of a model in which the iron atom was in an intermediate crystal field of slightly distorted octahedral symmetry. Nuclear magnetic resonance studies by the same group have been interpreted in terms of a similar model.⁽⁸⁶⁾

Another Mössbauer spectroscopic study of these complexes has recently been published.⁽⁸⁷⁾ The increase in quadrupole splitting with decreasing temperature is qualitatively interpreted in terms of the depopulation of the 6A_1 , high-spin, state. No unusual temperature dependence of the isomer shift was observed.

It was decided that a thorough investigation of the Mössbauer spectra of some iron(III) N,N dialkyldithiocarbamates was merited, in order to understand more fully both the spin equilibrium, and the nature of the iron-sulphur bond in a system in which the iron atom is coordinated to six sulphur atoms. Measurements were made over a wide temperature range, particular attention being paid to measurements at low temperatures and in external magnetic fields, when valuable information on the magnetic properties of the complexes can be obtained.

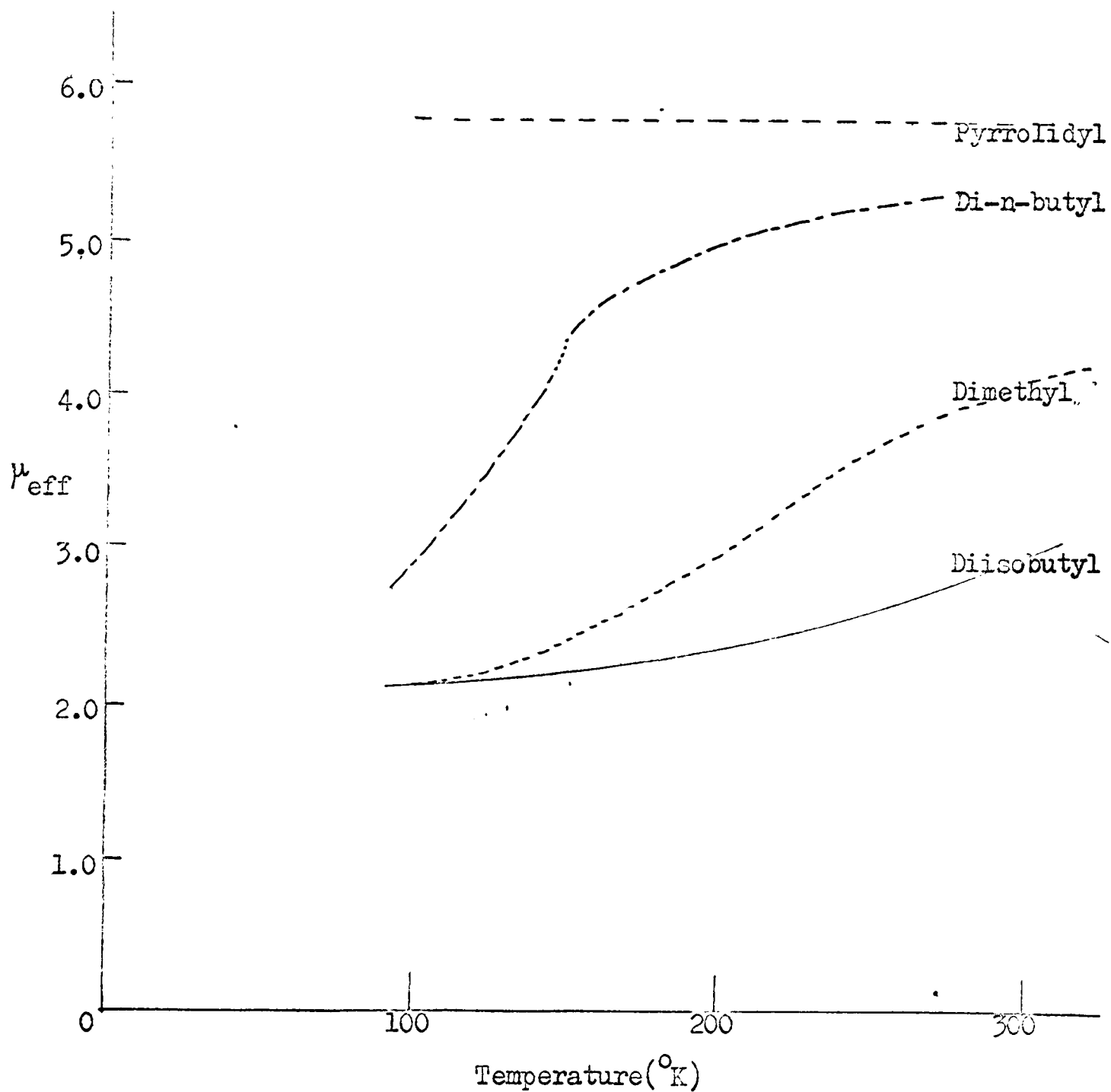
3.3. The present work.

The following work will be described in this chapter: Mössbauer Effect measurements have been carried out for four iron(III) N,N dialkyldithiocarbamates, for which detailed magnetic data is available⁽⁸⁰⁾. These were the pyrrolidyl, dimethyl, di-iso-butyl and di-n-butyl derivatives. Plots of the magnetic moments of these complexes vs.

temperature are shown in Figure 3.5. During the work it was felt that the study of a derivative with bulky alkyl groups would be useful in understanding the relaxation effects at low temperatures. The dicyclohexyl derivative was therefore prepared and studied. The results obtained are given in Table 3.1. Some of the spectra are illustrated in Figures 3.6 - 3.10. Some of the preliminary experimental results for this work were obtained in 1966 - 1967 and described in a dissertation submitted to fulfil the requirements of the Final Honour School of Natural Science, Chemistry Part II. The discussion was necessarily brief since the results available then were limited.⁽⁸⁸⁾

Preliminary results from the studies on iron(III) pyrrolidylthiocarbamate indicated that this high-spin complex exhibited unusual relaxation properties. Further Mössbauer Effect measurements have been carried out at temperatures from 1°K - 12°K to investigate the mechanism of the relaxation. The spectra obtained are shown in Figures 3.11 and 3.12.

It was interesting to compare the Mössbauer spectra of iron(III) pyrrolidylthiocarbamate with those of the five coordinate complexes, bis(N,N diethylthiocarbamato)iron chloride and bis(N,N diisopropylthiocarbamato)iron chloride. At low temperatures the Mössbauer spectra of all these compounds showed magnetic hyperfine interactions. Experiments have been carried out to establish the nature of the interaction producing the magnetic field at the iron nuclei in the different compounds.

Figure 3.5.

The temperature dependence of the magnetic moments of some iron(III)

N,N dialkyldithiocarbamates.

Mössbauer parameters for these samples are given in Table 3.3; the spectra are shown in Figures 3.13 and 3.14.

As a further extension of our work on the complexes of iron with dialkyldithiocarbamate ligands, a detailed Mössbauer Effect investigation of nitrosyliron bis(N,N diethyldithiocarbamate) has been carried out. The results obtained are given in Table 3.4. Some of the spectra are illustrated in Figures 3.15 and 3.16.

It was hoped that we should be able to complement our Mössbauer spectroscopic results on the iron(III) N,N dialkyldithiocarbamates with data from electron paramagnetic resonance studies. Previous attempts to detect epr in these complexes had been unsuccessful.⁽⁸⁹⁾ A sample of cobalt(III) N,N dimethyldithiocarbamate containing 1% of iron(III) N,N dimethyldithiocarbamate was prepared for this purpose. The epr spectrum obtained at 4.2°K is shown in Figure 3.17. The Mössbauer spectrum of a similar sample containing ^{57}Fe has been measured. The parameters are given in Table 3.2. The spectra obtained at low temperatures are shown in Figure 3.18.

3.4. Preparative methods.

(i) Iron(III) N,N dialkyldithiocarbamates.

These complexes were prepared by the method of White⁽⁷⁹⁾.

A slight excess of freshly precipitated ferric hydroxide was suspended in absolute ethanol. The appropriate secondary amine was added and the mixture stirred. Carbon disulphide, in amounts equimolar with the amine, was added

dropwise. The solution darkened and after about five minutes the reaction was complete. After filtration, the product was purified by dissolving in chloroform, filtering and reprecipitating by the gradual addition of absolute ethanol. The crystals were filtered off and dried in an oven at 50°C. The complexes tend to decompose in air and were freshly prepared shortly before use.

Analyses : Iron(III) pyrrolidylthiocarbamate, Found: C = 36.5% H = 5.2% N = 8.4%. Calc. for $((\text{CH}_2)_4\text{NCS}_2)_3\text{Fe}$, C = 36.4% H = 5.0% N = 8.5%.

Iron(III) N,N dimethyldithiocarbamate, Found: C = 26.5% H = 4.4% N = 10.2%. Calc. for $((\text{CH}_3)_2\text{NCS}_2)_3\text{Fe}$, C = 26.0% H = 4.4% N = 10.1%.

Iron(III) N,N diisobutyldithiocarbamate, Found: C = 48.7% H = 8.4% N = 6.3%. Calc. for $((^i\text{C}_4\text{H}_9)_2\text{NCS}_2)_3\text{Fe}$, C = 48.6% H = 8.1% N = 6.3%.

Iron(III) N,N di-n-butyldithiocarbamate, Found: C = 48.5% H = 8.4% N = 6.2%. Calc. for $((^n\text{C}_4\text{H}_9)_2\text{NCS}_2)_3\text{Fe}$, C = 48.6% H = 8.1% N = 6.3%.

Iron(III) N,N dicyclohexyldithiocarbamate, Found: C = 56.8% H = 7.9% N = 5.4%. Calc. for $((\text{C}_6\text{H}_{11})_2\text{NCS}_2)_3\text{Fe}$, C = 56.8% H = 8.1% N = 5.1%.

(ii) 1% iron(III) N,N dimethyldithiocarbamate in cobalt(III) N,N dimethyldithiocarbamate.

Cobalt(III) N,N dimethyldithiocarbamate was prepared by the addition of sodium dimethyldithiocarbamate (4.3g) in absolute ethanol (50ml) to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.4g) in absolute ethanol (50ml). The solution was stirred vigorously for two hours. The product was filtered off, recrystallised from chloroform/ethanol and dried in vacuo.

Analysis : Found, C = 27.4% H = 4.4% N = 10.5%. Calc. for $((CH_3)_2NCS_2)_3Co$,
C = 27.8% H = 4.6% N = 10.6%.

Cobalt(III) and iron(III) N,N dimethyldithiocarbamates were weighed out in 100:1 ratio and dissolved in the minimum quantity of chloroform. The solution was warmed and absolute ethanol was added. On cooling, crystals of the cobalt complex containing some iron complex were deposited. These were filtered off, washed thoroughly with absolute ethanol and dried in vacuo.

A sample containing ^{57}Fe was similarly prepared. ^{57}Fe was obtained from the Electromagnetic Separation Group, A.E.R.E., Harwell. It was dissolved in concentrated nitric acid. The solution was adjusted to pH 5. Addition of excess sodium dimethyldithiocarbamate precipitated the iron(III) complex which was thoroughly washed with absolute ethanol and dried in an oven at 50°C.

(iii) Bis(N,N dialkyldithiocarbamato)iron(III) chlorides.

These complexes were prepared by the method of Martin and White⁽⁷³⁾. The appropriate iron(III) N,N dialkyldithiocarbamate was dissolved in benzene. Concentrated hydrochloric acid was added dropwise. The mixture was shaken vigorously and the product precipitated. The product was filtered off, recrystallised from chloroform/carbon tetrachloride and dried in vacuo.

Bis(N,N diethyldithiocarbamato)iron(III) chloride, m.p. 254-256°C
(lit.⁽⁷³⁾ 250-255°C).

Bis(N,N diisopropyldithiocarbamato)iron(III) chloride, m.p. 299-300°C
(lit.⁽⁷³⁾ 300°C)

(iv) Nitrosyliron bis(N,N diethyldithiocarbamate).

This compound was prepared by the method of Adams and Raynor⁽⁹⁰⁾. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5g) was dissolved in dilute sulphuric acid (25ml, 2N). NaNO_2 (1.5g) and sodium diethyldithiocarbamate (10g) were added and the mixture was stirred vigorously for five minutes. The product was extracted with chloroform, from which it was also recrystallised. It was dried in vacuo.

Analysis : Found C = 31.8% H = 10.7% N = 5.0%. Calc. for $((\text{C}_{25}\text{H}_{52}\text{NCS})_2\text{FeNO})$,
C = 31.4% H = 10.4% N = 5.3%.

3.5. Results.Table 3.1.Mössbauer Effect data for some iron(III) N,N dialkyldithiocarbamates.

Compound	Temperature °K	Isomer shift δ mm.sec. ⁻¹	Quadrupole splitting ΔE_Q mm.sec. ⁻¹
$((CH_2)_4NCS_2)_3Fe$ Pyrrolidyl	300	0.40	0.36
	77	0.51	0.42
	4.2	0.53	0.20
$((CH_3)_2NCS_2)_3Fe$ Dimethyl	300	0.41	0.26
	195	0.43	0.47
	77	0.42	0.71
	4.2	0.49	0.78
	1.5	0.49	0.78
$((^iC_4H_9)_2NCS_2)_3Fe$ Di- isobutyl	300	0.39	0.33
	195	0.43	0.49
	77	0.46	0.59
$((^nC_4H_9)_2NCS_2)_3Fe$ Di-n-butyl	300	-	-
	253	0.4	-
	195	0.4	0
	77	0.44	0.66
$((C_6H_{11})_2NCS_2)_3Fe$ Dicyclohexyl	300	0.37	0.56
	195	0.43	0.66
	77	0.47	0.74

Table 3.2.

Mössbauer parameters for iron dimethyldithiocarbamate (1%) in cobalt dimethyldithiocarbamate.

<u>Temp. (°K)</u>	<u>δ mm.sec.⁻¹</u>	<u>ΔE_Q mm.sec.⁻¹</u>
300	0.42	0.23
195	0.40	0.46
77	0.41	0.71

Table 3.3.

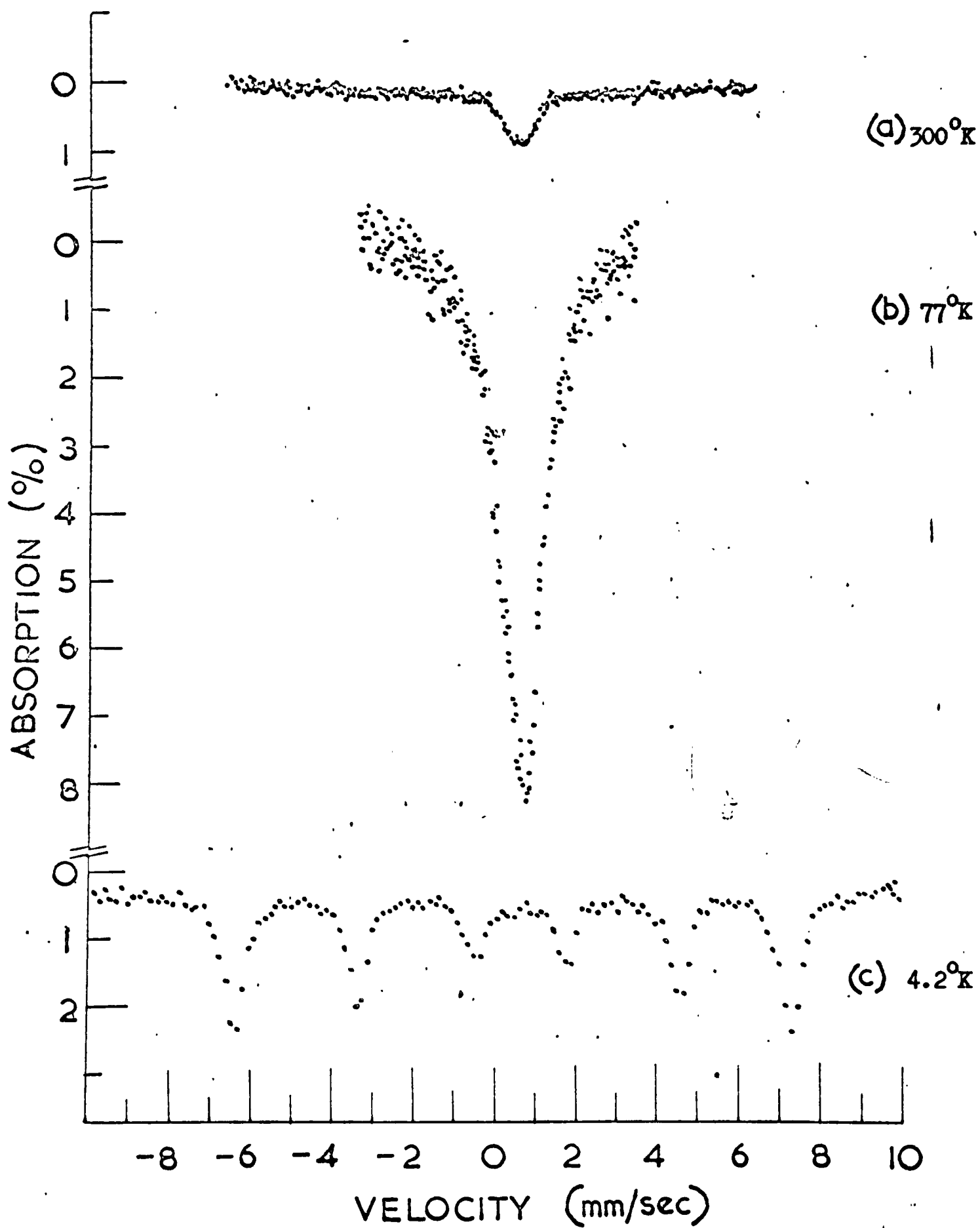
Mössbauer parameters for bis(N,N dialkyldithiocarbamato)iron(III) chlorides.

	<u>Temp. (°K)</u>	<u>δ mm.sec.⁻¹</u>	<u>ΔE_Q mm.sec.⁻¹</u>
Ethyl	4.2	0.53	2.68
Isopropyl	4.2	0.55	2.70

Table 3.4.

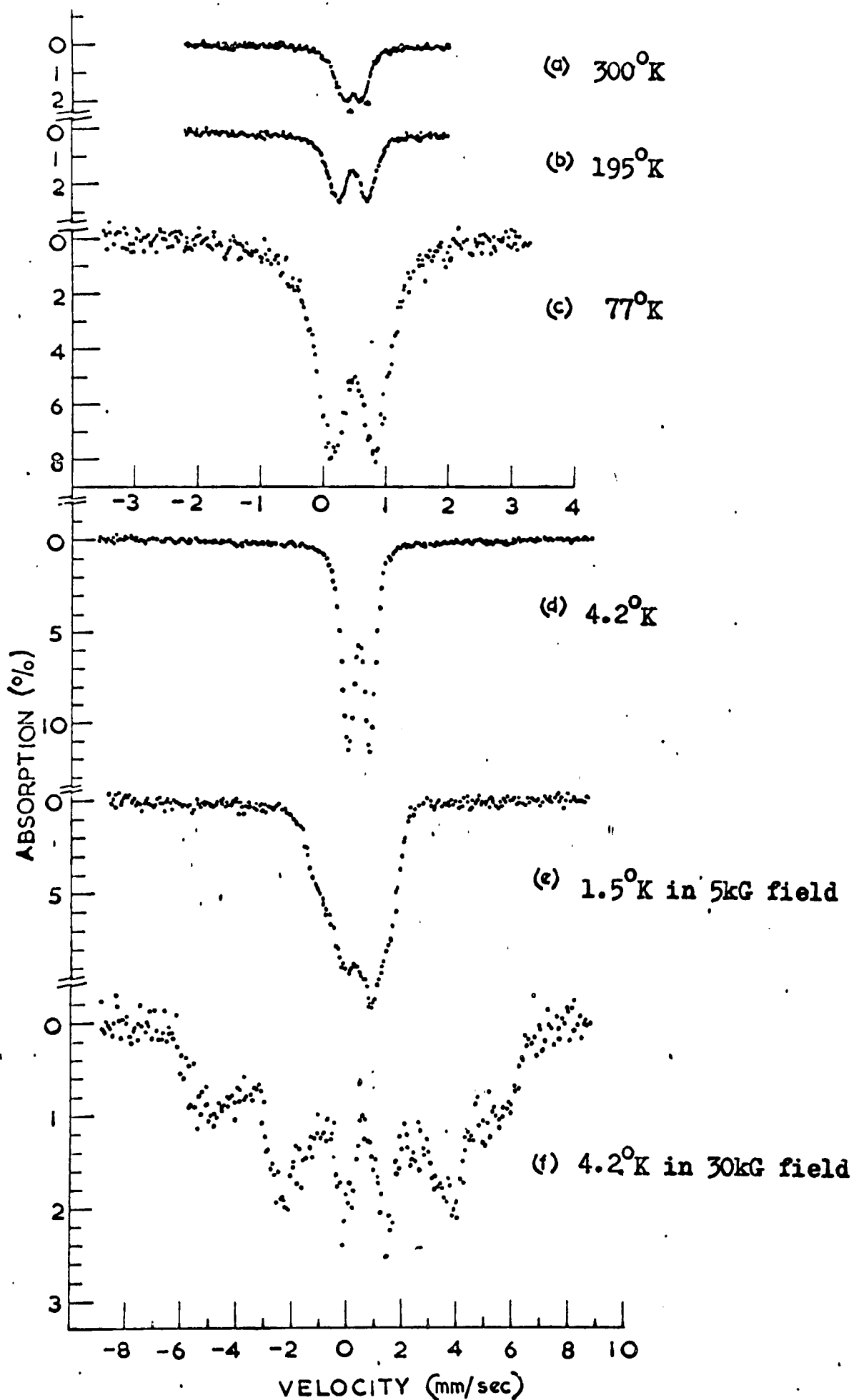
Mössbauer parameters for nitrosyliron bis(N,N diethyldithiocarbamate).

	<u>Temp. (°K)</u>	<u>δ mm.sec.⁻¹</u>	<u>ΔE_Q mm.sec.⁻¹</u>
	300	0.28	0.89
	77	0.34	0.87
	4.2	0.35	0.89
	1.3	0.38	1.03

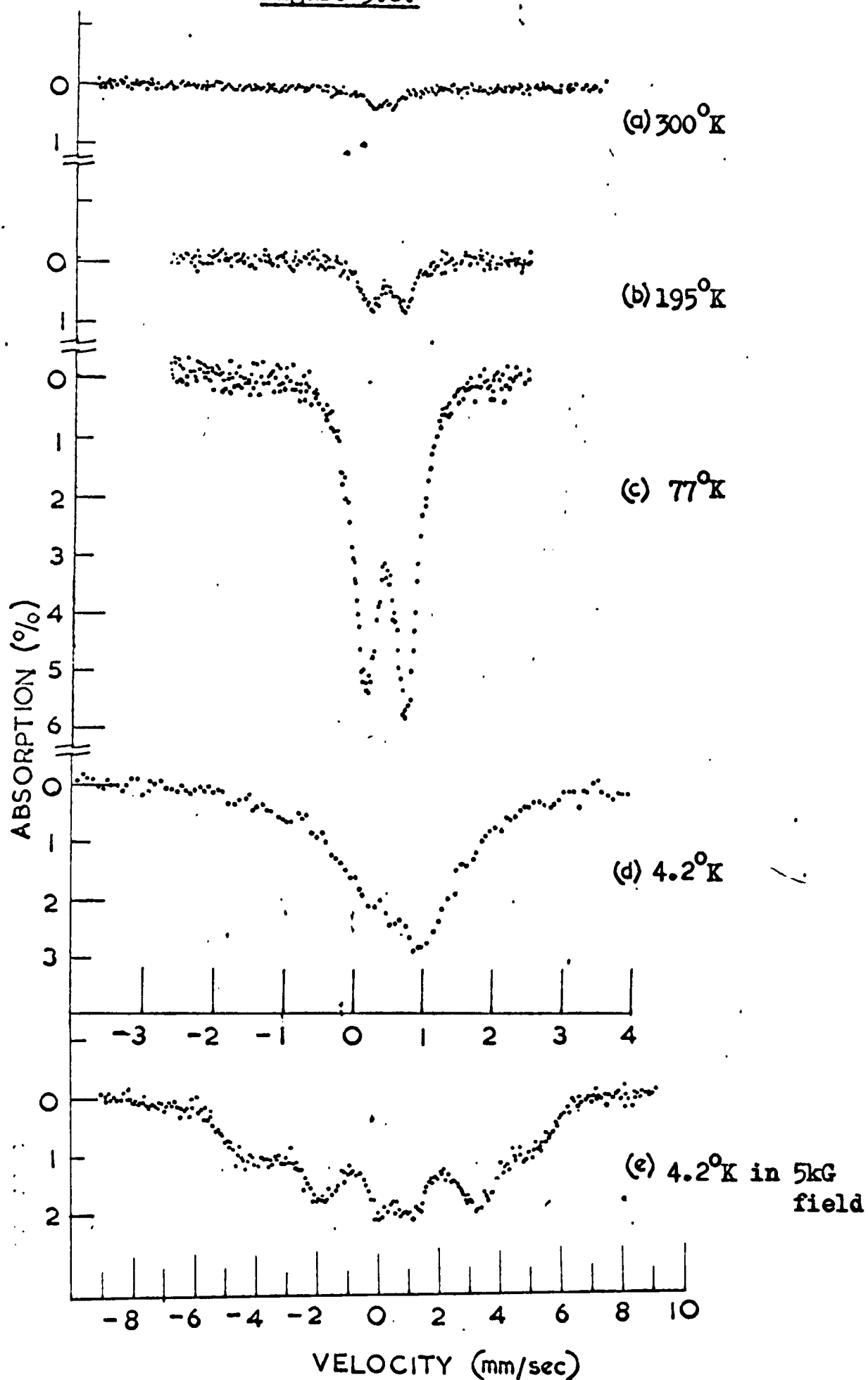
Figure 3.6.

Mössbauer spectra of iron(III) pyrrolidylthiocarbamate.

Figure 3.7.

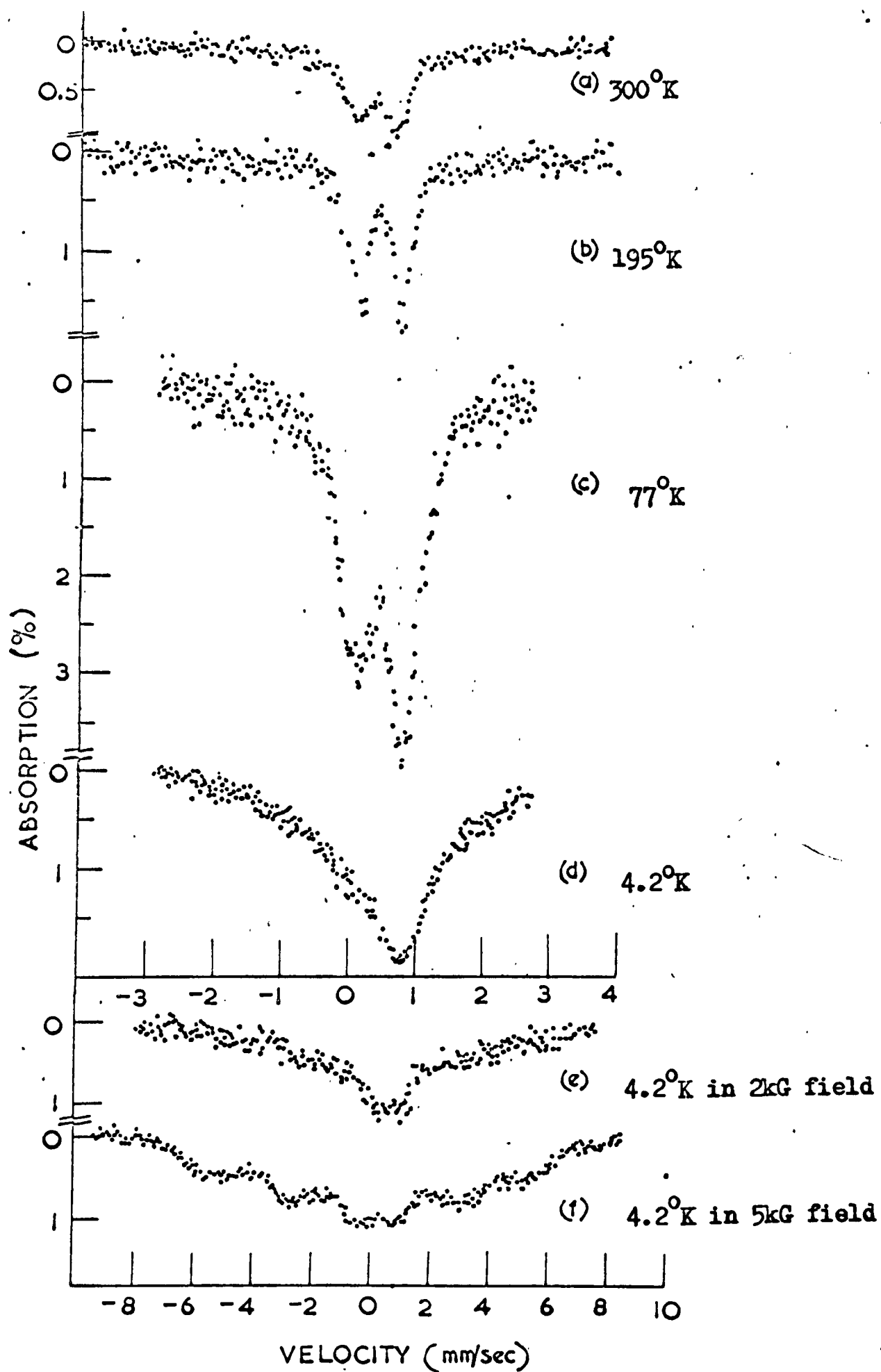


Mössbauer spectra of iron(III)-N,N dimethyldithiocarbamate.

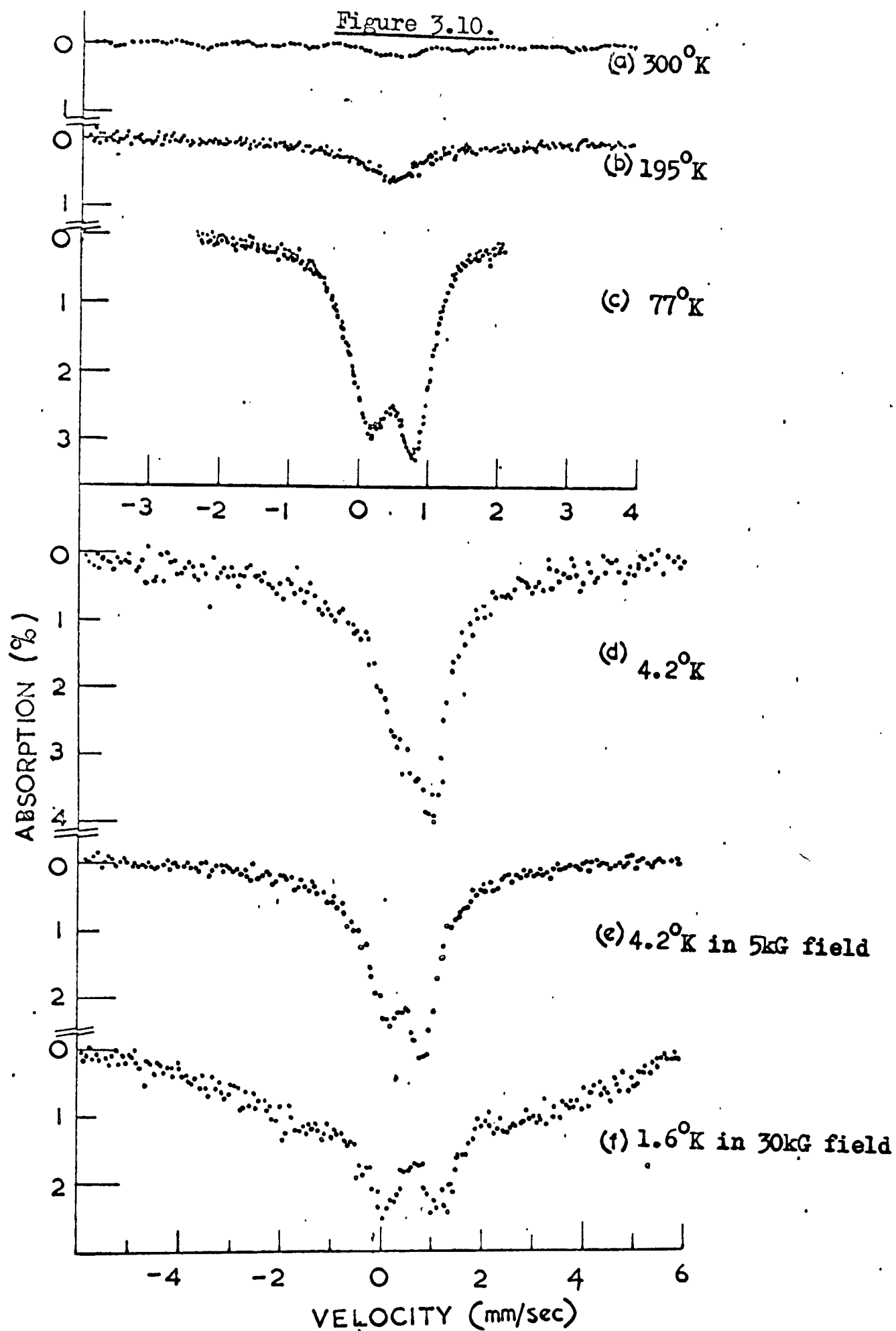
Figure 3.8.

Mössbauer spectra of iron(III) N,N diisobutyldithiocarbamate.

Figure 3.9.

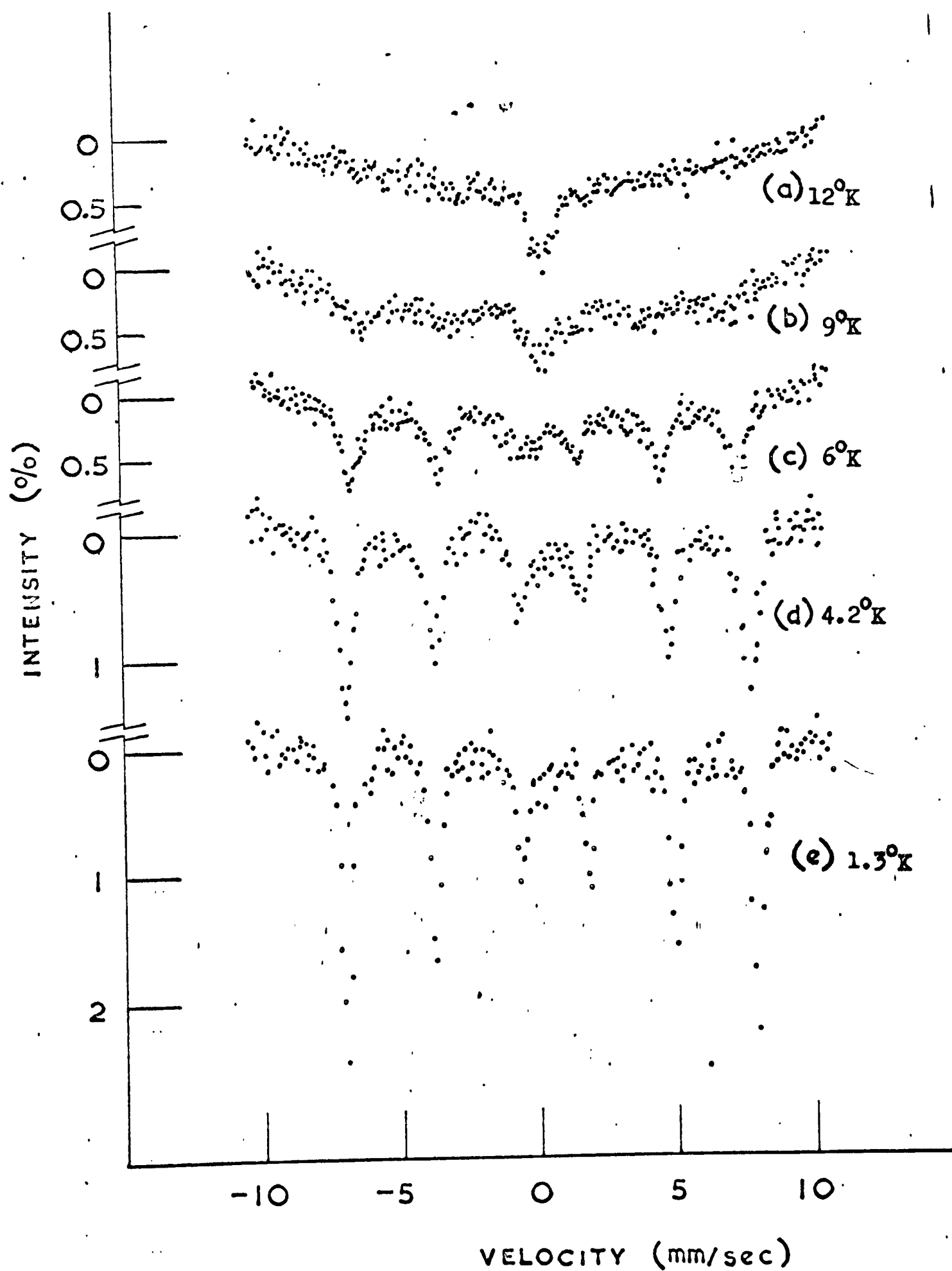


Mössbauer spectra of iron(III) N,N dicyclohexyldithiocarbamate.

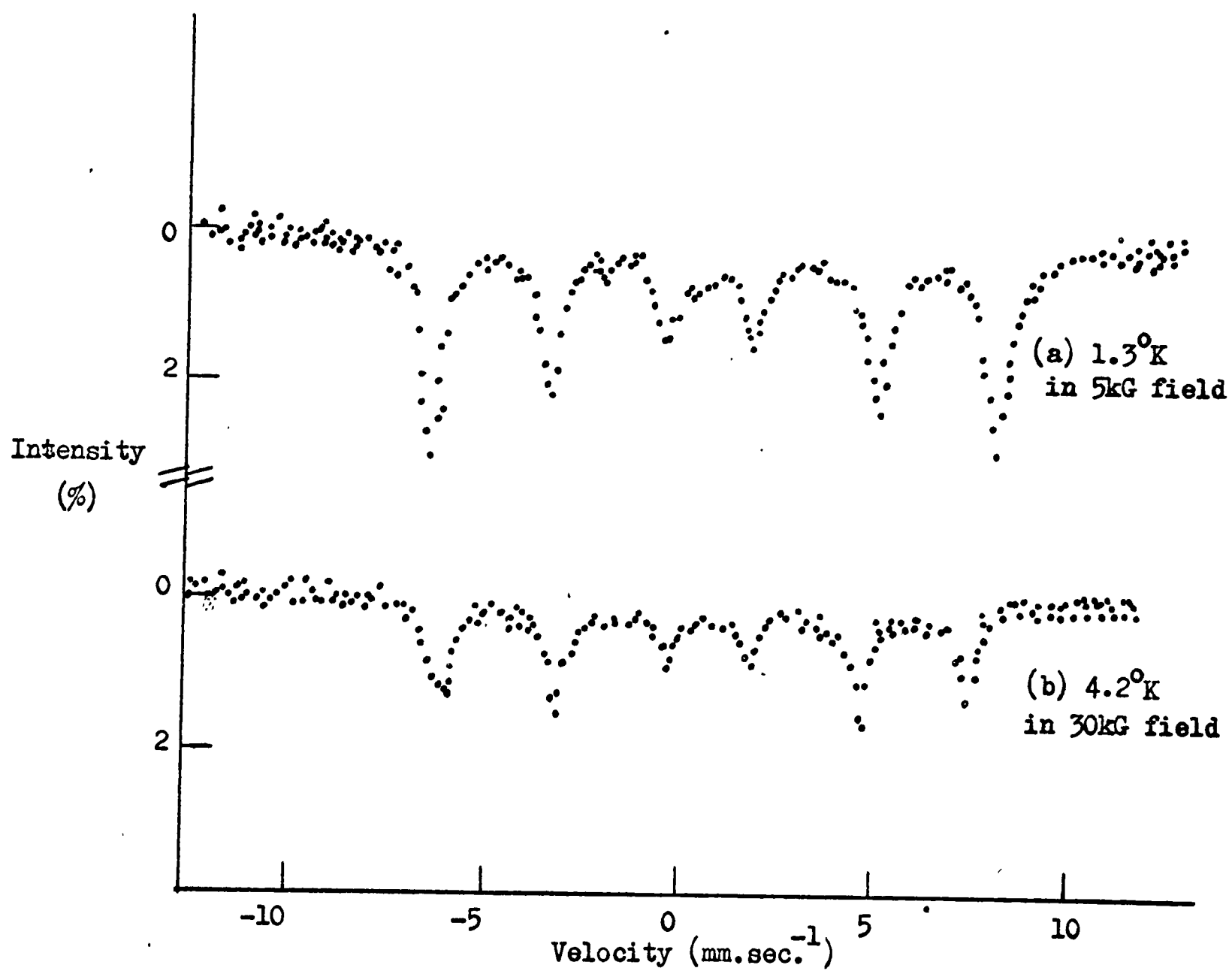


Mössbauer spectra of iron(III) N,N di-n-butyldithiocarbamate.

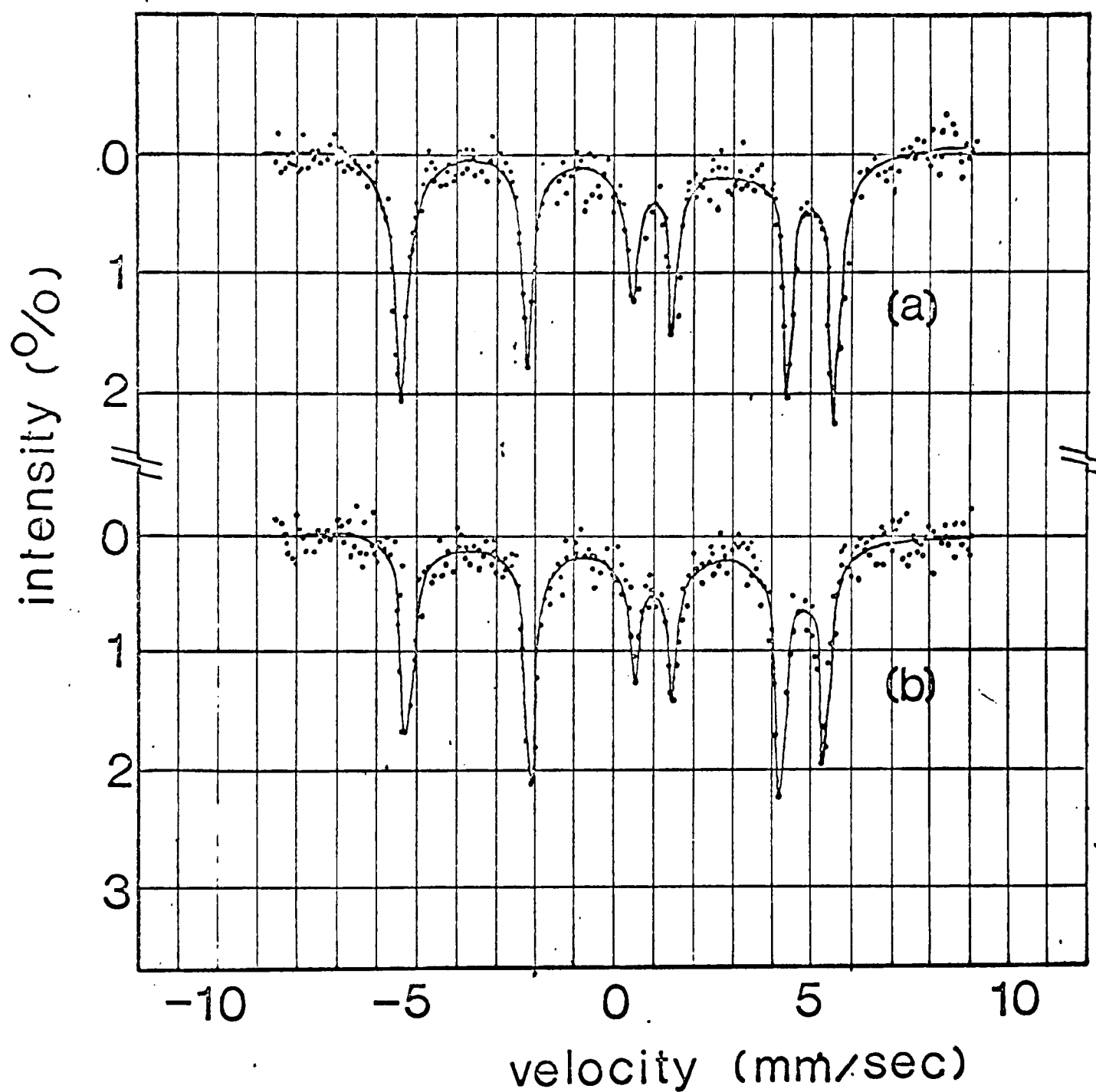
Figure 3.11.



Mössbauer spectra of iron(III) pyrrolidylthiocarbamate.

Figure 3.12.

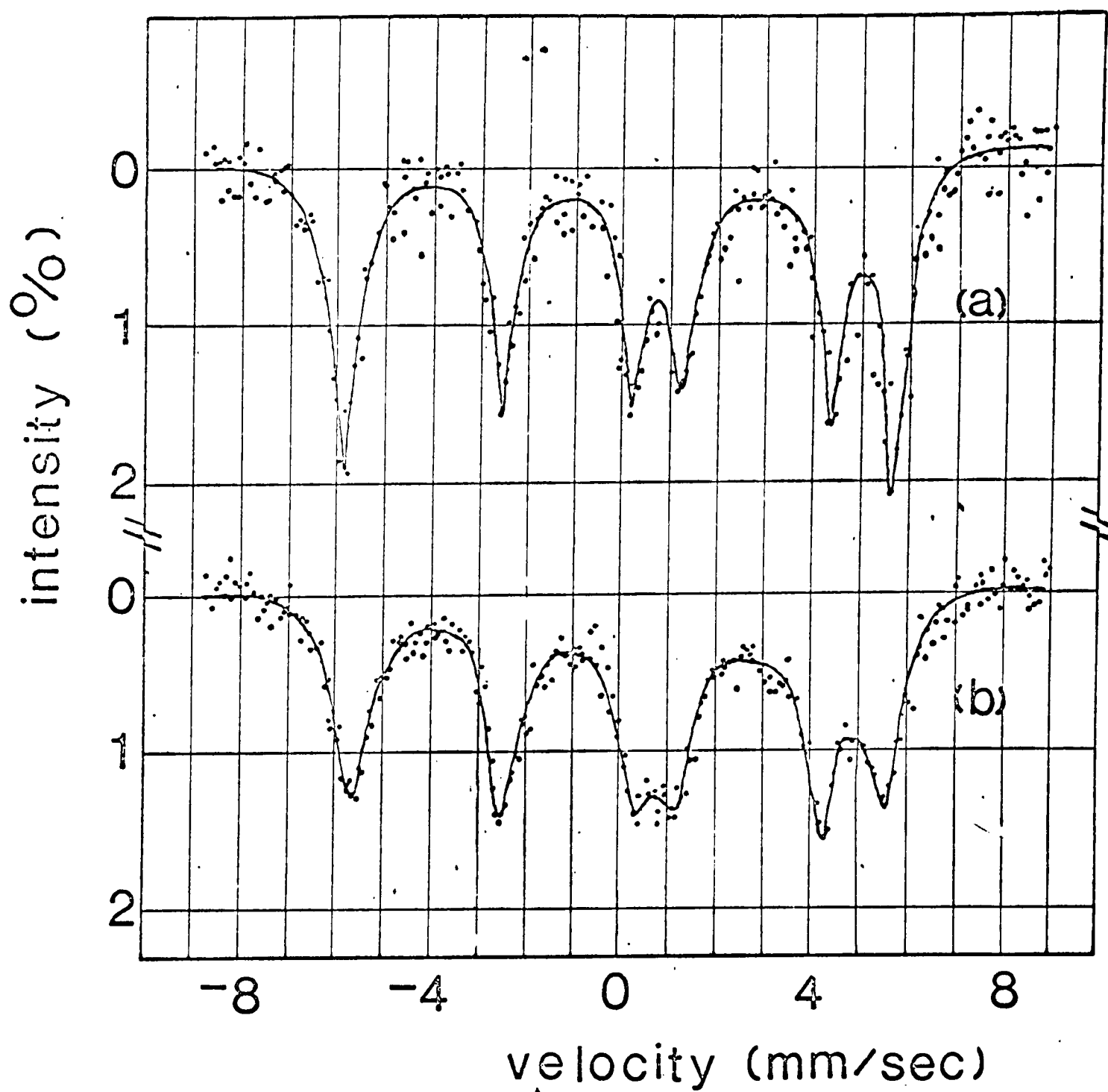
Mössbauer spectra of iron(III) pyrrolidylthiocarbamate.

Figure 3.13.

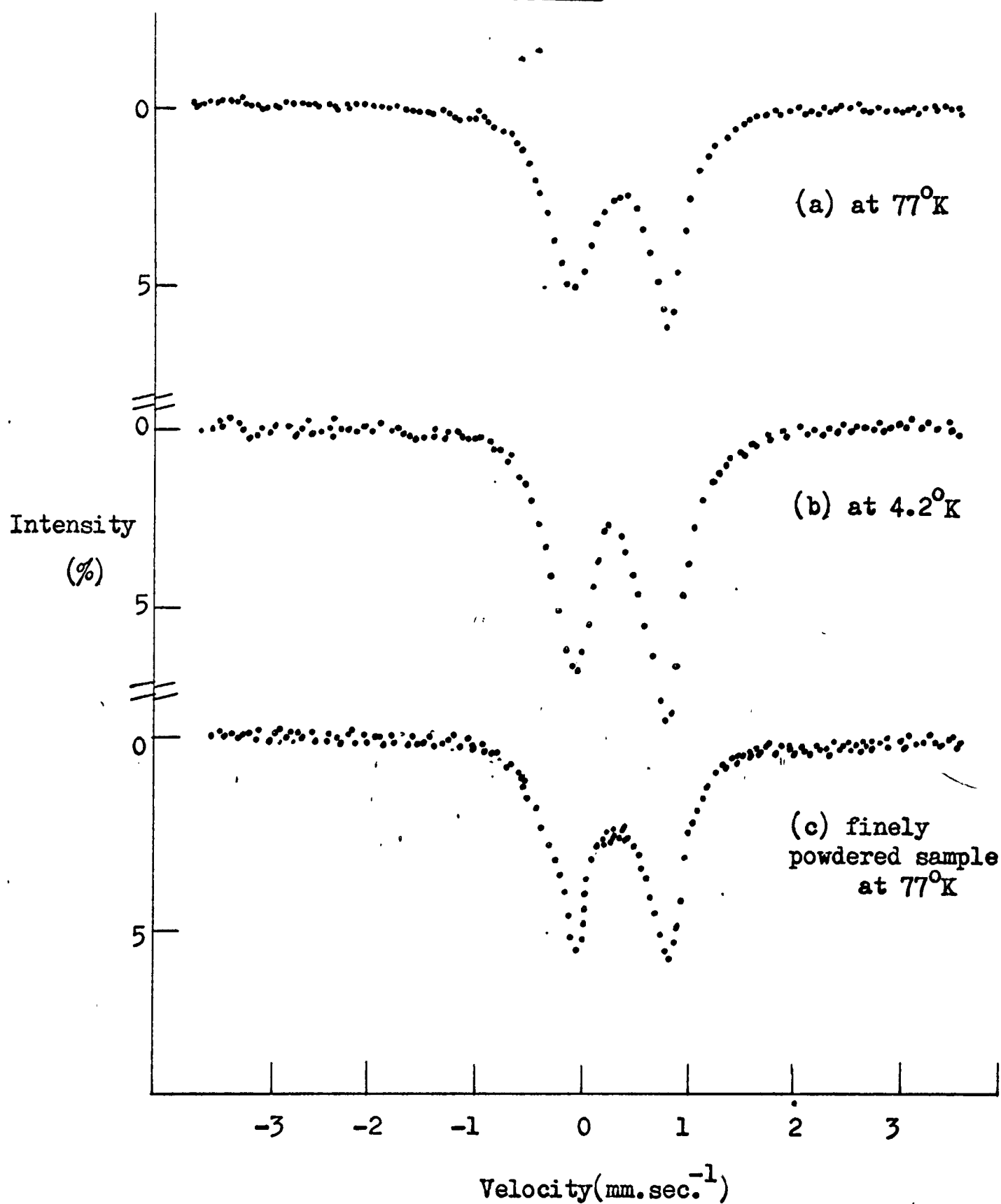
Mössbauer spectra of bis(N,N diethyldithiocarbamato)iron(III)

chloride, (a) at 1.6°K, (b) at 1.6°K in 30kG.

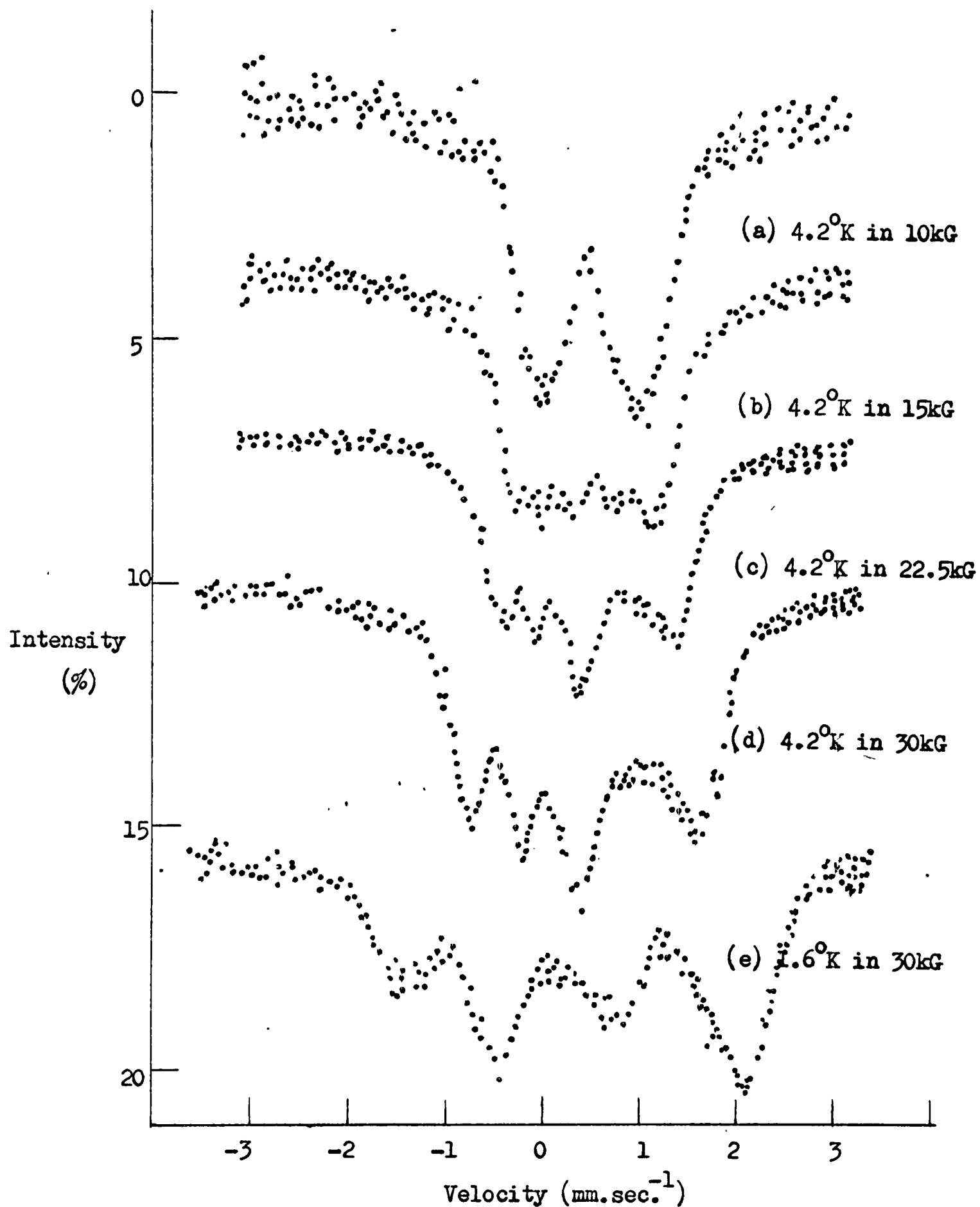
Figure 3.14.



Mössbauer spectra of bis(N,N diisopropyldithiocarbamato)iron chloride, (a) at 1.3°K, (b) at 1.3°K in 5kG field.

Figure 3.15.

Mössbauer spectra of nitrosyliron bis(N,N diethyldithiocarbamate).

Figure 3.16.

Mössbauer spectra of nitrosyliron bis(N,N diethyldithiocarbamate).

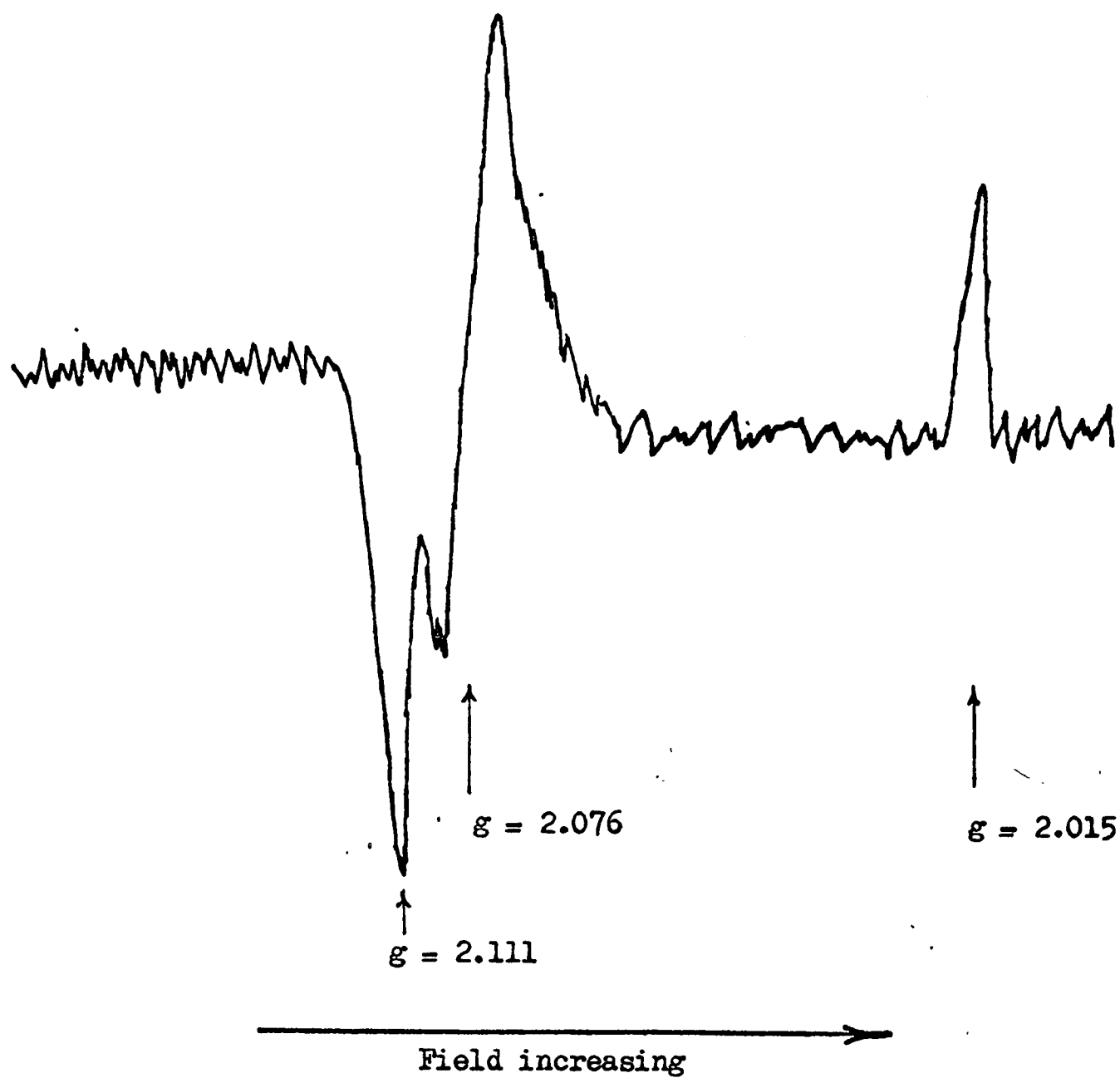
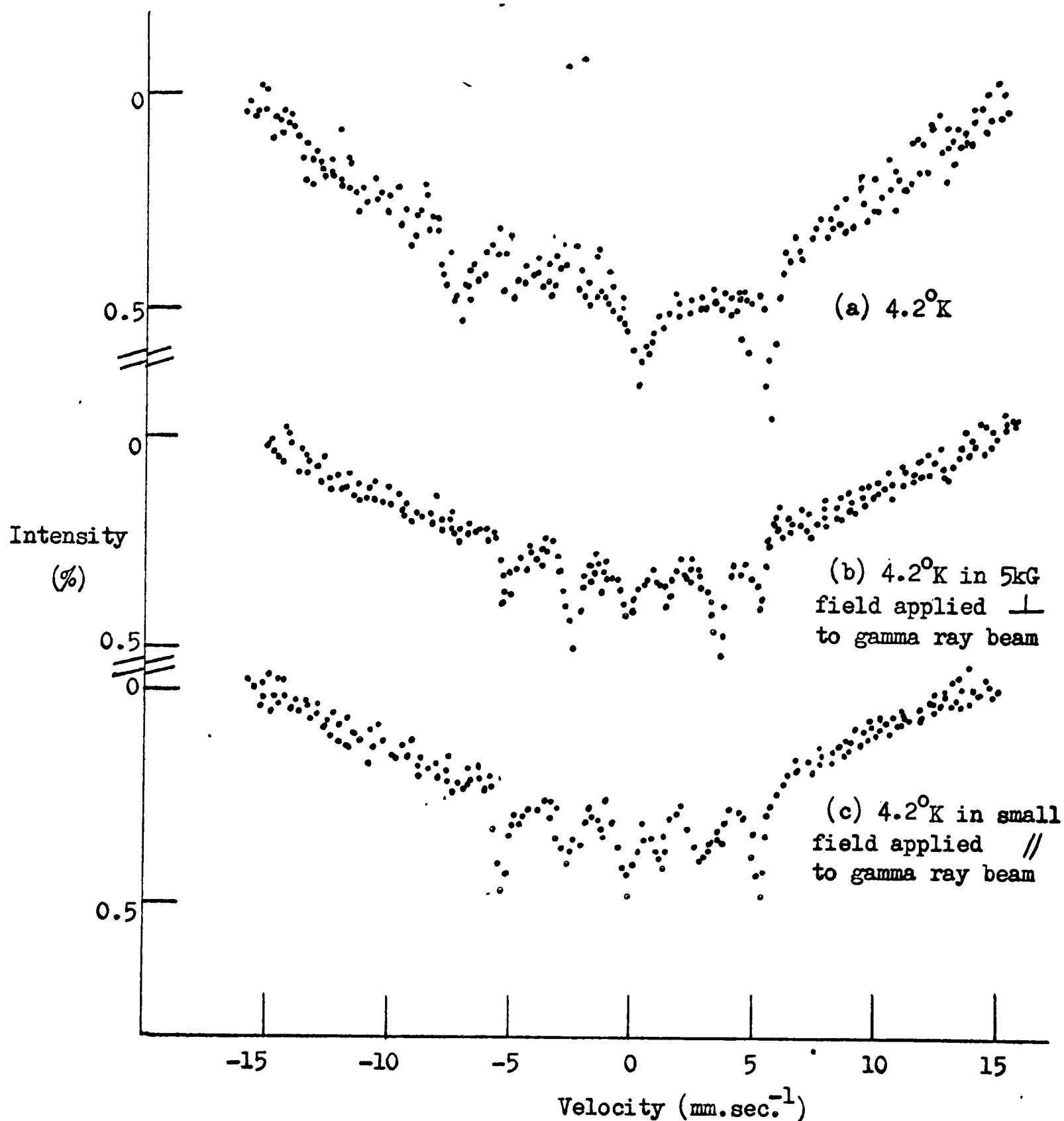
Figure 3.17.Temperature - 4.2°K Epr spectrum of iron(III) N,N dimethyldithiocarbamate, 1% in cobalt(III)N,N dimethyldithiocarbamate.

Figure 3.18.

Mössbauer spectra of ⁵⁷iron(III) N,N dimethyldithiocarbamate, 1% in
cobalt(III) N,N dimethyldithiocarbamate.

3.6. Discussion.

(i) The iron(III) N,N dialkyldithiocarbamates.

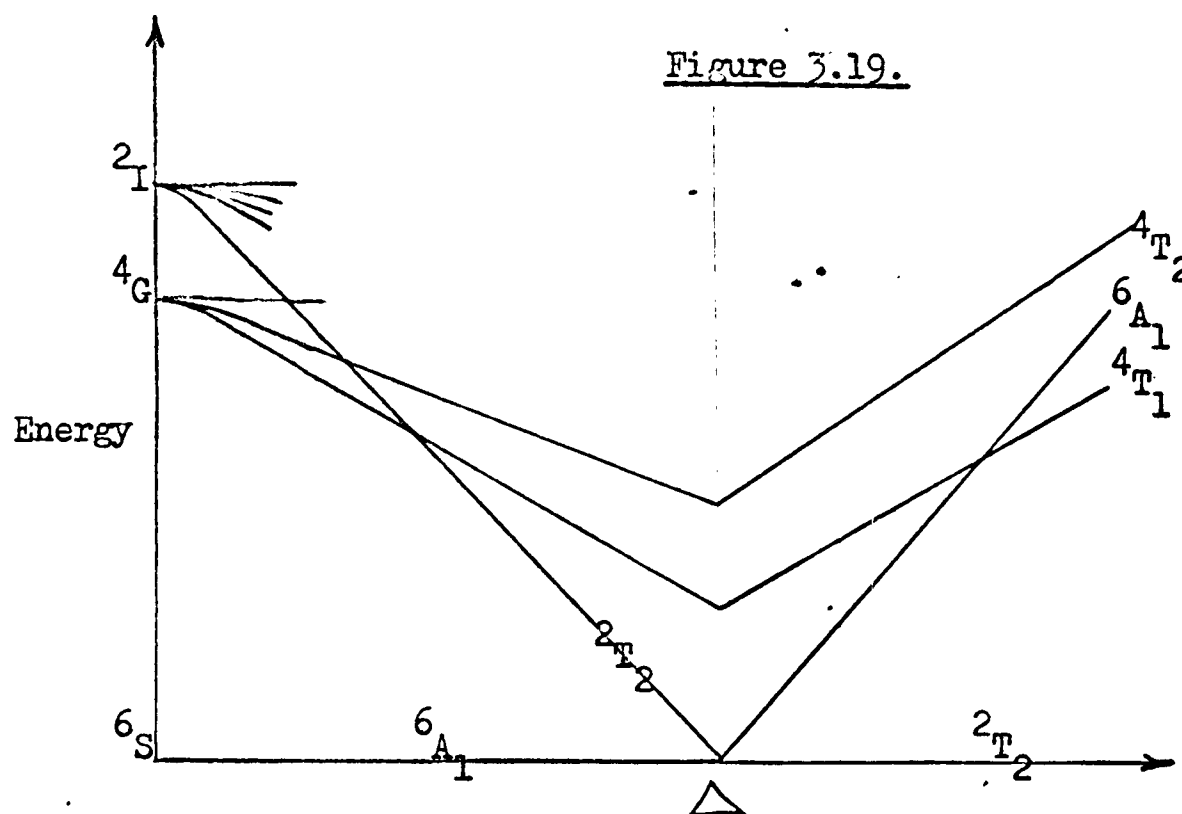
Before discussing in detail the results of the Mössbauer spectroscopic measurements on the iron(III) N,N dialkyldithiocarbamates, it will be useful to consider the conditions under which an equilibrium between high-spin and low-spin forms of the same complex can arise.

The crossover situation.

The magnetic moment, μ , of a transition metal complex with a d^5 electron configuration will depend on the symmetry and strength of the ligand field. The Tanabe-Sugano diagram⁽⁹¹⁾ for a d^5 ion in an octahedral field, (Figure 3.19), shows that the symmetry and spin of the ground state changes from 6A_1 to 2T_2 when the strength of the ligand field, Δ , passes through a certain value, often called the mean pairing energy, π . In most ferric compounds Δ has a value much greater, or much less than π , and magnetic moments of $\sim 2.0\mu_B$ or $5.9\mu_B$ are observed, corresponding to one or five unpaired electrons respectively. In complexes having Δ close to π , the low-spin and high-spin states will have nearly equal energies. The equilibrium between the two spin states will be revealed by anomalous magnetic behaviour.

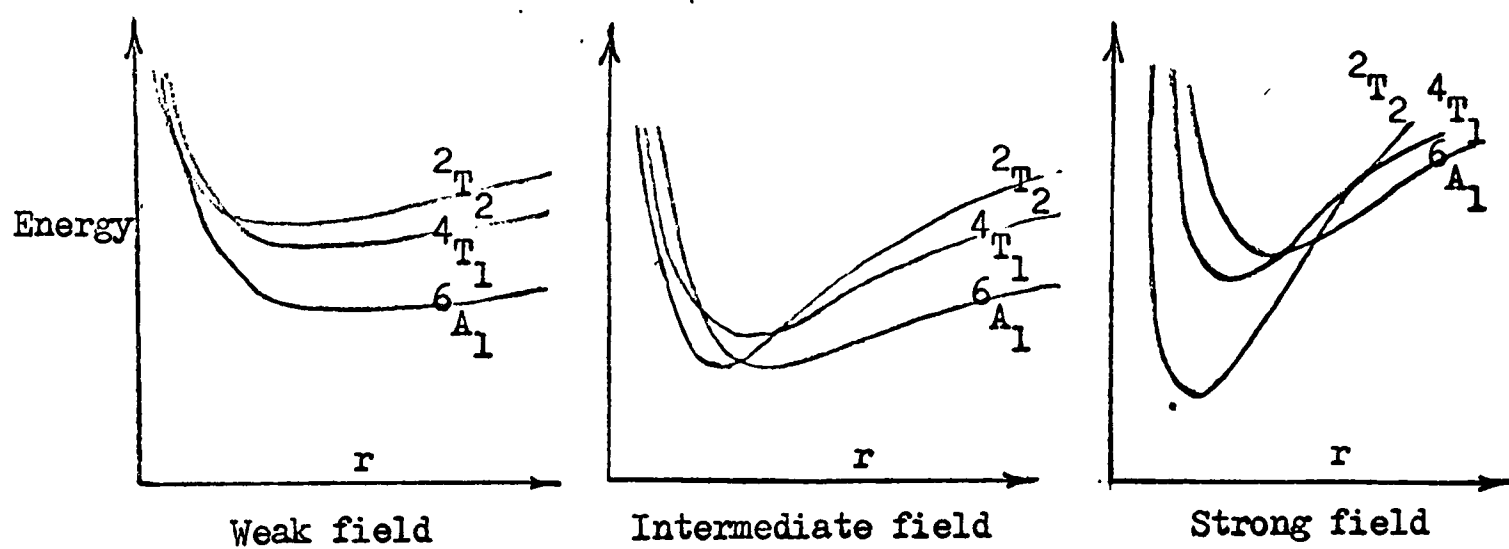
This simplified picture must be elaborated in order to obtain a better description of the conditions under which a spin

Figure 3.19.



Tanabe-Sugano diagram for a d^5 ion in an octahedral field. Only the lower energy levels are shown.

Figure 3.20.



Plots of total molecular energy as a function of metal-ligand distance.

equilibrium may occur. The Tanabe-Sugano diagram is of limited use since the molecular states in their equilibrium geometries do not have the same value of Δ . The transfer of an electron from the t_{2g} to the e_g orbitals results in an increase in the metal-ligand bond length and a consequent decrease in Δ ⁽⁹²⁾. To predict the properties of systems involving equilibria between states, estimates of the total molecular energies must be made.

Jørgensen⁽⁹³⁾ has calculated approximate potential energy curves for the d^5 configuration in the crossover region. The ligands are considered to be point charges, of magnitude proportional to a quantity q . The energies of the metal d-electrons in the octahedral field are superimposed on a potential of the form $k'r^{-9} - k''r^{-1}$, to yield total molecular potential energy functions. As q increases the 2T_2 state supplants the 6A_1 state as the ground state (Figure 3.20). It is to be noted that for octahedral symmetry the 4T_1 state never lies lowest.⁽⁹⁴⁾

A necessary and sufficient condition for the existence of equienergetic ground states is that:

$$\Delta(\text{high-spin}) < \Delta_x < \Delta(\text{low-spin})$$

where the Δ values refer to the complex in its equilibrium geometries and Δ_x is the value of Δ at which the 6A_1 and 2T_2 terms interact.

Δ_x may be identified with the mean pairing energy π ⁽⁸⁰⁾ so that:

$$\Delta(\text{high-spin}) < \pi < \Delta(\text{low-spin}).$$

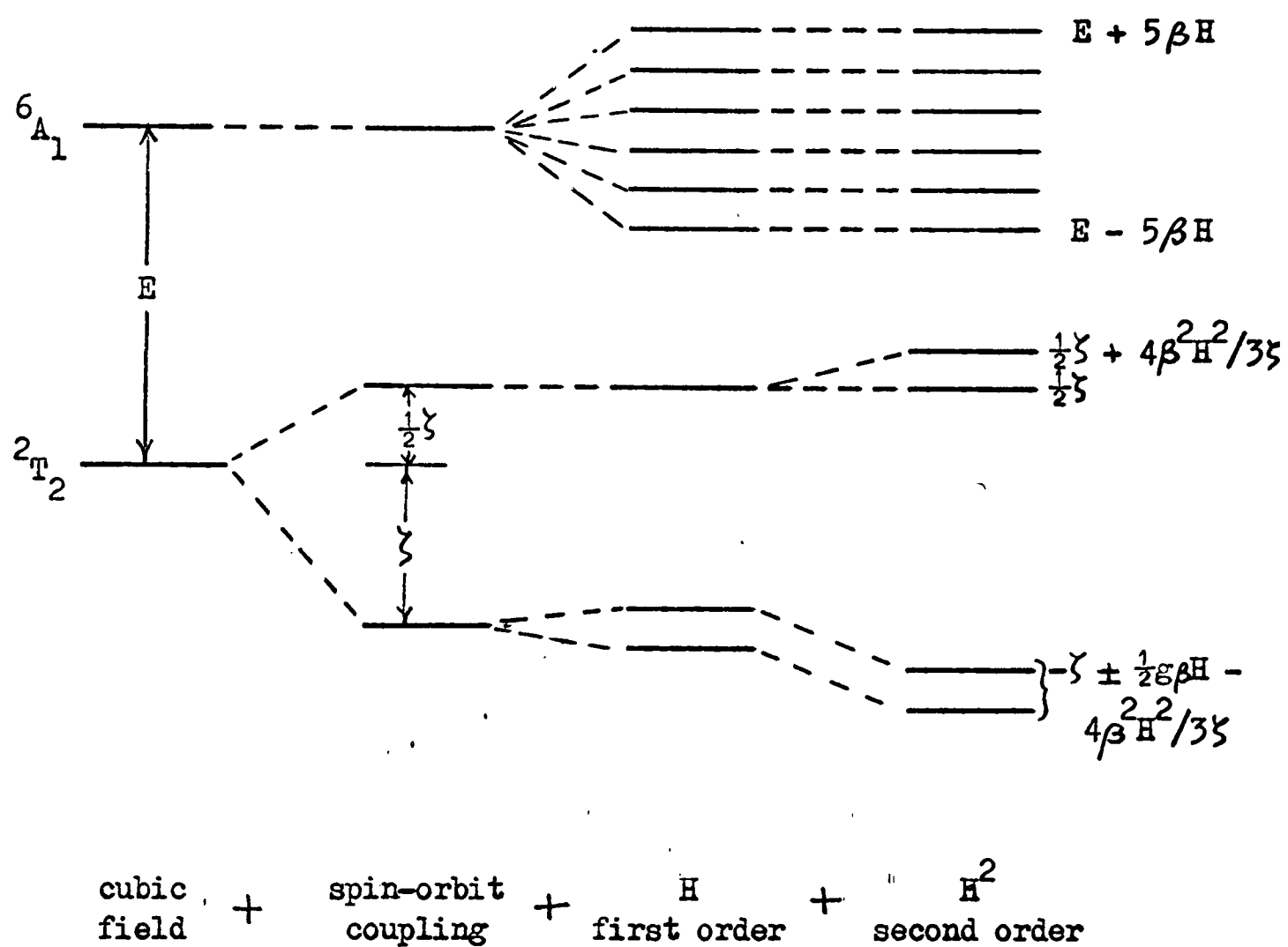
Ewald et al.⁽⁸⁰⁾ have shown that values of $\Delta(^6A_1)$, $\Delta(^2T_2)$ and Π , independently obtained, satisfy the above inequality for the case of the iron(III) N,N dialkyldithiocarbamates. The value of Π was calculated using the Racah parameters appropriate to the complexed iron(III) species. The ligand exhibits a pronounced nephelauxetic effect which reduces the value of Π to about one half of its estimated value in the free ion.

The same authors also found that the effects of temperature, pressure and minor modifications of the ligand molecule upon the magnetic and spectral properties of the iron(III) N,N dialkyldithiocarbamates were qualitatively in accord with theoretical predictions. The quantitative agreement of the temperature dependence of the magnetism with that calculated from the Van Vleck equation, was not good, however. The energy levels for the d^5 configuration in the crossover region may be drawn as in Figure 3.21. The Van Vleck equation applied to this situation gives:

$$\mu^2 = \frac{\frac{3}{4}g^2 + 105e^{-(1+E/\zeta)x} + 8x^{-1}(1 - e^{-3x/2})}{1 + 2e^{-3x/2} + 3e^{-(1+E/\zeta)x}} \quad (44)$$

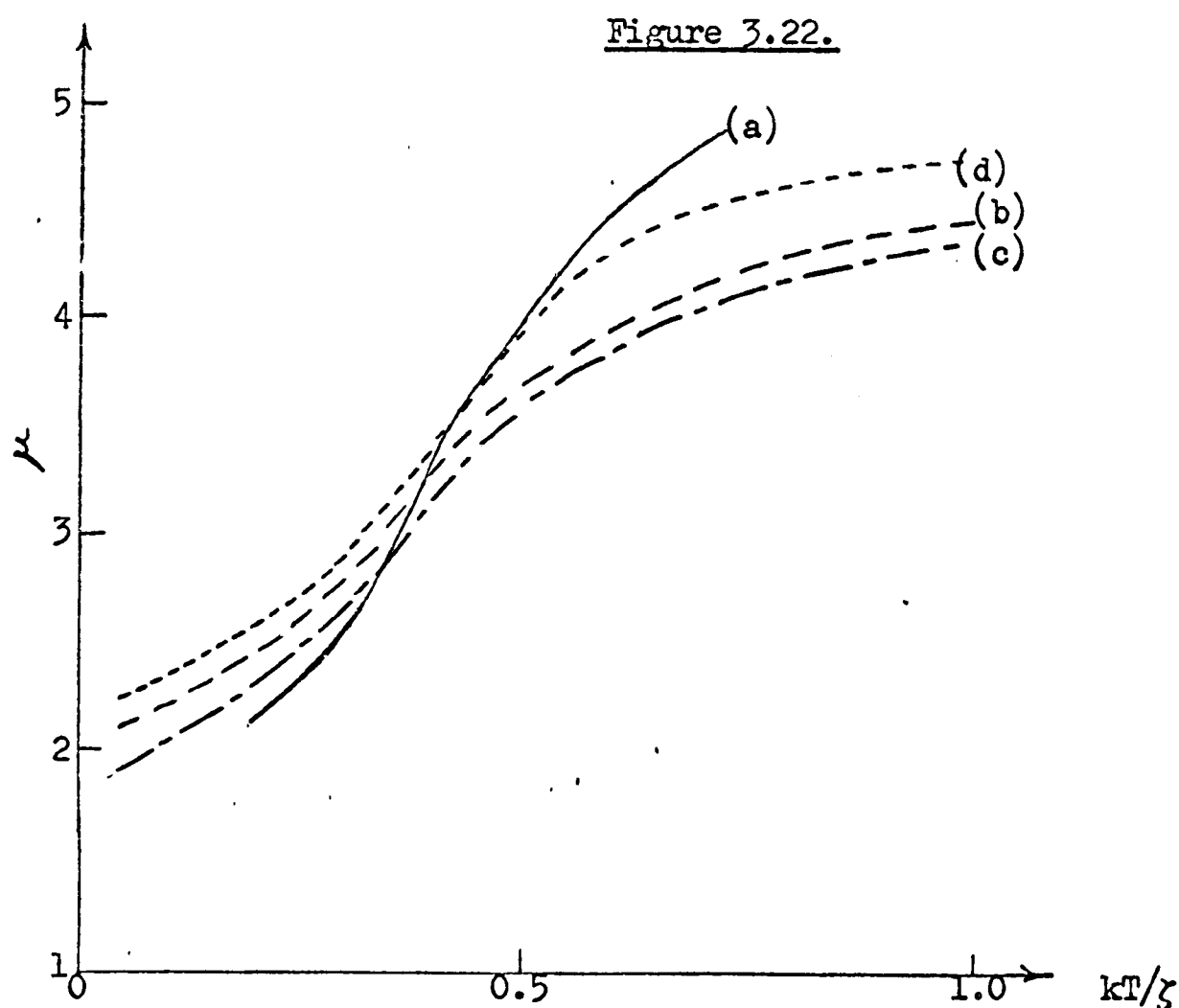
where $x = \zeta/kT$ and E is the separation between the zero point levels of the two states. ζ is the one electron spin-orbit coupling constant and g is a parameter taking account of the interaction with terms of higher energy. A comparison of the experimental temperature dependence of the magnetic moment of iron(III) N,N dimethyldithiocarbamate with

Figure 3.21.



Energy levels of the d^5 configuration in the crossover region.

that calculated from eq.(44) is shown in Figure 3.22. Golding and de Lisle⁽⁹⁵⁾ found that a marked improvement between theory and experiment was obtained when the effects of spin-orbit mixing of the 4T_1 state was taken into account. The inclusion of configurational mixing further improved the agreement (See Figure 3.22).



Experimental temperature dependence of the magnetic moment of iron(III) N,N dimethyldithiocarbamate (a). The calculated results using the Van Vleck formula (b), including spin-orbit coupling (c), and including (d) configurational mixing, are also shown.

The Mössbauer spectra.

All the iron(III) N,N dialkyldithiocarbamates that we have studied showed a single Mössbauer spectrum at all temperatures, and not a spectrum which could be analysed as a superposition of the two spectra expected for a mixture of a high-spin and a low-spin ferric compound. Studies by other workers have shown similar results⁽⁸³⁾⁽⁸⁵⁾, although Vainstein et al.⁽⁸⁴⁾ attempted to interpret their spectra in terms of contributions from different species. The time of change from one spin state to the other must therefore be faster than 1.5×10^{-7} sec., the lifetime of the ^{57}Fe excited state. The observed isomer shifts and quadrupole splittings are therefore averages depending on the proportions of high-spin and low-spin states in equilibrium at the temperature of measurement. Mössbauer studies of ferrous compounds with similar anomalous magnetic properties have, however, given spectra in which both high-spin and low-spin forms are evident⁽⁹⁶⁾⁽⁹⁷⁾. It would seem that in the latter case the anomalous behaviour is associated with a phase change, the low-spin species adopting a different crystal structure to that of the high-spin species. A cooperative collapse of the lattice presumably occurs at the crossover point⁽⁷⁰⁾. There is no evidence for this being the case in the iron(III) N,N dialkyldithiocarbamates.

The observation of an average Mössbauer spectrum may be explained as follows. In a ligand field of perfect cubic symmetry the $^6\text{A}_1$ and $^2\text{T}_2$ levels simply cross, and as there is no interaction

between the states and the observed Mössbauer spectrum would be a superposition of the spectra of the two individual states. However, when the ligand field has lower than cubic symmetry and spin-orbit coupling is taken into account, there are interactions between the 6A_1 and the 2T_2 states, via the 4T_1 state, which cause the energy levels to split and repel each other and which mix the states⁽⁹⁸⁾.

Because of the mixing there will be a rapid exchange between the states and the observed spectrum at high temperatures is a single averaged spectrum.

In general the spectra observed at room temperature consisted of a quadrupole split pair of lines. At lower temperatures the line widths increased as the electron spin relaxation times became comparable to the Larmor frequency of the nucleus. Due to the anomalous magnetic properties of the iron(III) N,N dialkyldithiocarbamates the Mössbauer parameters show unusual variations with temperature. The general features common to all the compounds will first be discussed. More detailed considerations of the spectra of the individual compounds will be dealt with later.

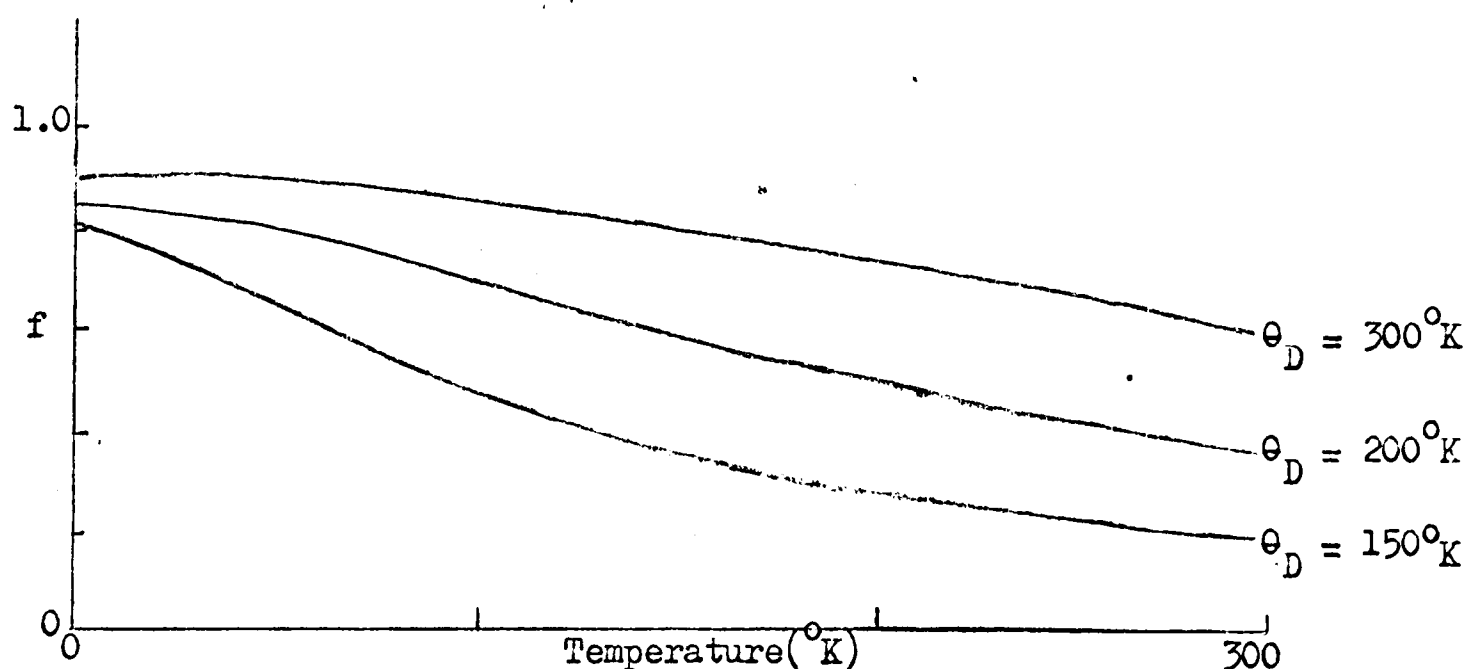
The recoilless fraction.

All the compounds showed a large increase, by a factor of between four and eight, in the intensity of the Mössbauer Effect on lowering the temperature from 300°K to 77°K . This is indicative of a low effective Debye temperature for iron in these compounds. In Figure 3.24

is plotted the calculated dependence of the recoilless fraction, f , on temperature for certain values of the Debye temperature, θ_D . The intensity is proportional to the recoilless fraction. The large variation of intensity with temperature observed in these compounds is consistent with θ_D values of $\sim 150^\circ\text{K}$. In comparison θ_D for metallic iron has been estimated from Mössbauer spectroscopy to be 490°K ⁽⁹⁹⁾. It was not considered worthwhile to evaluate θ_D any more accurately. It is sufficient to note that the low Debye temperatures reflect the weak nature of the binding of the iron in these compounds, and that the temperature dependence of the intensity of the spectrum of the high-spin pyrrolidyl compound is similar to that of the other derivatives.

The di-n-butyl derivative was remarkable in that there was no effect observable at room temperature, whilst at 77°K the intensity of its Mössbauer spectrum was comparable to those of the other compounds.

Figure 3.24.



Plot of recoilless fraction vs. temperature for various values of θ_D .

The isomer shift.

Typical isomer shift values for high-spin iron(III) complexes are about $0.5 \text{ mm. sec.}^{-1}$, and for low-spin ferric complexes about $0.1 \text{ mm. sec.}^{-1}$ (43). The values of the isomer shifts at 300°K for all the iron(III) N,N dialkyldithiocarbamates studied are close to $0.40 \text{ mm. sec.}^{-1}$ and differ barely significantly for the high-spin pyrrolidyl derivative and for the other compounds, which contain varying admixtures of the low-spin state. The isomer shifts in these compounds are therefore much closer to the weak ligand field case than to the strong field situation.

The temperature dependence of the shifts is interesting. The pyrrolidyl compound shows a decrease in shift of $0.11 \text{ mm. sec.}^{-1}$ on raising the temperature from 77°K to 300°K , which is close to the increase expected from the second order Doppler Effect. The decrease in the shifts of the diisobutyl and dicyclohexyl compounds is slightly smaller. Both these compounds have magnetic moments at room temperature $\sim 1\mu_B$ greater than the expected value for a low-spin ferric compound. The decrease in the shift of the dimethyl compound over the same temperature range is only $0.01 \text{ mm. sec.}^{-1}$. At 300°K the magnetic moment of this compound is $4.17\mu_B$. It seems that the expected decrease in shift due to the second order Doppler Effect is offset by population of the high-spin state with its higher isomer shift. Unfortunately, the di-n-butyl compound, which has an even higher magnetic moment at room temperature ($\mu_{\text{eff}} = 5.32\mu_B$), did not show a spectrum at 300°K , so that

this point could not be conclusively established.

The magnetic properties of the iron(III) N,N dialkyl-dithiocarbamates should be sensitive to pressure, which should shift the equilibrium towards the state of lower molecular volume. Ewald et al. investigated this pressure dependence and estimated that there is a decrease in volume of 0.7% during the transition ${}^6A_1 \rightarrow {}^2T_2$ for iron(III) N,N di-n-butylthiocarbamate⁽⁸⁰⁾. Pound, Benedek and Drever⁽¹⁰⁰⁾ have investigated the pressure dependence of the isomer shift. A volume decrease of 0.7% would give rise to a decrease in shift of 0.01 mm.sec.⁻¹ according to their measurements. This effect is too small to be of importance in the present measurements.

The high value of the isomer shift implies a low s-electron density at the iron nucleus. The bonding of the ferric ion with the dithiocarbamate ligands can affect the isomer shift in two ways. Firstly, donation of electrons from the ligand σ -orbitals into the metal e_g orbitals will increase the d-electron density. The increased shielding of the metal s-electrons from the nucleus will result in an increased isomer shift. Secondly, delocalisation of the metal d-electrons into empty ligand π -orbitals will decrease the shielding of the s-electrons from the nucleus and give rise to a decreased isomer shift. In the present case the first interaction is evidently the dominant one.

The magnetic hyperfine interactions.

The effects of electron spin relaxation are important and are best considered before a detailed discussion of the quadrupole splitting is given, since it is generally necessary to take the magnetic hyperfine interactions into account in order to determine the values of the quadrupole splitting.

As described in Chapter 2, magnetic hyperfine interactions may be observed in paramagnetic compounds, even in the absence of an external magnetic field, if the electron spin relaxation rates are slow relative to the nuclear precession frequency. These rates may be decreased by lowering the temperature, when the spin lattice relaxation time becomes long, or by using materials in which the interionic separations are large, when the spin-spin relaxation time becomes long.

Relaxation effects are seen in all the compounds studied. The pyrrolidyl compound shows a broadened and asymmetric spectrum at 300°K and 77°K. At 4.2°K the hyperfine field is fully resolved into six lines (Figure 3.6(c)). The spectra are not unexpected since the complex contains only high-spin ferric ions for which the spin-lattice relaxation times are long even at high temperatures. For the remaining compounds, which are low-spin at 0°K, no relaxation broadening is observed at 300°K. It develops as the temperature is lowered to 77°K and 4.2°K. The dicyclohexyl compound

shows the largest broadening at 77°K suggesting that the long relaxation times may be associated with the large alkyl groups and consequent large interionic separation. The dimethyl compound showed no line broadening even at 4.2°K , which is consistent with the smaller iron - iron distance resulting from the packing of the relatively small methyl groups.

The application of an external magnetic field to the samples at low temperatures enables additional information on the hyperfine interactions to be obtained. This will be discussed more fully later. It is sufficient now to consider that the hyperfine interactions observed in the presence of an external magnetic field may arise from one of two mechanisms. For fast relaxation rates, as observed in the dimethyl compound, the effective magnetic field at the nuclei is proportional to the magnetisation, H/T . In a magnetic field of 30 kG at 4.2°K a six line spectrum is observed (Figure 3.7(f)). The lines are broad as the specimen is a polycrystalline material with an anisotropic susceptibility tensor and quadrupole effect, so that the observed spectrum is a superposition of many similar six line spectra.

When the relaxation rates are slower, as in the dicyclohexyl compound, so that hyperfine broadening appears in zero magnetic field, a six line spectrum is observed when the applied field is strong enough to decouple the electron and nuclear spins. In this case the effective field at the nucleus is not proportional to the

magnetisation. An even better example of this is provided by the spectra of the iron dimethyl compound diluted in cobalt(III) N,N dimethyldithiocarbamate. In zero field at 4.2°K a broad six line spectrum is observed, (Figure 3.18(a)), as the large iron - iron distance results in very slow spin-spin relaxation times. An applied field of 500 gauss is sufficient to decouple the electron and nuclear spins and produce a well resolved six line spectrum, (Figure 3.18(b)). A field of 30 kG does not alter the magnitude of the internal field.

The quadrupole splitting.

A high-spin ferric ion in a cubic environment shows zero quadrupole splitting. The spectrum of iron(III) pyrrolidyl-dithiocarbamate at 300°K and 77°K is a single broad line, (Figures 3.6(a) and 3.6(b)), which is resolved by a computer fit of the data into a quadrupole split line. The splitting is $0.36 \text{ mm. sec.}^{-1}$ and $0.40 \text{ mm. sec.}^{-1}$ respectively. These small values presumably arise from charges on the neighbouring atoms and indicate that the environment of the iron atom is not exactly cubic. The quadrupole splitting is also more or less independent of temperature, as is expected when the contributions to the electric field gradient come from the lattice. At 4.2°K a six line spectrum is observed, (Figure 3.6(c)). The separation between the lowest velocity pair of lines is greater than that between the highest velocity pair of lines. The quadrupole interaction therefore raises the $\pm 1/2$ levels and the component of the electric field gradient in the direction

of the field is negative. The magnitude of the quadrupole splitting at 4.2°K is $0.20 \text{ mm. sec.}^{-1}$

The remaining compounds are low-spin at low temperatures. The ground state is 2T_2 . An electric field gradient arises from the raising of the degeneracy of the 2T_2 state by the combined effect of the ligand field and spin-orbit coupling, (Fig.2.11), and is largest at low temperatures when only one doublet is populated. As the temperature is increased other orbital states become populated and the quadrupole coupling decreases. The situation has been treated quantitatively by Golding⁽¹⁰¹⁾. The wave functions of the three doublets of Figure 2.11 are written (eq.40):

$$\begin{aligned}\psi_i &= A_i |1^+\rangle + B_i |\zeta_i^-\rangle + C_i |-1^+\rangle \\ \psi'_i &= A_i |-1^-\rangle - B_i |\zeta_i^+\rangle + C_i |1^-\rangle\end{aligned}$$

where $i = 1, 2$ or 3 . The quadrupole splitting is then:

$$\Delta E_Q = \frac{\sum_i \Delta E_{Qi} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \quad (45)$$

where:

$$\Delta E_{Qi} = \frac{2}{7} e^2 Q (1 - \gamma_{\infty}) \langle r^{-3} \rangle (s_i^2 + t_i^2)^{\frac{1}{2}}$$

and

$$\begin{aligned}s_i &= B_i^2 - \frac{1}{2}(A_i^2 + C_i^2) \\ t_i &= \sqrt{3} A_i C_i\end{aligned}$$

If the g -values are known, the values of A , B and C can be determined

and the quadrupole splitting can be calculated. When the g -values are unknown, it may be shown that eq.(45) can be expressed in terms of a covalency parameter, α , and a distortion parameter, δ . Then:

$$\Delta E_Q = \frac{e^2 Q (1 - \gamma_\infty) \langle r^{-3} \rangle \alpha^2 \sum_i A_i e^{-E_i/kT}}{14 \sum_i e^{-E_i/kT}} \quad (46)$$

where:

$$A_1 = 1 - 3\left(\frac{1}{2} - 3x\right)X^{-1}$$

$$A_2 = 1 + 3\left(\frac{1}{2} - 3x\right)X^{-1}$$

$$A_3 = -2$$

$$E_1 = -\left(\frac{1}{4} + \frac{x}{2} + \frac{X}{2}\right)\lambda'$$

$$E_2 = -\left(\frac{1}{4} + \frac{x}{2} - \frac{X}{2}\right)\lambda'$$

$$E_3 = \left(\frac{1}{2} + x\right)\lambda'$$

$$X = \alpha^2 / (5/4 - 3x - 9x^2)$$

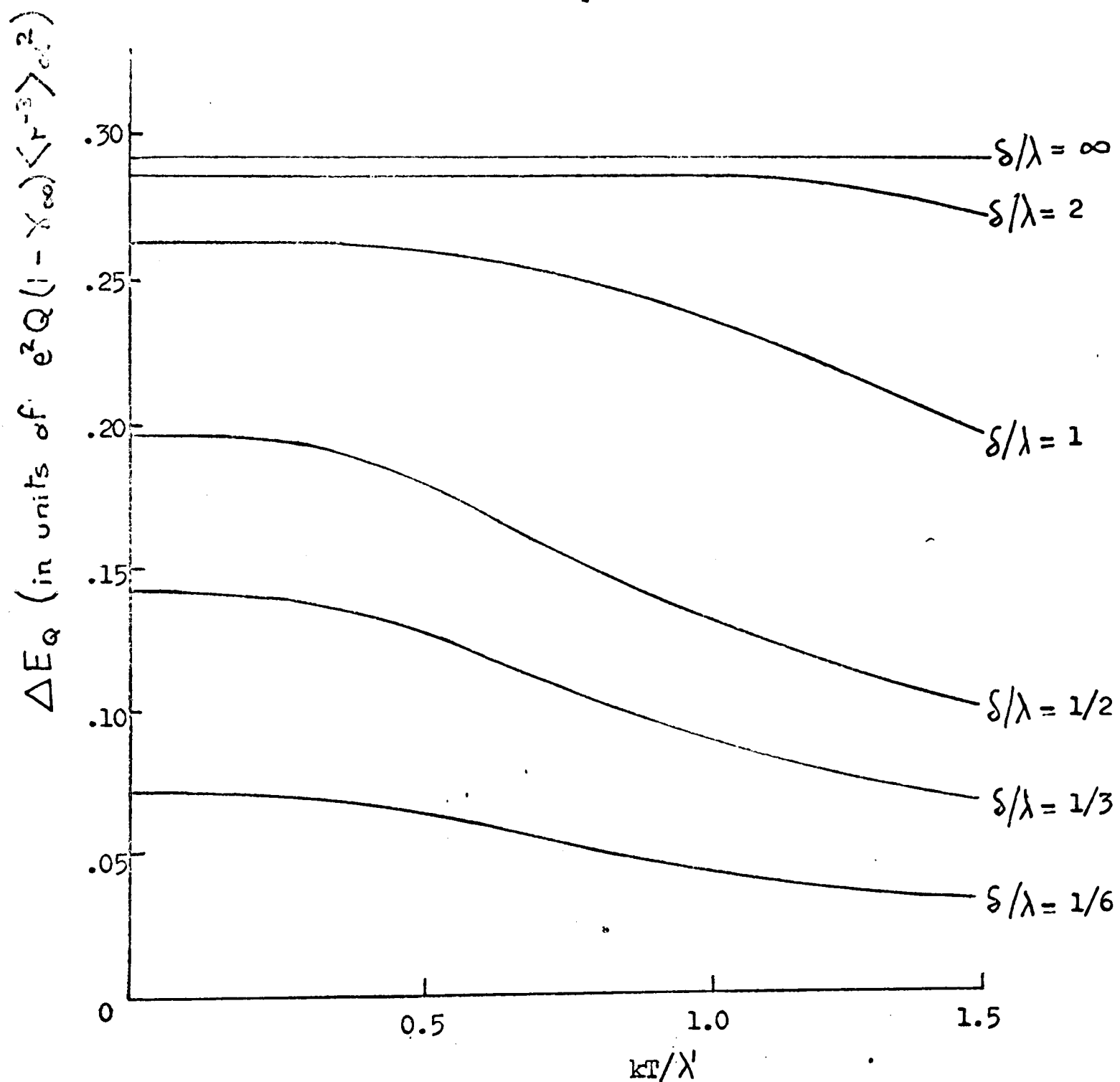
$$x = \delta/\lambda$$

α is given by $\alpha^2 = \lambda'/\lambda$ where λ is the free ion spin orbit coupling constant and λ' is the spin orbit coupling constant of the complexed species. δ is the splitting of the 2T_2 levels caused by the ligand field in the absence of spin orbit coupling. The values of λ' and δ depend on the coefficients of eq. (44).

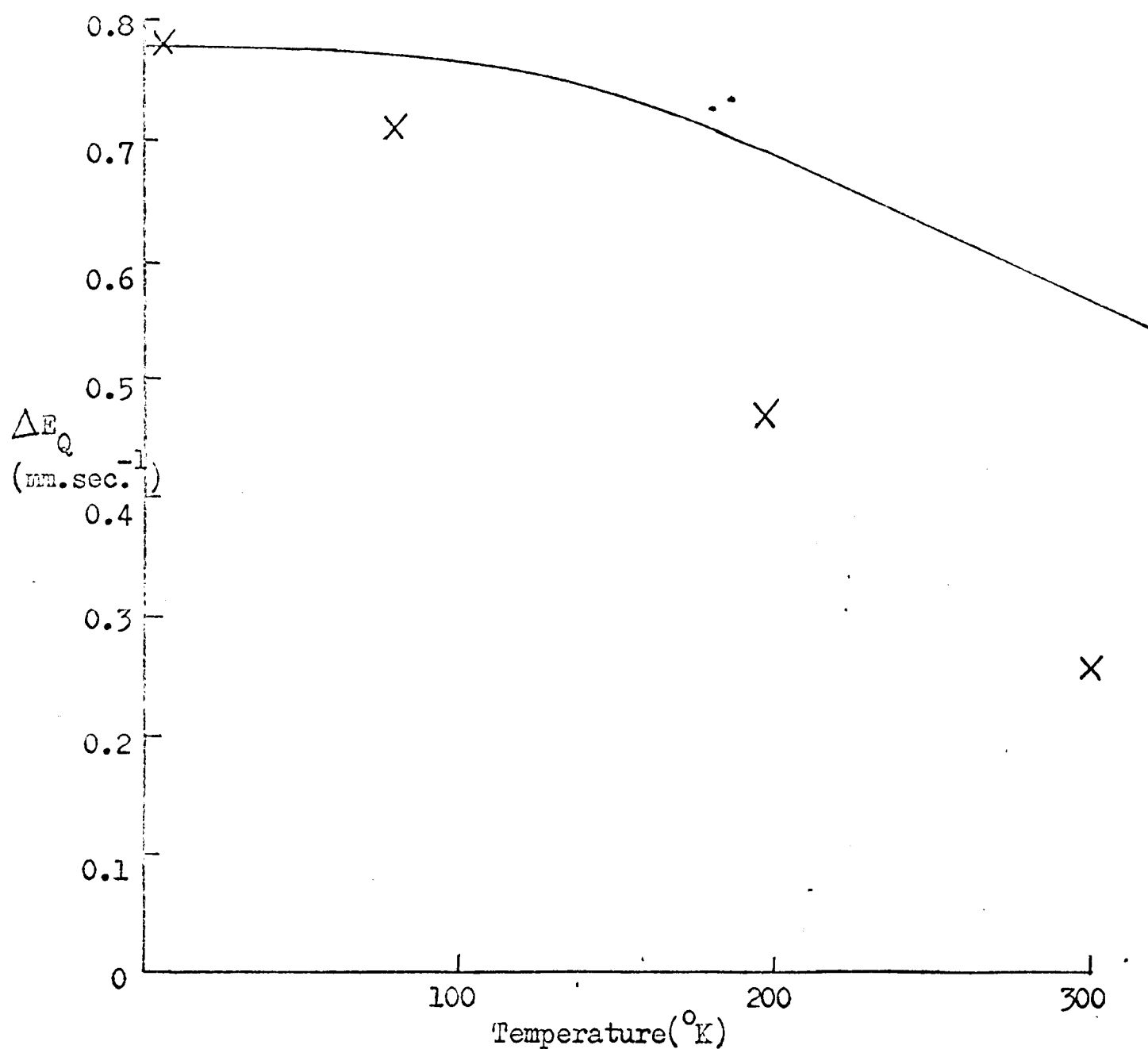
The dependence of the quadrupole splitting upon temperature for various ratios of δ/λ is plotted in Figure 3.25.

In Figure 3.26 is plotted the calculated curve for $\delta/\lambda = 0.25$

with $\lambda' = 300 \text{ cm.}^{-1}$ which fits the data best for iron(III) N,N dimethyl-

Figure 3.25.

The temperature dependence of the quadrupole splitting for low-spin ferric compounds. (After Golding⁽¹⁰¹⁾).

Figure 3.26.Plot of quadrupole splitting against temperature.

The solid line is the theoretical curve for a low spin compound with $\Delta E_Q = 0.78 \text{ mm.sec.}^{-1}$ at 4.2°K , with $\delta/\lambda = \frac{1}{4}$ and $\lambda' = 300 \text{ cm.}^{-1}$. The experimental points (X) are for iron(III) N,N dimethyldithiocarbamate.

dithiocarbamate at low temperatures. The experimental points are also plotted. It is seen that they lie well below the calculated curve at high temperatures. The large decrease in quadrupole splitting observed as the temperature increases, evidently cannot be satisfactorily explained simply by considering the 2T_2 levels. As the temperature increases the high-spin, 6A_1 , state becomes populated. We have already seen in the pyrroliidyl compound that this state has a small electric field gradient compared to the low-spin compounds, and hence the abnormally large decrease in quadrupole splitting can be explained. A similar decrease is found in the other compounds, but the effect is greatest in the dimethyl compound which has the greatest increase in μ_{eff} , that is, the greatest population of the 6A_1 state at room temperature.

The position of the equilibrium.

Ewald et al.⁽⁸⁰⁾ have pointed out the difficulties in estimating the relative populations of the two spin states from the magnetic measurements, due principally to the uncertainty in estimating a magnetic moment for the low-spin species. We had hoped that Mössbauer spectroscopic measurements might be useful in resolving this problem. However, since only an averaged spectrum was observed the estimation of relative concentrations from intensity measurements is not possible. The temperature dependence of the quadrupole splitting correlates well with the temperature dependence of the magnetic moment, but in

attempting to determine the population of the high- and low-spin states the problem arises of estimating the quadrupole splitting for the low-spin species. This is essentially the same problem as estimating μ_{eff} since unknown contributions to both quantities from spin-orbit coupling are important. More hope would seem to lie with isomer shift measurements, but as we have seen the temperature dependence of the shift due to the second order Doppler Effect, must then be taken into account. Furthermore the temperature dependence of the isomer shift is very small, and the accuracy of its determination is limited by instrumental factors. The position of the equilibrium can therefore be estimated only very approximately from our measurements.

We have seen qualitatively how the Mössbauer parameters are affected by the high-spin, low-spin equilibrium, and have shown how they yield confirmation for this phenomenon. We shall now examine in more detail the Mössbauer spectra observed at low temperatures and in external magnetic fields. Important information about the ground state of the iron(III) *N,N* dialkyldithiocarbamates is obtained. We shall concentrate our attention on two compounds, the typical low-spin compound, (at low temperatures), iron(III) *N,N* dimethyldithiocarbamate, and the high-spin iron(III) pyrrolidyl-dithiocarbamate.

Iron(III) N,N dimethyldithiocarbamate.

Information on the ground state of this compound can be obtained from the electric field gradient data. Inspection of the Mössbauer spectrum of this compound at 4.2°K and in a 30 kG external field, (Figure 3.7(f)), shows that the sign of the major component of the electric field gradient is positive and perpendicular to the direction of magnetisation. If the electric field gradient produced by the lattice is neglected, the quadrupole splitting is given by:

$$\Delta E_Q = \frac{1}{2} e^2 q Q (1 - R) \alpha^2 \quad (47)$$

If V_{xx} , V_{yy} and V_{zz} are the components along the principal axes of the ligand field of the second derivative of the electrostatic potential, V , then:

$$eq = \left[V_{zz}^2 + \frac{(V_{xx} - V_{yy})^2}{3} \right]^{\frac{1}{2}} \quad (48)$$

V_{xx} , V_{yy} and V_{zz} may be expressed in terms of A, B, and C, the coefficients of eq.(40).

$$\begin{aligned} V_{zz} &= \frac{-2}{7} \langle r^{-3} \rangle \langle \psi | L_z^2 - 2 | \psi \rangle \\ &= \frac{-2}{7} \langle r^{-3} \rangle (-A^2 + 2B^2 + C^2) \\ V_{xx} - V_{yy} &= \frac{-2}{7} \langle r^{-3} \rangle \langle \psi | L_+^2 + L_-^2 | \psi \rangle \\ &= 6AC \end{aligned} \quad (49)$$

Since

$$V_{xx} + V_{yy} = -V_{zz}$$

$$V_{xx} = \frac{1}{2}(-\frac{2}{7}) \langle r^{-3} \rangle ((A^2 - 2B^2 + C^2) + 6AC) \quad (50)$$

and

$$V_{yy} = \frac{1}{2}(-\frac{2}{7}) \langle r^{-3} \rangle ((A^2 - 2B^2 + C^2) - 6AC) \quad (51)$$

We also use the fact that for a pure d-orbital the electric field gradient is $4/7 \langle r^{-3} \rangle$ and the quadrupole splitting may be taken as $2.54 \text{ mm. sec.}^{-1} (101)$

The g-values are given by eqs.(41),(42) and (43).

Taking the orbital reduction factor, k, as one for simplicity, we have:

$$g_z = 2(2A^2 - B^2)$$

$$g_x = 2(\sqrt{2A + B})(\sqrt{2C + B})$$

$$g_y = 2(\sqrt{2A + B})(\sqrt{2C + B})$$

If $p = \sqrt{2A + B}$ then:

$$4p^2(4 - p^2) = g_x^2 + g_y^2 + g_z^2 = 3g_{av}^2$$

At low temperatures we may take g_{av} as 2 (corresponding to $\mu_{eff} = \sqrt{3}$).

The effective direction of magnetisation of a polycrystalline sample in a magnetic field will tend to be perpendicular to the symmetry axis of the ligand field, unless the g-values are highly anisotropic, (or more strictly, the product gH_n where H_n is the magnetic hyperfine field tensor), with $g_z \gg g_x, g_y$. The observed spectrum, (Figure 3.7(f)), shows that the average magnetisation tends to be perpendicular to z, the symmetry axis of the ligand field. Therefore g and H_n are almost certainly not very anisotropic, corresponding to only small distortions of the molecule. g_x and g_y are not necessarily the maximum g-values but they will not be much less than g_z .

We can now attempt to fit our data to the theory.

The data we require to fit are:

- (i) the magnitude and sign of the quadrupole coupling;
- (ii) the observation that the component of the electric field gradient is negative in the direction of magnetisation of a polycrystalline sample in a magnetic field, that is, V_{xx} is negative;
- (iii) the average value of g .

No set of values of A , B and C can be found to simultaneously account for all these data. A reasonable fit is obtained when $A = 0.822$, $B = 0.570$ and $C = 0$, corresponding to a small distortion giving a ground state consisting of equal amounts of $|xz\rangle$ and $|yz\rangle$ with slightly less of $|xy\rangle$. This satisfies all the above conditions except that the magnitude of the quadrupole splitting ($0.04 \text{ mm. sec.}^{-1}$) is much smaller than that observed. The calculated g -values are close to 2, being $g_x = g_y = 1.975$, $g_z = 2.05$.

Difficulties have been encountered by other workers attempting to interpret measurements on low-spin ferric complexes. Bleaney and O'Brien⁽¹⁰²⁾ found that the values of A , B and C that accounted for the anisotropy of the g -tensor in $K_3\text{Fe}(\text{CN})_6$ gave values which were too large. In a Mössbauer study of the same complex, Oosterhuis, Lang and deBenedetti were unable to account for

the temperature dependence of the quadrupole splitting over the whole range from 4.2°K to 300°K.⁽¹⁰³⁾

The discrepancies are presumably associated with the neglect of the lattice contributions to the electric field gradient, and with the assumption of pure d-functions. In this compound the neglect of the nearby excited 6A_1 state may also be important.

In order to study further the ground state of this compound, a specimen of iron(III) N,N dimethyldithiocarbamate doped in cobalt(III) N,N dimethyldithiocarbamate was prepared and studied. Iron(III) N,N dimethyldithiocarbamate diluted in cobalt(III) N,N dimethyldithiocarbamate.

Mössbauer spectra.

In attempting to establish further information about the ground state of iron(III) N,N dimethyldithiocarbamate from the Mössbauer and epr spectra of the diluted complex, it was important firstly to ensure that the energy levels of the complex were not perturbed when it was doped into the host lattice of cobalt(III) N,N dimethyldithiocarbamate.

The Mössbauer spectrum of the sample of the diluted complex containing ${}^{57}\text{Fe}$ iron(III) N,N dimethyldithiocarbamate was measured at 300°K, 195°K and 77°K. The values of the isomer shift and quadrupole splitting were found to be equal within experimental

error to the values observed in the concentrated sample (Table 3.2). The spin equilibrium would therefore seem to persist in the diluted sample, which is perhaps surprising due to the minor structural modifications that are required to shift the position of the equilibrium. Furthermore, at low temperatures and in external magnetic fields, the transitions in the Mössbauer spectra showing magnetic hyperfine interactions occur at the same energies as in the concentrated sample. It is therefore justifiable to apply the results from our measurements on this sample to a discussion of the nature of the ground state of iron(III) N,N dimethyldithiocarbamate.

At 4.2°K the electron spin relaxation times are long for this sample, (Figure 3.18(a)), and a field of 500 gauss applied perpendicularly to the gamma ray beam is sufficient to decouple the electron and nuclear spins and produce a spectrum showing well resolved magnetic hyperfine interactions (Figure 3.18(b)). The lines are now much sharper than those observed in the spectrum of the concentrated sample at 4.2°K in a 30 kG field (Figure 3.7(f)), where the sample is actually magnetised. The intensities of the six lines are approximately in the ratio 3:4:1:1:4:3. When a small field is induced parallel to the gamma ray beam the intensities of the lines change, those of the second and fifth lines decreasing. The expected ratio of 3:0:1:1:0:3 is not observed, however.

Electron paramagnetic resonance.

Previous attempts to detect the epr spectra of iron(III) N,N dimethyldithiocarbamates have not been successful, even when the measurements have been conducted at 4.2°K⁽⁸⁹⁾. We were unable to detect an epr spectrum in our sample at high temperatures ($> 100^\circ\text{K}$). This may be due to the presence of the nearby excited 6A_1 state giving rise to fast relaxation rates. For a sample of (unenriched) iron(III) N,N dimethyldithiocarbamate diluted in cobalt(III) N,N dimethyldithiocarbamate the epr spectrum shown in Figure 3.17 was observed at 4.2°K. The g-values are:

$$g_1 = 2.015, g_2 = 2.076, g_3 = 2.111 \quad (\pm 0.005)$$

An attempt to observe hyperfine interactions due to the ^{57}Fe , $I = 1/2$, was unsuccessful. The sample enriched with ^{57}Fe showed broad lines in its epr spectrum, presumably arising from exchange interactions. The epr and Mössbauer data that we have obtained, have therefore come from different samples

The g-values can be fitted to eqs.(41)(42)(43), taking the values $A = 0.825$, $B = 0.595$, $C = 0.0035$ and the orbital reduction factor, $k = 1$. These values give excellent agreement with experiment, giving $g_z = 2.015$, $g_x = 2.077$ and $g_y = 2.112$, although the normalisation condition is not exactly satisfied since $A^2 + B^2 + C^2 = 1.03$. The values of A, B, and C are also in good agreement with those estimated earlier from the electric field gradient data.

The matrix of the spin-orbit coupling and the low symmetry field is given by⁽⁶⁰⁾:

$$\begin{array}{ccc}
 |1^+\rangle & |3_1^-\rangle & |-1^+\rangle \\
 \text{(or } |-1^-\rangle \text{)} & \text{(or } -|3_1^+\rangle \text{)} & \text{(or } |1^-\rangle \text{)} \\
 |1^+\rangle \text{ (or } |-1^-\rangle \text{)} & \frac{1}{2}\lambda & \frac{1}{2}\lambda\sqrt{2} & \frac{1}{2}V \\
 |3_1^-\rangle \text{ (or } -|3_1^+\rangle \text{)} & \frac{1}{2}\lambda\sqrt{2} & \Delta & 0 \\
 |-1^+\rangle \text{ (or } |1^-\rangle \text{)} & \frac{1}{2}V & 0 & -\frac{1}{2}\lambda
 \end{array} \quad (52)$$

The secular equations associated with this matrix are:

$$\begin{aligned}
 \left(\frac{1}{2}\lambda - E\right)A + \frac{1}{2}\lambda\sqrt{2}B + \frac{1}{2}VC &= 0 \\
 \frac{1}{2}\lambda\sqrt{2}A + (\Delta - E)B &= 0 \\
 \frac{1}{2}VA + \left(-\frac{1}{2}\lambda - E\right)C &= 0
 \end{aligned} \quad (53)$$

which can be solved for Δ/λ and V/λ , giving in this case 0.302 and -0.0043 respectively. Taking λ as 300 cm^{-1} , the orbital separations associated with the single hole are 91 cm^{-1} and 1.2 cm^{-1} respectively.

The distortion from cubic symmetry is indeed very small.

The calculated quadrupole splitting is $0.03 \text{ mm. sec.}^{-1}$

in poor agreement with experiment. Contributions from covalency, the lattice and the effects of the excited $6A_1$ state are evidently important in determining the magnitude of the quadrupole splitting.

Iron(III) pyrrolidylthiocarbamate.

We have already seen that this complex shows slow electron spin relaxation rates at 4.2°K , resulting in the observation of magnetic hyperfine splittings in its Mössbauer spectrum.

The structure of the complex has not yet been determined, but the metal - metal distance is expected to be small as it is in related compounds. For example, the Co - Co distance in cobalt(III) N,N diethyldithiocarbamate is only about $5.3 \text{ \AA}^{(71)}$. Spin-spin relaxation times are therefore expected to be short. Spin-lattice relaxation times will be long however, since the compound contains only high-spin ferric ions.

The Mössbauer spectrum at 4.2°K shows six absorption lines, (Figure 3.11(d)), and the effective field at the nucleus is $440 \pm 5 \text{ kG}$. At 1.3°K , (Figure 3.11(e)), the spectrum is slightly different, the effective field having increased to $460 \pm 5 \text{ kG}$ over this small temperature range. As the temperature is increased to 6°K , (Figure 3.11(c)), and 9°K , (Figure 3.11(b)), the lines of the spectrum become increasingly broad and at 12°K , (Figure 3.11(a)), they have collapsed to a single broad line.

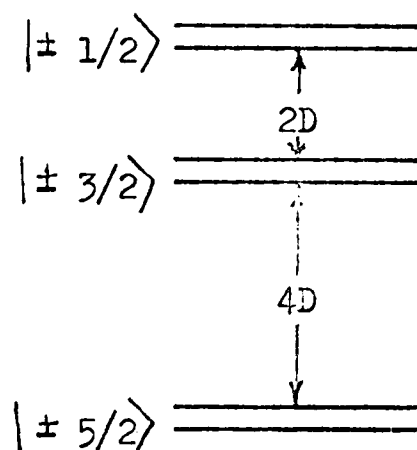
The observed effects can be explained by the variation of the spin-spin relaxation time with temperature. The spectra in the temperature range $1.3^{\circ}\text{K} - 4.2^{\circ}\text{K}$ can be interpreted on a model with a large zero field splitting, D, of the ^6S state

according to the spin-Hamiltonian:

$$\mathcal{H} = D(S_z^2 - 35/12) + AS.I$$

When D is negative the Kramers doublet $|\pm 5/2\rangle$ lies lowest and the separations of the Kramers doublets are as shown in Figure 3.26.

Figure 3.26.



If $4|D|/k$ is greater than 4.2°K only the lowest doublet will be populated at helium temperatures. Transitions between the $|+ 5/2\rangle$ and the $|- 5/2\rangle$ levels are forbidden so that the spectrum observed is a superposition of two identical six line spectra with $H_{\text{eff}} = 5A/2g_n\beta_n$

The situation may be compared with the case of dilute Fe^{3+} in Al_2O_3 (104). Again relaxation times are long, but now D is small so that all the levels are populated and three separate spectra for the $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ levels are observed.

In iron(III) pyrrolidylthiocarbamate, at 1.3°K the occupation of the $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ levels is negligible, but as the temperature is raised to 4.2°K the $|\pm 3/2\rangle$ levels become populated to a small extent. Relaxation between the $|+ 5/2\rangle$ and $|+ 3/2\rangle$ and the $|- 5/2\rangle$ and $|-3/2\rangle$ levels is now possible since transitions are allowed between the two components of this doublet. The effective field averages out between these pairs of states and decreases with increasing temperature as observed. As the temperature is further raised the $|\pm 1/2\rangle$ levels eventually become appreciably populated. The relaxation rate then increases rapidly with temperature and the Mössbauer spectrum collapses to a single broad line.

The explanation of the relaxation mechanism is supported by other observations. Firstly, we were unable to detect an epr spectrum for this compound at 4.2°K , consistent with the concept of a large zero field splitting with the $|\pm 5/2\rangle$ levels lying lowest. Secondly, an applied magnetic field has a negligible effect on the Mössbauer spectrum at 1.3°K (Figure 3.12). If the $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ levels were quite close in energy to the $|\pm 5/2\rangle$ levels the splitting of these states in a magnetic field should result in some population of these states and the consequent appearance of extra lines in the spectrum⁽³⁰⁾. This is not seen. The slight broadening observed in the spectrum at 4.2°K compared to 1.3°K is

attributable to second order effects⁽¹⁰⁵⁾.

The Mössbauer spectra of this complex enable us to estimate the value of D from a comparison of the effective magnetic field at 4.2°K and 1.3°K . Since the population of the $|\pm 1/2\rangle$ doublet is negligible, we can write:

$$H_{\text{eff}}^{(T)} = \frac{\frac{5}{2} + \frac{3}{2} e^{-4|D|/kT}}{\frac{5}{2}(1 + e^{-4|D|/kT})} H_{\text{eff}}^{(0)} \quad (54)$$

where $H_{\text{eff}}^{(T)}$ is the effective field at $T^{\circ}\text{K}$. From our data $4|D|/k$ is estimated as 9.3°K , taking $H_{\text{eff}}^{(0)}$ as 470 kG.

The large value of D may be associated with the presence in this complex of a nearby excited 2T_2 state. Large values of D are also found in some haemoglobin compounds where there is also a close approach of higher states⁽¹⁰⁶⁾.

The component of the electric field gradient tensor in the direction of the magnetic field is negative. The major components of the electric field gradient and zero field splitting tensors will have the same axes. Since the $S_z = \pm 5/2$ states lie lowest, the major component of the electric field gradient will be parallel to the axis of magnetisation. If the molecule is assumed to be subject to a trigonal distortion, the negative sign of the major component of the electric field gradient corresponds to an elongation.

Iron(III) N,N di-n-butylthiocarbamate.

This compound has many anomalous properties.

Its magnetic moment vs. temperature curve shows a marked and reproducible discontinuity at about 140°K (see Figure 3.5), which has been associated with a phase change⁽⁶⁰⁾. Also, unlike most of the other derivatives, its magnetic moment in solution is appreciably lower than in is in the solid state⁽⁷⁹⁾.

We have also observed peculiarities in its Mössbauer spectra. Although prolonged runs were made at room temperature with several different samples of this compound, we were unable to detect a Mössbauer Effect. Only small effects were observable at 253°K and 195°K , but at 77°K the intensity of the spectrum was comparable to that of the other compounds.

It has recently been shown that the compound can exist in two crystalline forms. It is interesting to note that the spin equilibrium is present in both forms, although the position of the equilibrium is not the same⁽⁷⁰⁾. We consider that the absence of a Mössbauer Effect at 300°K is a consequence of a low Debye - Waller factor associated with the crystalline modification stable at room temperature.

It was also impossible to obtain well resolved magnetic hyperfine interactions for this compound, even at 1.2°K in an external magnetic field of 30 kG.

ii) Magnetic hyperfine interactions in bis(N,N dialkyldithiocarbamato)iron(III) chlorides.

The magnetic field at the Mössbauer nucleus may arise in a number of ways. Thus ferromagnetic, antiferromagnetic and paramagnetic compounds may in suitable circumstances all show similar Mössbauer spectra. It was interesting to compare the spectra obtained at low temperatures for iron(III) pyrrolidylthiocarbamate with similar spectra obtained for bis(N,N diethyldithiocarbamato)iron(III) chloride.

Magnetic susceptibility and magnetisation measurements on bis(N,N diethyldithiocarbamato)iron(III) chloride have shown it to be a $S = 3/2$ ferromagnet with a Curie temperature of 2.5°K ⁽¹⁰⁷⁾. Previous Mössbauer Effect measurements showed line broadening due to relaxation effects, and did not distinguish between this ferromagnet and some slowly relaxing paramagnets of similar structure⁽¹⁰⁸⁾⁽¹⁰⁹⁾. We have carried out Mössbauer Effect measurements on this compound at low temperatures and in external magnetic fields, and the spectra that we have obtained confirm that the compound is ferromagnetic. For comparison, similar experiments were performed on the related paramagnetic compound bis(N,N diisopropylthiocarbamato)iron(III) chloride.

The spectrum obtained for the diethyl compound at 4.2°K (Table 3.3), was identical to that reported previously⁽¹⁰⁷⁾.

At 1.6°K a six line spectrum was observed, (Figure 3.13(a)), from which the value of the effective field at the iron nucleus was estimated as 322 ± 5 kG. In order to confirm that the sample was ferromagnetic, the spectrum was then measured in an externally applied field of 30 kG.

When an external magnetic field is applied to a ferromagnetic absorber the Mössbauer spectrum is perturbed in two ways. Firstly, the relative line intensities change from 3:2:1:1:2:3 to 3:4:1:1:4:3 when the field is applied perpendicular to the gamma ray direction, as the atomic spins of the ferromagnet align themselves parallel to the external field. In the spectrum of bis(N,N diethyldithiocarbamate)iron(III) chloride, the intensities of lines 2 and 5 increase relative to lines 1 and 6 when the external field is applied (Figure 3.13(b)). As the absorber is polycrystalline, of finite thickness and the environment of the ^{57}Fe atoms is not exactly cubic, the changes in intensity are not exactly as predicted.

The second effect of the external field is to alter the value of the effective field at the iron nucleus, H_{eff} .

H_{eff} is given by:

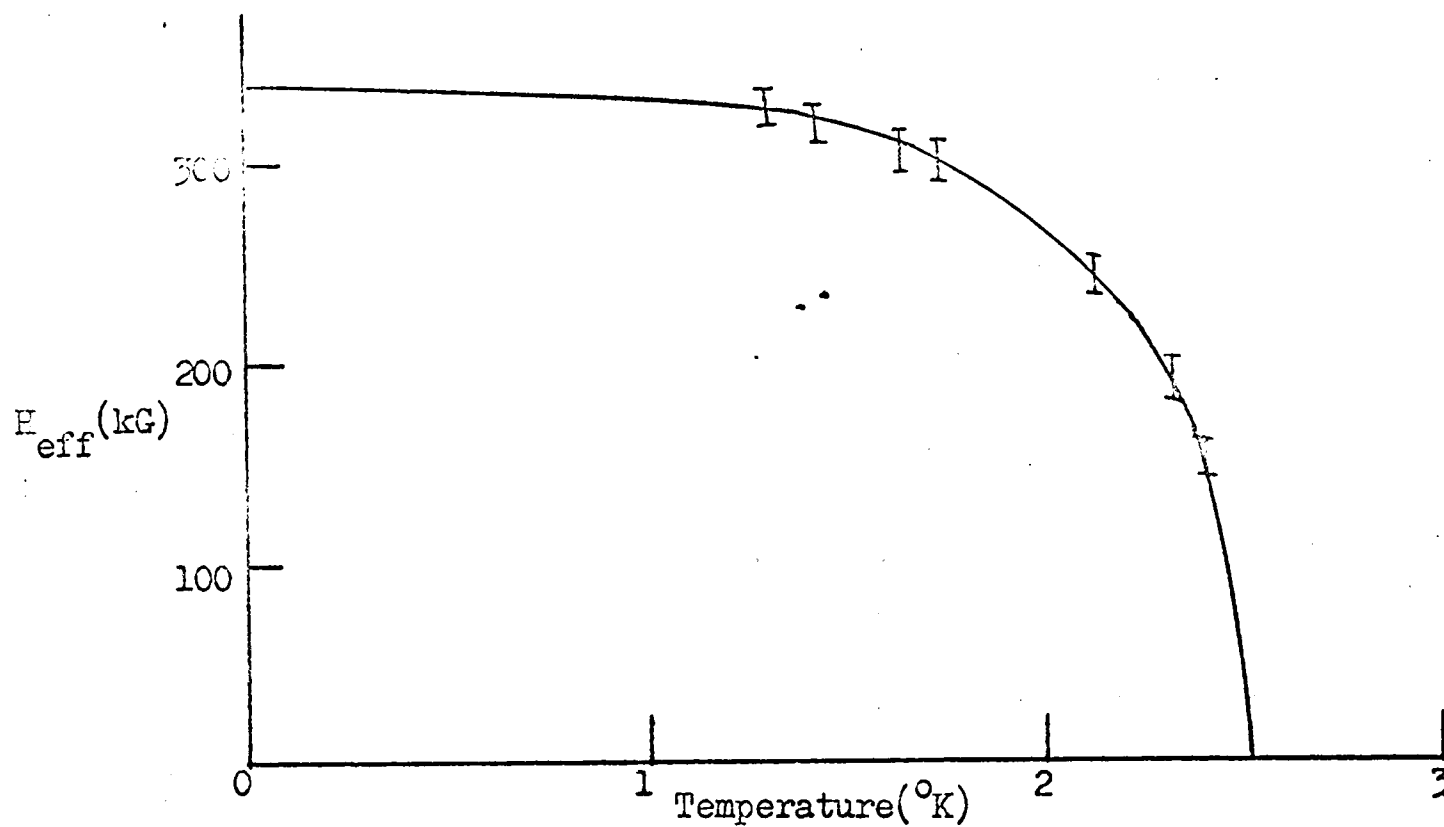
$$H_{\text{eff}} = \left\langle \frac{S}{S} \right\rangle H_n - H \quad (55)$$

where H_n is the saturation value of the hyperfine field, H is the external field and S is the spin. The application of a 30 kG field at 1.6°K reduces the value of $|H_{\text{eff}}|$ to 300 ± 5 kG. The internal

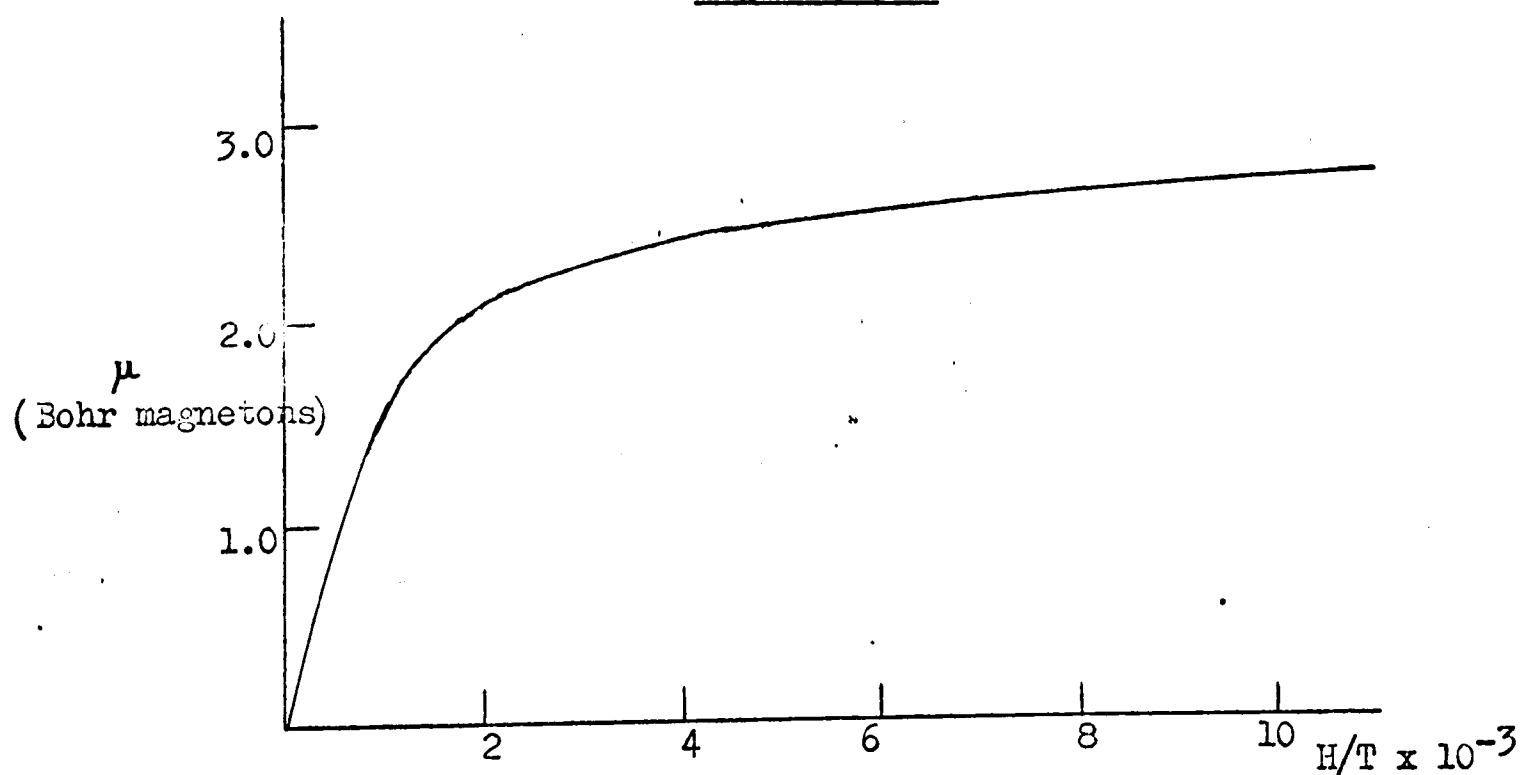
field is therefore negative. It is also field dependent; one would expect it to decrease by 30 kG instead of 22 kG. This behaviour can be understood with reference to the plot of H_{eff} against temperature shown in Figure 3.27, which has been compiled from the data of Wickmann et al.⁽¹⁰⁷⁾ together with our data. A temperature of 1.6°K is not far below the Curie point for this compound, and at this temperature the value of the internal field has not attained the saturation value H_n . The expectation value of the magnetic moment, $\langle \mu \rangle$, is estimated from our data as about $2.8 \mu_B$ at 1.6°K. From the magnetic data of Wickmann et al.⁽¹⁰⁷⁾, (Figure 3.28), $\langle \mu \rangle$ at $H/T = 30/1.6 \text{ kG/}^\circ\text{K}$ is estimated as about $2.9 \mu_B$. When the external field is applied therefore, $\langle \mu \rangle$ is increased from $2.8 \mu_B$ to $2.9 \mu_B$ and the decrease in H_{eff} is not equal and opposite to the applied field.

Both the changes in intensity of the absorption lines, and the field and temperature dependence of H_{eff} are consistent with the compound being ferromagnetic and are not consistent with antiferromagnetism or paramagnetism.

For comparison the Mössbauer spectra of the diisopropyl compound may be considered. At 1.3°K it shows a six line spectrum typical of magnetic ordering (Figure 3.14(a)). The effect of an externally applied field on this spectrum is however quite different from the previous ferromagnetic case. Epr studies on this

Figure 3.27.

Plot of effective field at the iron nucleus vs. temperature for $(\text{Et}_2\text{NCS}_2)_2\text{FeCl}$.

Figure 3.28.

Magnetisation curve for $(\text{Et}_2\text{NCS}_2)_2\text{FeCl}$ at 1.5°K (from ref (107)).

compound have shown that the zero field splitting of the two Kramer's doublets is $-4.0 \pm 0.5^\circ\text{K}^{(110)}$. The $|\pm 3/2\rangle$ doublet lies lowest and at 1.3°K the $|\pm 1/2\rangle$ doublet is not populated. The application of an external field of 5kG splits the Kramer's levels and some population of the $|\pm 1/2\rangle$ levels is now possible. Extra transitions can now occur, resulting in the observed broadening of the lines of the Mössbauer spectrum (Figure 3.14(b)).

iii) Nitrosyliron bis(N,N diethyldithiocarbamate).

As a continuation of the study of complexes of iron with dialkyldithiocarbamate ligands, the Mössbauer Effect in nitrosyliron bis(N,N diethyldithiocarbamate) was investigated. The crystal and molecular structure of this complex has been established⁽⁷⁴⁾, and the electronic structure has been discussed. On the basis of absorption spectroscopic measurements and epr data Gray, Bernal and Billig⁽¹¹¹⁾ have proposed the molecular scheme shown in Figure 3.29. The epr spectrum has also been investigated by other workers⁽⁷⁶⁾⁽¹¹²⁾. The complex may be considered to be an iron(I) complex, indeed epr measurements on the ⁵⁷Fe enriched complex show that the unpaired electron is about 80% localised on the iron atom⁽⁷⁶⁾. Mössbauer Effect measurements at room temperature have been reported previously⁽¹¹³⁾.

The Mössbauer spectrum.

The spectrum between 300°K and 1.3°K consisted of a quadrupole split pair of lines of unequal intensity. The anisotropy of the line intensities was presumably due to preferred orientation of the crystals in the sample, and not due to relaxation phenomena or to the Gol'danskii Effect, as it was temperature independent and could be reduced by finely powdering the sample. However, it was not possible to obtain line intensities that were exactly equal, (Figure 3.15).

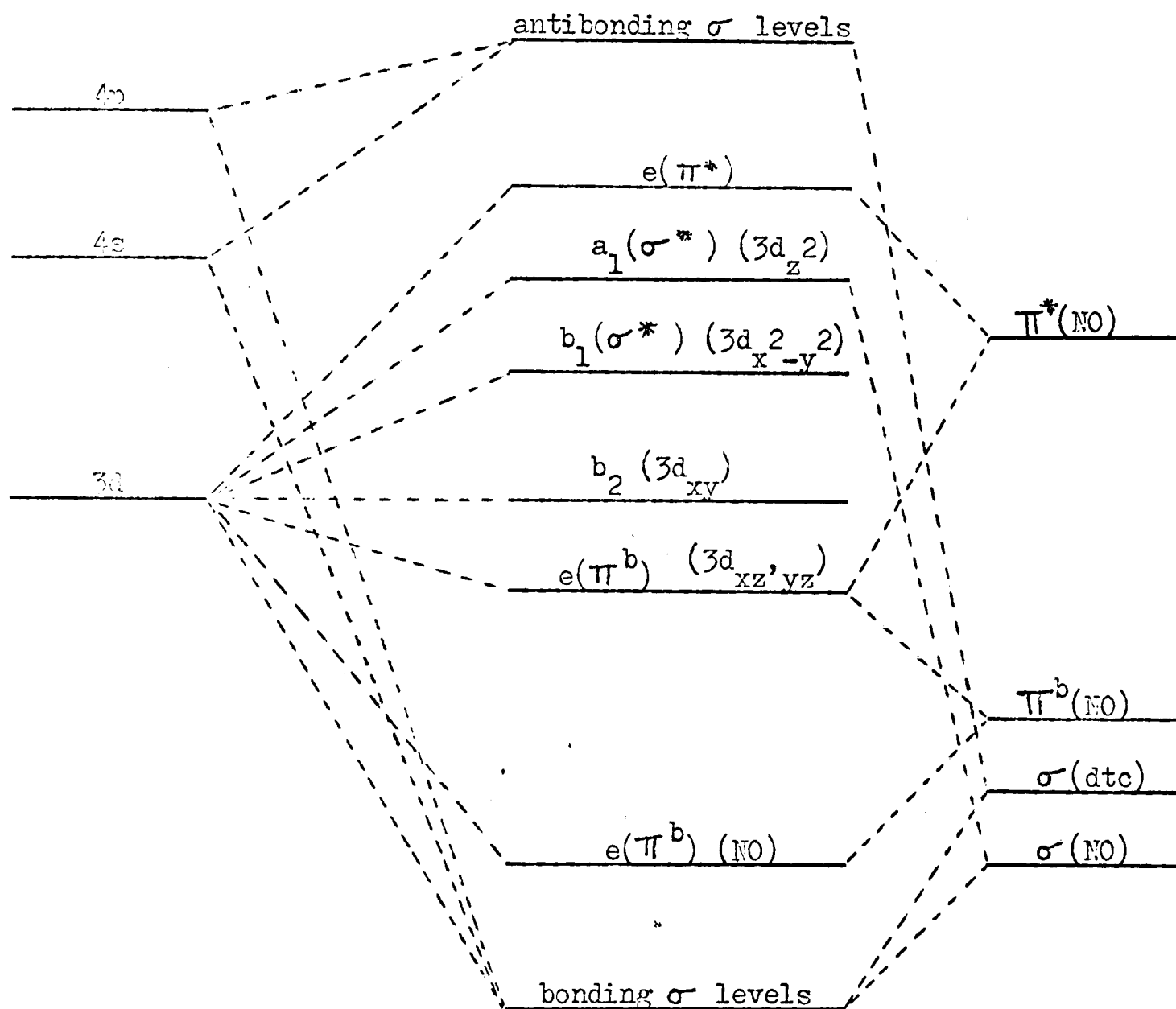
The intensity of the absorption increased by a factor of about six on cooling from 300°K to 77°K, indicating a low

Figure 3.29.

Metal orbitals

M.O.- levels

Ligand orbitals



Molecular orbital energy level scheme for $((C_5H_5)_2NCS)_2FeNO$, after Gray.

effective Debye temperature for iron in this compound, as in the other dithiocarbamate complexes investigated.

The isomer shift.

The isomer shift increased from $0.28 \text{ mm. sec.}^{-1}$ at 300°K to $0.34 \text{ mm. sec.}^{-1}$ at 77°K , which is about the increase expected from the second order Doppler Effect. The value of the isomer shift is quite similar to the values found in the iron(III) N,N dialkyl-dithiocarbamates (compare Tables 3.1 and 3.4). The similar values can be accounted for if the metal d-orbitals are considered to have considerable ligand character. Occupation of these orbitals by electrons will then affect relatively little the s-electron density at the iron nucleus.

The quadrupole splitting.

The quadrupole splitting is $0.89 \text{ mm. sec.}^{-1}$ at 300°K and has the same value at 4.2°K , showing little dependence on temperature over the whole temperature range. On the application of a magnetic field of 15 kG or more at 4.2°K , the left hand line of the quadrupole split pair splits into three components and the right hand line splits into two (Figure 3. 16).

Ruby and Flinn⁽¹¹⁴⁾ first showed that the sign of the quadrupole splitting can be determined by magnetically perturbing the energy levels. Collins⁽⁴⁴⁾ has given a fuller treatment for the case of ferrocene. It is assumed that the symmetry is axial and

that H makes an angle θ with the z -axis, which is also the principal axis of the electric field gradient. The magnetic Hamiltonian (eq.(15)), then becomes:

$$\mathcal{H}_M = g_{e,n} \mu_N H (I_z \cos\theta + I_x \sin\theta \cos\phi + I_y \sin\theta \sin\phi) \quad (56)$$

where the projection of I on to the xy plane makes an angle ϕ with the x -axis. The matrix associated with the magnetic and quadrupole Hamiltonian for the excited state is:

$$\begin{array}{cccc} E + \frac{3\alpha \cos\theta}{2} & \frac{\sqrt{3}\alpha \sin\theta (\cos\phi - i\sin\phi)}{2} & 0 & 0 \\ \frac{\sqrt{3}\alpha \sin\theta (\cos\phi + i\sin\phi)}{2} & -E + \frac{\alpha \cos\theta}{2} & \alpha \sin\theta (\cos\phi - i\sin\phi) & 0 \\ 0 & \alpha \sin\theta (\cos\phi + i\sin\phi) & -E - \frac{\alpha \cos\theta}{2} & \frac{3\alpha \sin\theta (\cos\phi - i\sin\phi)}{2} \\ 0 & 0 & \frac{3\alpha \sin\theta (\cos\phi + i\sin\phi)}{2} & E - \frac{3}{2} \cos\theta \end{array}$$

where $E = \frac{1}{2}e^2 qQ$ and $\alpha = g_{e,n} \mu_N H$.

Neglecting the mixing in of $|3/2, 3/2\rangle$ with $|3/2, 1/2\rangle$ and of $|3/2, -3/2\rangle$ with $|3/2, -1/2\rangle$, the energy levels and wave functions of the excited state become:

$$\begin{array}{ll} E + \frac{3\alpha \cos\theta}{2} & |3/2, 3/2\rangle \\ -E + \frac{\alpha}{2} \sqrt{4 - 3\cos^2\theta} & |3/2, +\rangle \\ -E - \frac{\alpha}{2} \sqrt{4 - 3\cos^2\theta} & |3/2, -\rangle \\ E - \frac{3\alpha \cos\theta}{2} & |3/2, -3/2\rangle \end{array}$$

$$\begin{aligned}\text{where } |3/2, +\rangle &= -\sin\delta |3/2, -1/2\rangle + \cos\delta |3/2, 1/2\rangle \\ |3/2, -\rangle &= \cos\delta |3/2, -1/2\rangle + \sin\delta |3/2, 1/2\rangle\end{aligned}$$

and,

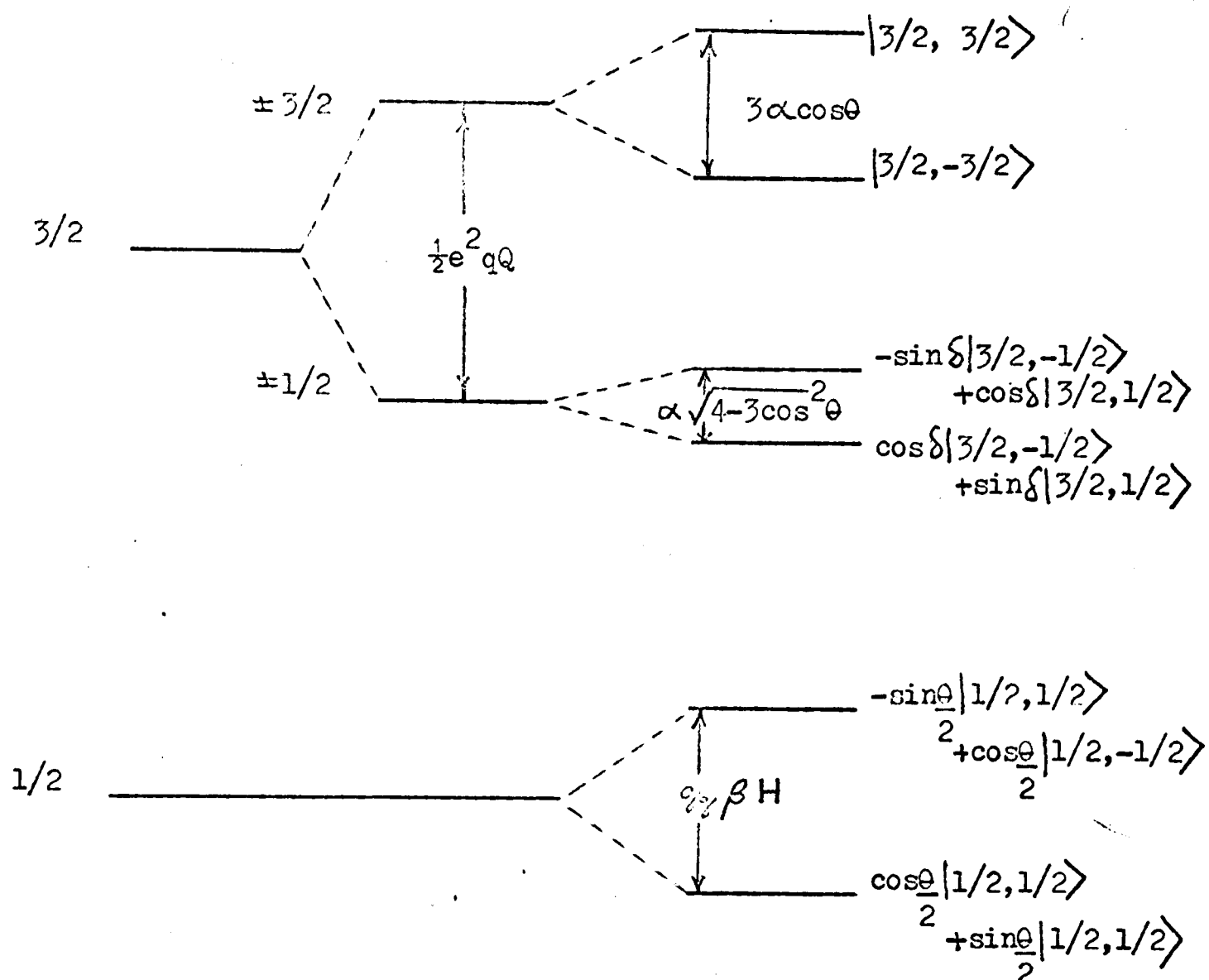
$$\tan\delta = \left[\frac{(4 - 3\cos^2\theta)^{\frac{1}{2}} - \cos\theta}{(4 - 3\cos^2\theta)^{\frac{1}{2}} + \cos\theta} \right]^{\frac{1}{2}}$$

The energy levels and wave functions for the ground state are:

$$\begin{aligned}-\frac{g_n \mu_N H}{2} & \cos\frac{\theta}{2} |1/2, 1/2\rangle + \sin\frac{\theta}{2} |1/2, -1/2\rangle \\ \frac{g_n \mu_N H}{2} & -\sin\frac{\theta}{2} |1/2, 1/2\rangle + \cos\frac{\theta}{2} |1/2, -1/2\rangle\end{aligned}$$

The energy levels and wave functions of the various states are illustrated in Figure 3.30.

The selection rules are $\Delta m_I = 0, \pm 1$, so that now there are four possible transitions from the ground state to the $|3/2, \pm 3/2\rangle$ states and sixteen from the ground state to the states arising from the $|3/2, \pm 1/2\rangle$ states. The transition probabilities have been determined by Collins⁽⁴⁴⁾. To obtain the powder spectrum the transitions must be weighted by the solid angle $d\theta$, and the complete summation carried out over all angles. It is found that the line due to the $\pm 3/2$ states is broadened into a doublet and that due to the $\pm 1/2$ states is broadened into a triplet⁽⁴⁴⁾⁽¹¹⁵⁾. The two lines of the zero field spectrum can thus be identified and the sign of the major component of the electric field gradient can be established.

Figure 3.30.

Perturbation of the quadrupole energy levels by an external magnetic field.

Therefore, from the spectra observed in external magnetic fields for bis(N,N diethyldithiocarbamate), we can ascribe the higher velocity line to the $|1/2, \pm 1/2\rangle \rightarrow |3/2, \pm 3/2\rangle$ transition. The major component of the electric field gradient tensor is therefore positive in sign. If it can be assumed that the major contribution to the electric field gradient comes from electrons localised on the metal, so that:

$$q = - \langle 3\cos^2\theta - 1 \rangle \langle r^{-3} \rangle$$

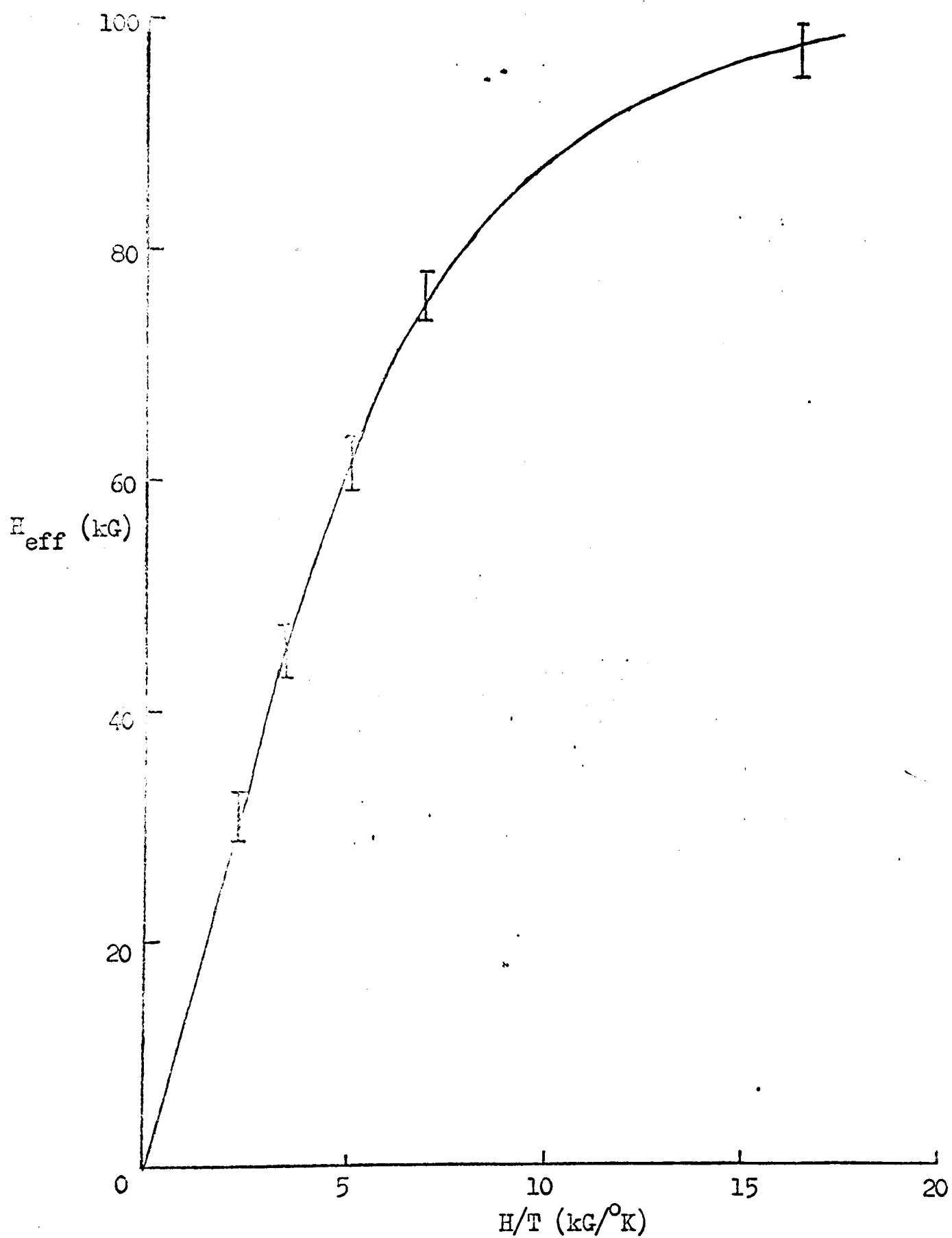
then the d^7 electron configuration corresponding to the positive sign would be $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{x^2-y^2})^1$, the order of the levels being the same as that proposed by Gray⁽¹¹¹⁾.

However, since the metal and ligand orbitals of this compound are likely to be well mixed, contributions to the electric field gradient from bonding electrons will be appreciable. Furthermore, the metal ion is not centrosymmetric in the complex so that lattice contributions to the electric field gradient may also be appreciable. The orbital ground state is thus not readily ascertained solely from a consideration of the sign of q .

Magnetic hyperfine interactions.

Magnetic hyperfine interactions are observed in the Mössbauer spectrum of this compound in external magnetic fields at temperatures of 4.2°K and below (Figure 3.16). In Figure 3.31 are plotted the values of the effective hyperfine field at

Figure 3.31.



Plot of the effective field at the iron nucleus vs. H/T for $(Et_3NCS)_2FeNO$.

The solid line is $\mu_B (H/T)$ where H is $-110kG$.

the iron nucleus, H_{eff} , obtained from the Mössbauer spectra, against H/T , where H is the applied field and T is the absolute temperature.

The values can be fitted to a relation of the form:

$$H_{\text{eff}} = H_n B_s(\mu H/kT) - H \quad (57)$$

where μ is the magnetic moment and $B_s(\mu H/kT)$ is the Brillouin function for spin S . Agreement is found when $S = 1/2$, that is when:

$$B_{\frac{1}{2}}(\mu H/kT) = \tanh(\mu H/kT)$$

The solid line in Figure 3.31 is the theoretical curve. The sign of the hyperfine field has been assumed to be negative. At low values of H/T the value of H_{eff} is proportional to the value of H/T . This indicates that interactions between ions are small and that the susceptibility of the compound at low temperatures is that expected for a compound with a free spin S of $1/2$, a fact which has not yet been established by classical magnetic susceptibility measurements. As H/T increases the value of H_{eff} approaches the saturation value H_n of 110 ± 5 kG.

The orbital contribution to the hyperfine field will be negligible since the g -values for this complex are close to 2⁽¹¹²⁾. The major contribution to the effective field at the nucleus must therefore arise from H_s , the Fermi contact term and from H_d the dipolar field. Calculated unrestricted Hartree Fock values of the hyperfine field for Fe(III) ($S = 5/2$) and for Fe(II) ($S = 2$) are -630 kG and -550 kG respectively⁽¹¹⁶⁾. Experimental

values confirm these calculated values. The low value of H_n is therefore of the order expected for $S = 1/2$ and confirms that the oxidation state Fe(I) adequately describes the nature of the iron in nitrosyliron bis(N,N diethyldithiocarbamate).

The orbital ground state.

In the presence of an external magnetic field, H , the hyperfine interaction between the nucleus and the surrounding electrons is described by the Hamiltonian:

$$\mathcal{H}_n = g_n \beta_n \underline{H} \cdot \underline{I} + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + \mathcal{H}_Q \quad (58)$$

where A_x , A_y and A_z are the components of the magnetic hyperfine interaction tensor parallel to the x, y and z axes, and are related to the components H_{ni} of the hyperfine field tensor by:

$$g_n \beta_n H_{ni} = A S_i \quad (59)$$

where $i = x, y$ or z . S and I are the electron and nuclear spin operators, g_n is the nuclear gyromagnetic ratio and β_n is the nuclear magneton. $\mathcal{H}_Q$ is the quadrupole Hamiltonian. The values of A_x , A_y and A_z are strongly influenced by the spatial distribution of the spin, since they are in part determined by the angular dependent dipolar and orbital terms. From eqs. (17) and (59), neglecting H_L , the hyperfine interaction for a single electron outside filled T_{2g} orbitals is given by:

$$A_z = 2g_n \beta_n (-K \pm 4/7) \langle r^{-3} \rangle \quad (60)$$

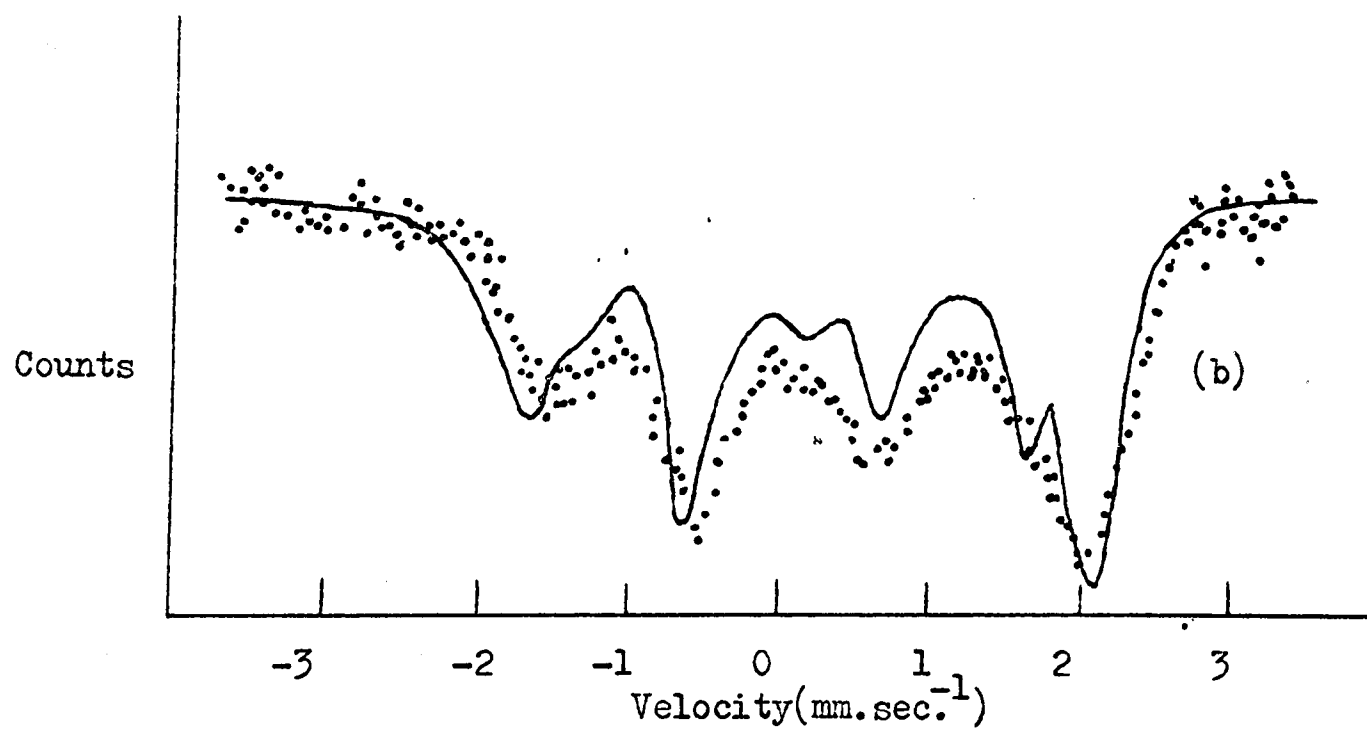
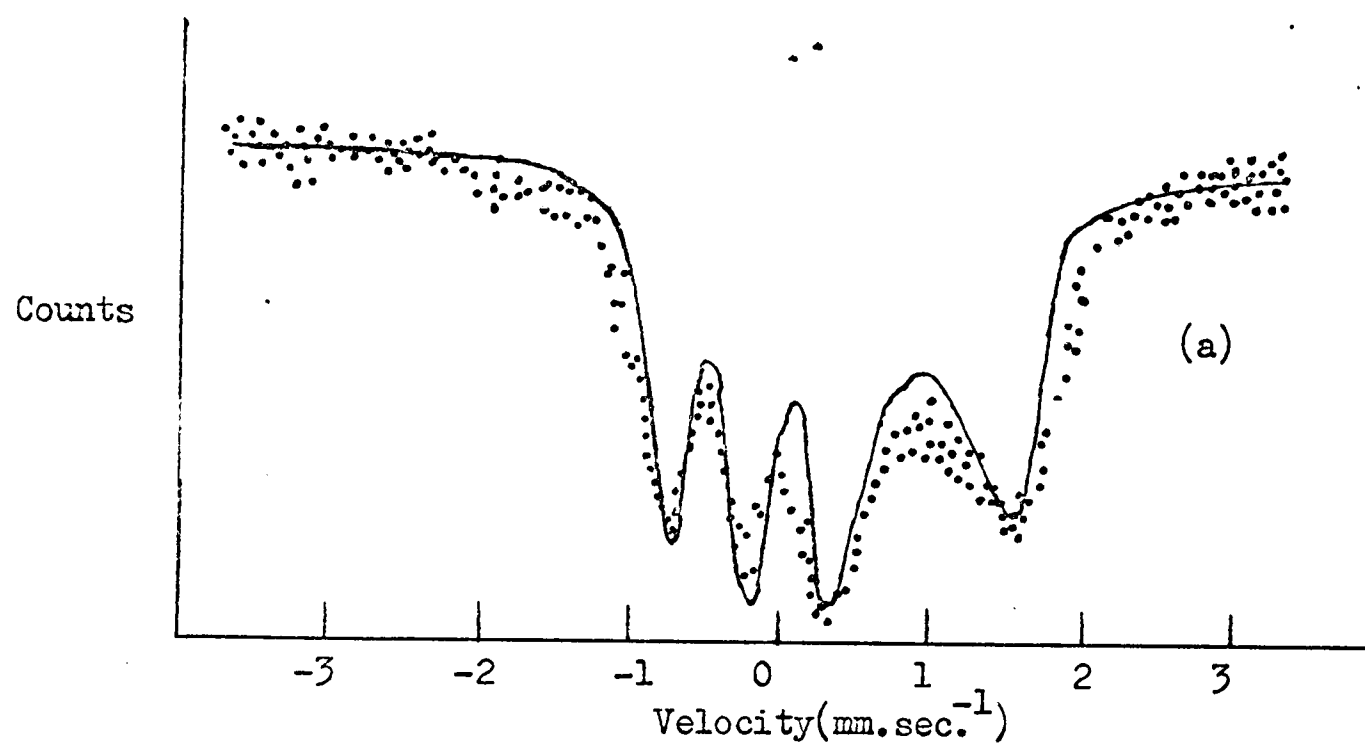
$$A_x = 2g_n \beta_n (-K \mp 2/7) \langle r^{-3} \rangle \quad (61)$$

the upper or lower sign depending on whether the ground state wave function is d_{z^2} or $d_{x^2-y^2}$ respectively.

Dr. G. Lang calculated the Mössbauer spectra for the compound in a 30kG external field at temperatures of 4.2°K and 1.6°K, from the above spin-Hamiltonian, assuming different electronic configurations. A computer program was used which averaged for a polycrystalline specimen over all possible directions of the magnetic field. The experimental g-values and quadrupole splitting were used and κ was taken as 0.35⁽⁵⁴⁾. Assuming the unpaired electron occupied the $d_{x^2-y^2}$ orbital, and taking values for the ground state of $A_z c/E_\gamma = 3.8 \text{ mm. sec.}^{-1}$ and $A_x c/E_\gamma = A_y c/E_\gamma = 0.3 \text{ mm. sec.}^{-1}$ gave poor agreement with experiment. For an electron in the $d_{x^2-y^2}$ orbital the effective field would act parallel to the xy plane. The resulting lines in the powder Mössbauer spectrum will be broad in contrast to the observations.

Excellent agreement with the experimental spectra was obtained for a d_{z^2} configuration, with $A_x c/E_\gamma = A_y c/E_\gamma = 2.8 \text{ mm. sec.}^{-1}$ and $A_z c/E_\gamma = -0.9 \text{ mm. sec.}^{-1}$. For the d_{z^2} orbital the anisotropy of the hyperfine interaction causes the effective field to act close to the xy plane, which is the direction favoured by geometry, and hence relatively sharp lines are observed in the Mössbauer spectrum. The calculated and the observed spectra are compared in Figure 3.32. The agreement is good, except that the sign of the quadrupole splitting

used in the calculation is opposite to that observed experimentally. An explanation compatible with the observations is that the electronic configuration is d^9 with a d_{z^2} hole, but this is obviously untenable. It seems therefore that the observed sign of q differs from the calculated sign due to contributions from the lattice and bonding electrons. We conclude that the orbital ground state corresponds to the unpaired electron occupying the d_{z^2} orbital.

Figure 3.32.

Calculated (—) and experimental spectra for nitrosyliron bis(N,N-diethyldithiocarbamate), (a) at 4.2 K in 30kG, (b) at 1.6 K in 30kG.

CHAPTER FOUR. STUDIES OF SOME IRON-SULPHUR COMPLEXES PROPOSED AS
MODELS FOR THE NON-HAEM IRON PROTEINS.

4.1. Introduction.

The use of simple metallo-organic compounds as model systems for complex biological molecules is well established. The model is chosen so that it reproduces some physical or chemical property of the system. From investigations of the model it may be possible to relate information to the properties of the more complicated biological system. Much success has been achieved in this field, particularly in the study of metal porphyrin complexes as models for haemoglobin compounds⁽¹¹⁷⁾ and vitamin B₁₂⁽¹¹⁸⁾. For the non-haem iron proteins the situation is less hopeful, for the reasons discussed in Chapter One. Several simple model complexes have, however, been proposed. We have studied a number of them, restricting our investigations to complexes of iron with sulphur ligands.

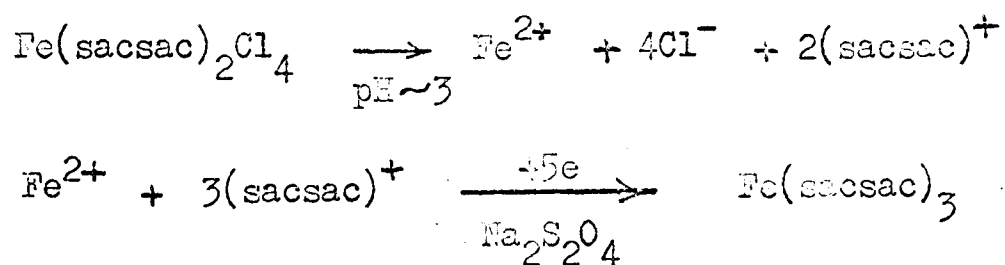
4.2. The systems studied.

The proposal that that the iron atoms of the non-haem iron proteins possess sulphur ligands, arising from the cysteine residues of the protein, has stimulated the search for stable model compounds which contain Fe-S-R, Fe-S-S-R and Fe-S-S-Fe groupings. Coucouvanis⁽¹¹⁹⁾ has prepared some complexes containing

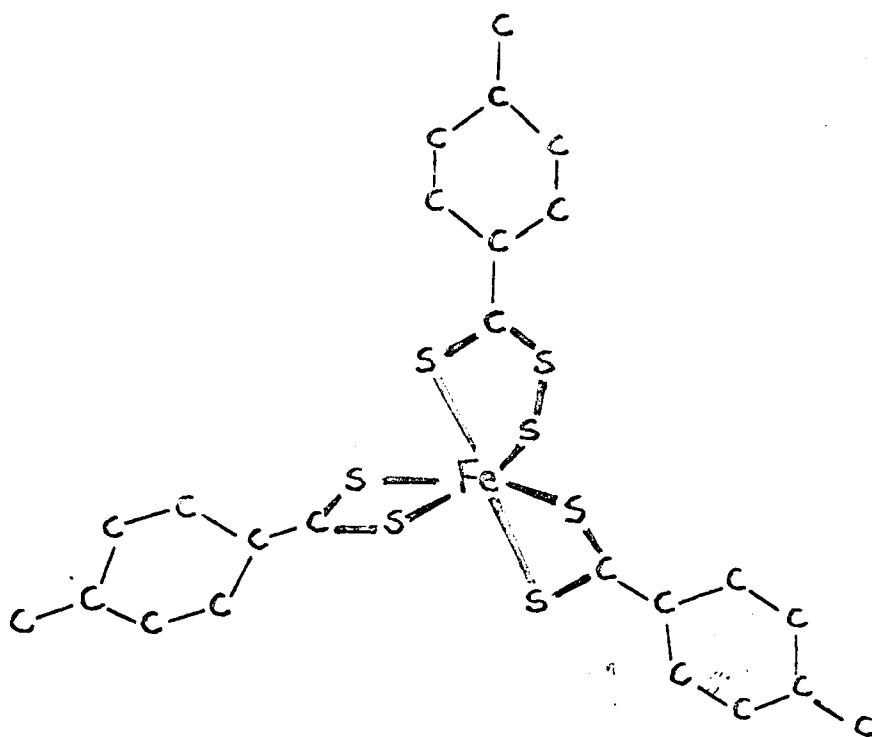
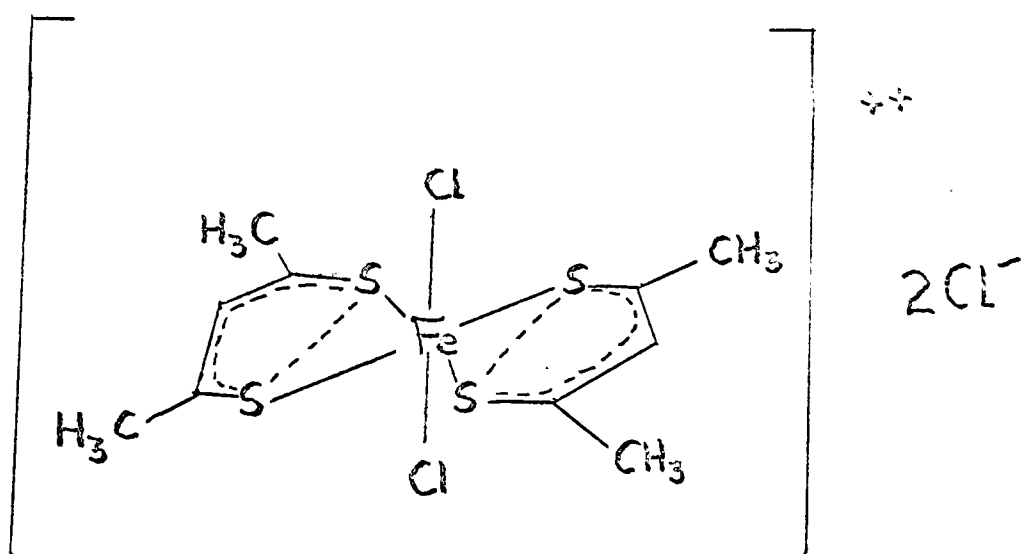
the Fe-S-S-R linkage. These are six coordinate, low-spin iron(III) complexes of the ligands thio-p-toluyldisulphide, $\text{CH}_3-\text{C}_6\text{H}_4-\text{CS}_2^-$ (TTD), and dithio-p-toluate, $\text{CH}_3-\text{C}_6\text{H}_4-\text{CS}_2^-$ (DTT). The structure of the complex $\text{Fe}(\text{TTD})(\text{DTT})_2$ has been solved⁽¹²⁰⁾, and is shown in Figure 4.1.

We have prepared the complexes $\text{Fe}(\text{TTD})_2(\text{DTT})$, $\text{Fe}(\text{TTD})(\text{DTT})_2$ and $\text{Fe}(\text{DTT})_3$. The results of the Mössbauer spectroscopic measurements made on these complexes are given in Table 4.1. Some of the Mössbauer spectra are shown in Figures 4.3 - 4.5. The epr spectra 10^{-3} M chloroform solutions of $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ were measured at 100°K . The spectra are illustrated in Figures 4.6 and 4.7.

Knauer, Hemmerich and van Voorst⁽¹²¹⁾ prepared a complex of iron with dithioacetylacetone (sacsac), which was believed to contain the $\begin{smallmatrix} \text{S} & & \text{S} \\ & \diagdown & / \\ & \text{Fe} & \\ & / & \diagdown \\ \text{S} & & \text{S} \end{smallmatrix}$ coordination shown in Figure 4.2. Dissolution in weakly acid solution and reduction with sodium dithionite yielded the low-spin ferric complex, $\text{Fe}(\text{sacsac})_3$:



The formal oxidation state of the iron is increased on reduction of the complex. The system was proposed as a model for the non-haem iron proteins, in which the characteristic epr spectrum appears only on reduction of the complex, but is believed to belong to low-spin

Figure 4.1.Structure of $\text{Fe}(\text{TFD})(\text{DTE})_2$ (120)Figure 4.2.Proposed structure of $\text{Fe}(\text{sacsac})_2\text{Cl}_2$ (121)

iron(III) atoms.

The Mössbauer studies of $\text{Fe}(\text{sacsac})_2\text{Cl}_4$ presented here indicate that the initially proposed structure is incorrect. Mössbauer Effect measurements on the related complex $\text{Fe}(\text{Ph}_2\text{C}_3\text{HS}_2)_2\text{Cl}_4$ have also been carried out. The results from both these sets of measurements are given in Table 4.2. The spectra are shown in Figures 4.8. and 4.9.

There have been several attempts to duplicate other properties of the non-haem iron proteins. The characteristic epr spectrum, with g_{av} less than 2 and two principal g-values below 2, has been one obvious target. Röder and Bayer⁽¹²²⁾ have shown that an epr spectrum, similar to that of reduced plant ferredoxin, can be obtained from solutions containing cysteine methyl ester, sulphur and iron(III), under suitable conditions. Turton⁽¹²³⁾ attempted to isolate the epr active species but was unsuccessful, mainly because the observed epr spectrum in fact arises from only ~5% of the total iron present. Mossbauer studies on the system in frozen solution were also unsuccessful.

An epr spectrum qualitatively similar to that of the reduced non-haem iron proteins, and showing a temperature dependence of intensity very like that of the non-haem iron proteins, was observed by Cotton and Gibson⁽¹²⁴⁾ for the complex tristetraphenylphosphonium trisdicyano-1,2-dithioleneiron. We have carried out a

a Mössbauer spectroscopic investigation of this complex. The results are presented in Table 4.3, and the spectra are shown in Figure 4.10.

Finally, we have investigated a complex that has been prepared and characterised by previous workers, but which has not been studied before as a model for the non-haem iron proteins. The complex $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2^{(125)}$ is readily oxidised to the paramagnetic species $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2^+$, which can be isolated as the hexafluoroantimonate salt⁽¹²⁶⁾. This paramagnetic complex appears to be a promising model system. It has some structural similarities to the non-haem iron proteins, having a two iron atom paramagnetic centre and containing bridging sulphur ligands. It also shows an epr spectrum similar to that of the reduced non-haem iron proteins. The Mössbauer parameters obtained for the complex are given in Table 4.4. The Mössbauer spectra are shown in Figure 4.11. The epr spectrum obtained from a 10^{-3} M acetone solution of the complex at 100°K is illustrated in Figure 4.12.

4.3. Preparative methods.

(i) The 'persulphide' complexes.

$\text{Fe(TTD)}_2(\text{DTT})$ was prepared by the method of Coucouvanis⁽¹¹⁹⁾ by the reaction of ferric chloride with Zn(TTD)_2 . Zn(TTD)_2 was prepared by the method of Fackler⁽¹²⁷⁾ and was recrystallised from carbon disulphide/absolute ethanol.

$\text{Fe}(\text{TID})_2(\text{DTT})$

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.8g) in absolute ethanol (100ml) was added to $\text{Zn}(\text{TID})_2$ (1.0g) in tetrahydrofuran (30ml). The blackish precipitate was filtered off, washed with methanol and recrystallised from carbon disulphide/petroleum ether. It was dried in vacuo.

Analysis: Found C = 46.8% H = 3.49%. Calc. C = 46.4% H = 3.38%.

 $\text{Fe}(\text{TID})(\text{DTT})_2$

Coucouvanis prepared this complex by treating $\text{Fe}(\text{TID})_2(\text{DTT})$ with triphenylphosphine. We found that it was difficult to obtain a pure product by this method as some $\text{Fe}(\text{DTT})_3$ was also formed. A double decomposition method similar to that used for $\text{Fe}(\text{TID})_2(\text{DTT})$ was developed.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5g) in methanol (10ml) was added to $\text{Zn}(\text{TID})_2$ (1.5g) in tetrahydrofuran (50ml). Addition of petroleum ether precipitated a purplish solid which was repeatedly recrystallised from carbon disulphide/petroleum ether and dried in vacuo.

Analysis: Found C = 49.4% H = 3.92%. Calc. C = 48.9% H = 3.60%.

 $\text{Fe}(\text{DTT})_3$

$\text{Fe}(\text{TID})_2(\text{DTT})$ was dissolved in chloroform. An equal weight of triphenylphosphine was added, and the solution boiled for 10 minutes. The solution turned dark green and upon addition of a little petroleum ether and allowing to cool, dark green crystals

were deposited. The product contains chloroform of crystallisation⁽¹¹⁹⁾.

Analysis: Found C = 45.0% H = 3.64%. Calc. C = 44.5% H = 3.41%.

(ii) Dithioacetylacetonateiron complexes

The complexes $\text{Fe}(\text{sacsac})_2\text{Cl}_4$ and $\text{Fe}(\text{Ph}_2\text{C}_2\text{S}_2)_2\text{Cl}_4$ were kindly supplied by Dr. G. Mackenzie of the University of Sheffield.

(iii) Tristetraphenylphosphonium triscyano-1,2-dithiolene iron

This complex was prepared by the method of McCleverty et al.⁽¹²⁸⁾

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.40g) in acetone (20ml) under nitrogen was treated with $\text{Na}_2\text{S}_2\text{C}_2(\text{CN})_2$ (1.11g) in degassed acetone - water (1:5 v/v, 30ml). Ph_4Cl in degassed ethanol (1.63g in 30ml) was added. On standing for one hour, red-brown crystals separated which were filtered off, washed with ethanol, water, again with ethanol and finally with ether. The complex was dried in air.

Analysis: Found C = 67.9% H = 4.3% N = 5.7%. Calc. C = 67.5% H = 4.0% N = 5.6%.

(iv) $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2\text{SbF}_6$

This compound was prepared by Mr. M. Clare according to the literature method⁽¹²⁶⁾.

4.4. Results.Table 4.1.Mössbauer Effect data for the 'persulphide' complexes

Compound	Temperature °K	Isomer shift δ mm.sec. ⁻¹	Quadrupole splitting ΔE_Q mm.sec. ⁻¹
Fe(TTD) ₂ (DTT)	300	0.17	1.83
	77	0.29	1.86
	4.2	0.31	1.86
	1.3	0.33	1.82
Fe(TTD)(DTT) ₂	300	-	-
	77	0.31	1.73
	4.2	0.31	1.74
	1.3	0.31	1.73
Fe(DTT) ₃ .CHCl ₃	300	-	-
	77	0.37	1.86
	4.2	0.37	1.84
	1.3	0.37	1.85

Table 4.2.Mössbauer Effect data for the dithioacetylacetonatoiron complexes

Complex	Temperature °K	Isomer shift δ mm.sec. ⁻¹	Quadrupole splitting ΔE_Q mm.sec. ⁻¹
Fe(sacsac) ₂ Cl ₄	300	0.90	1.48
	77	1.02	2.99
	4.2	1.11	3.18
Fe(Ph ₂ C ₃ HS ₂) ₂ Cl ₄	300	0.94, 0.93	2.10, 1.32
	195	1.05, 1.05	2.67, 2.04
	77	1.20	2.96
	4.2	1.21	3.04

Table 4.3.

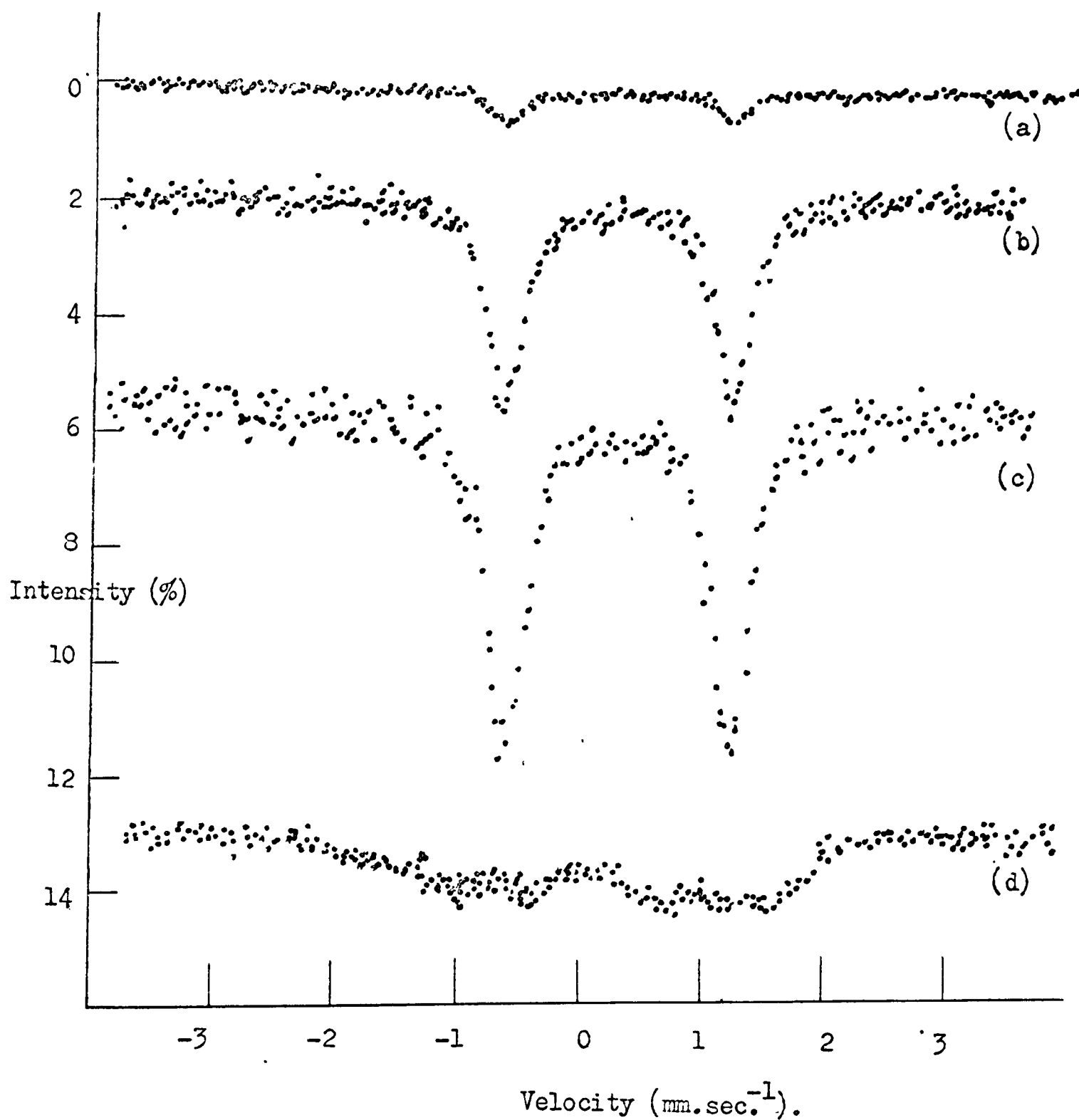
Mössbauer Effect data for tristetraphenylphosphonium trisdicyano-
1,2-dithiolene iron

Temperature °K	Isomer shift δ mm.sec. ⁻¹	Quadrupole splitting ΔE_Q mm.sec. ⁻¹	Relative intensity
300	0.29	1.65	1.04
195	0.38	1.69	0.58
77	0.41	1.85	0.53
77 5kG	0.41	1.84	0.87
4.2	0.43	1.82	0.51
1.3	0.42	1.82	0.54

Table 4.4.

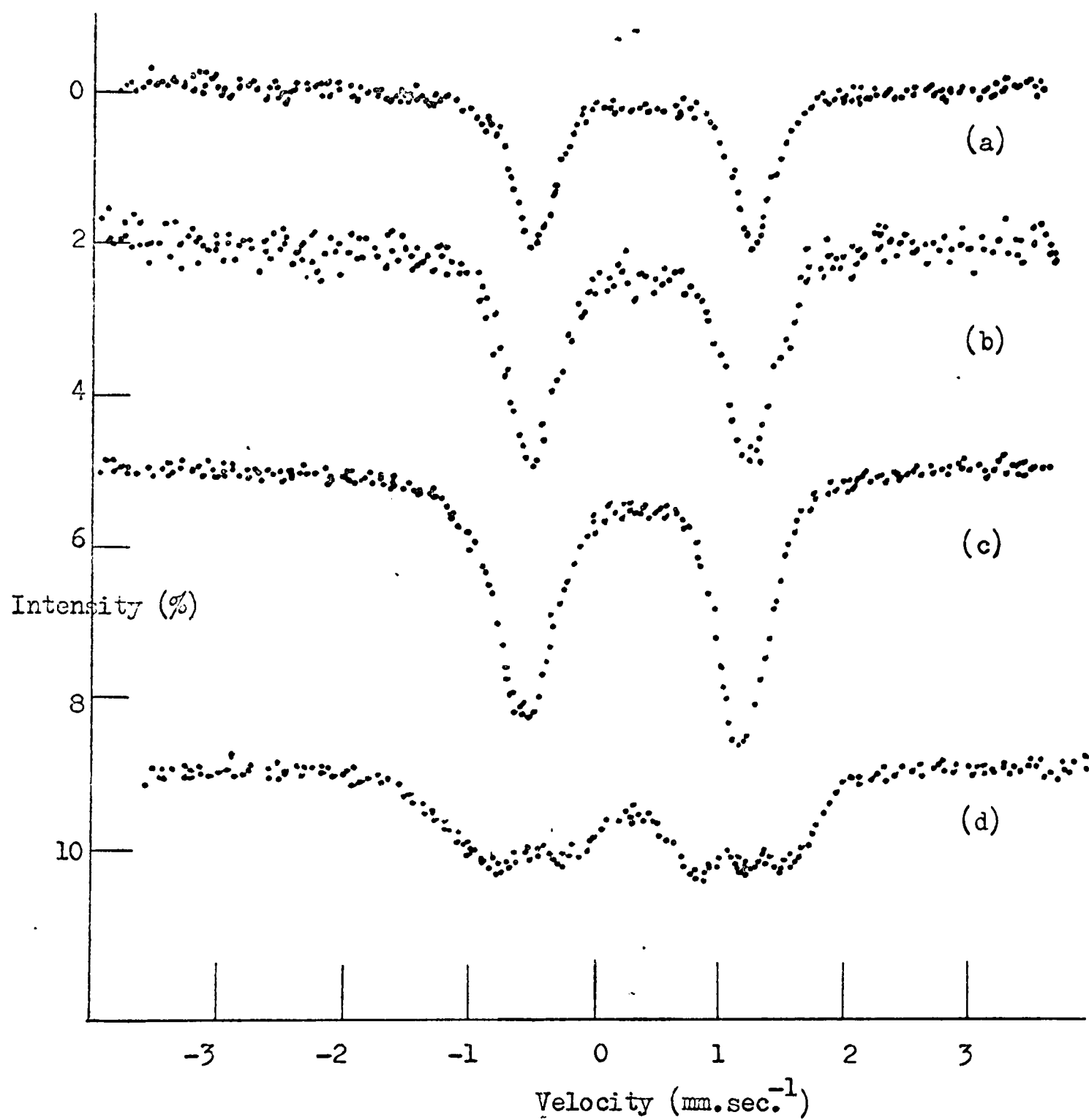
Mössbauer parameters for ($\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe}$) SbF_6

Temperature °K	Isomer shift δ mm.sec. ⁻¹	Quadrupole splitting ΔE_Q mm.sec. ⁻¹
300	0.18	1.76
77	0.27	1.79
4.2	0.30	1.78

Figure 4.3.

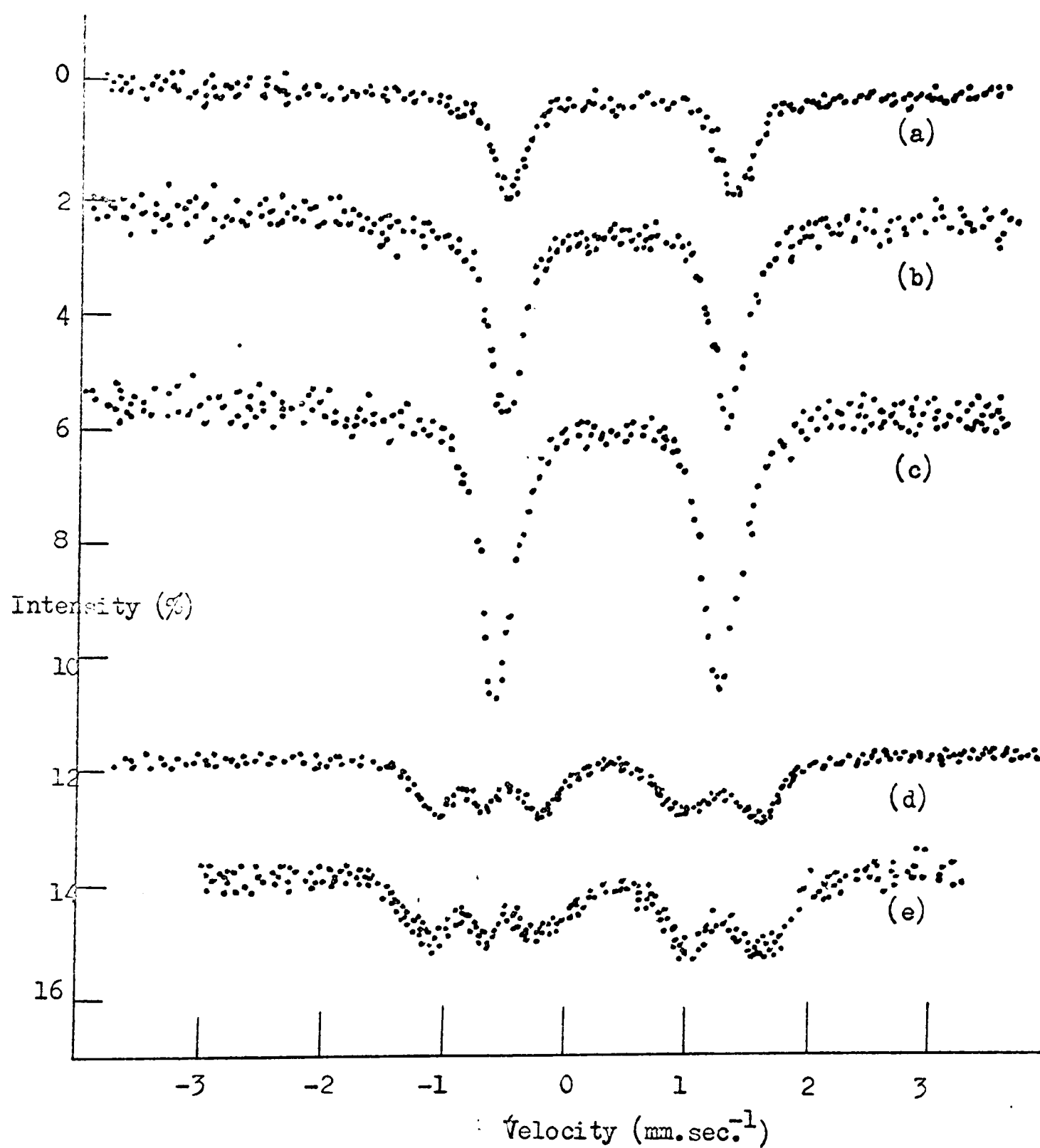
Mössbauer spectra of Fe(TTD)₂(DTT) (a) at 300°K, (b) at 77°K, (c) at 4.2°K,

(d) at 4.2°K in 30kG field.

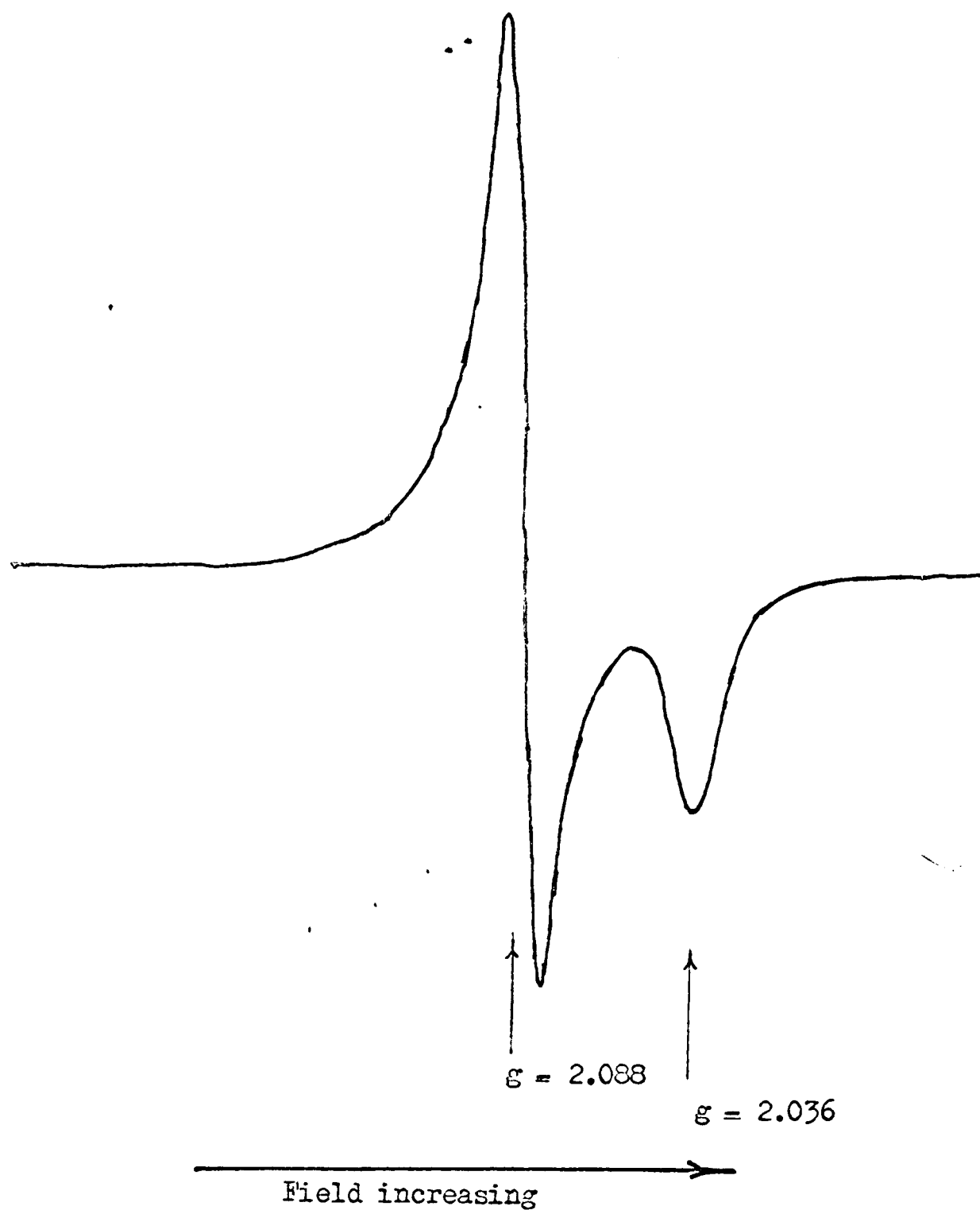
Figure 4.4.

Mössbauer spectra of Fe(TTD)(DTT) (a) at 77°K, (b) at 4.2°K, (c) at 1.3°K,
(d) at 4.2°K in 30kG field.

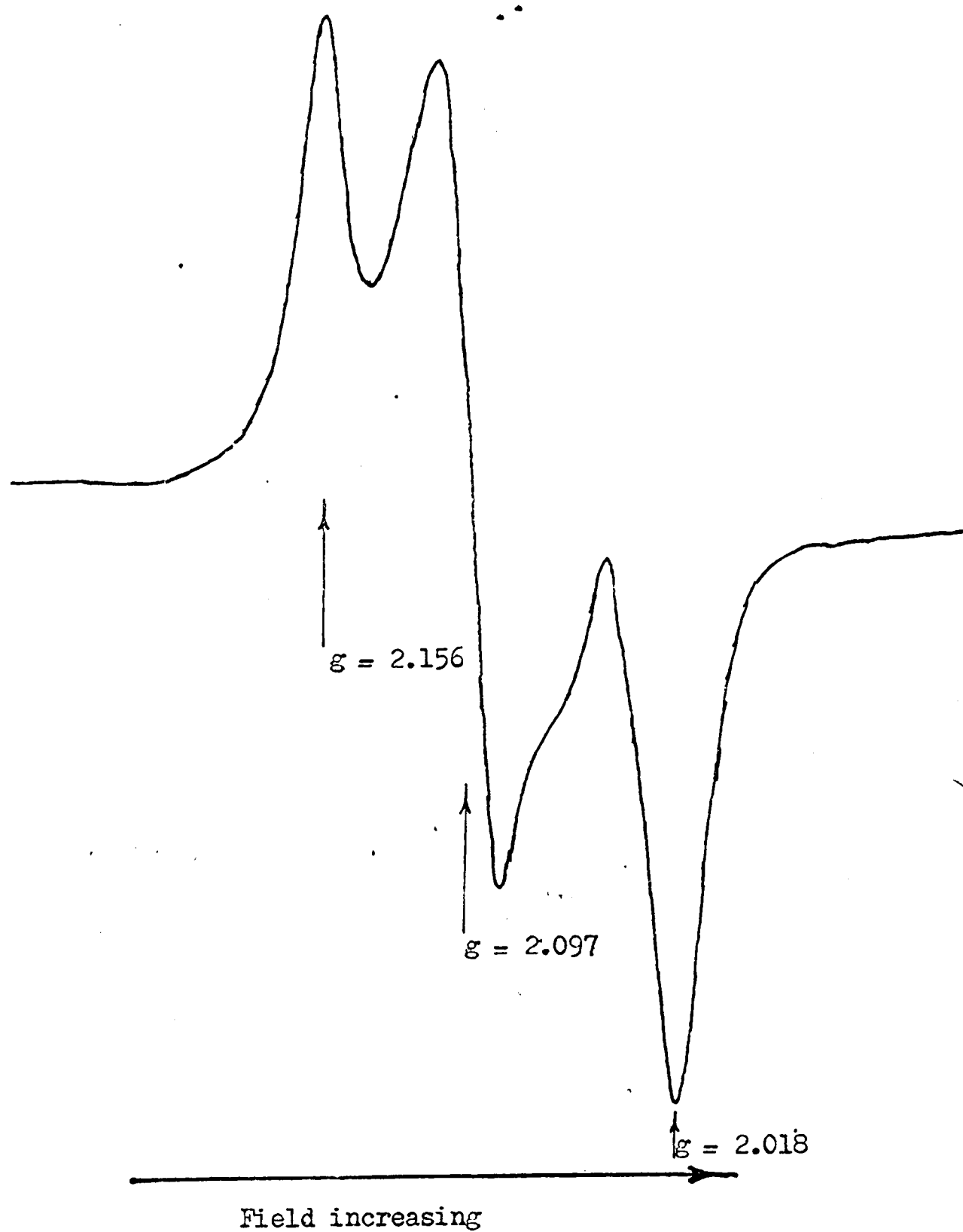
Figure 4.5.



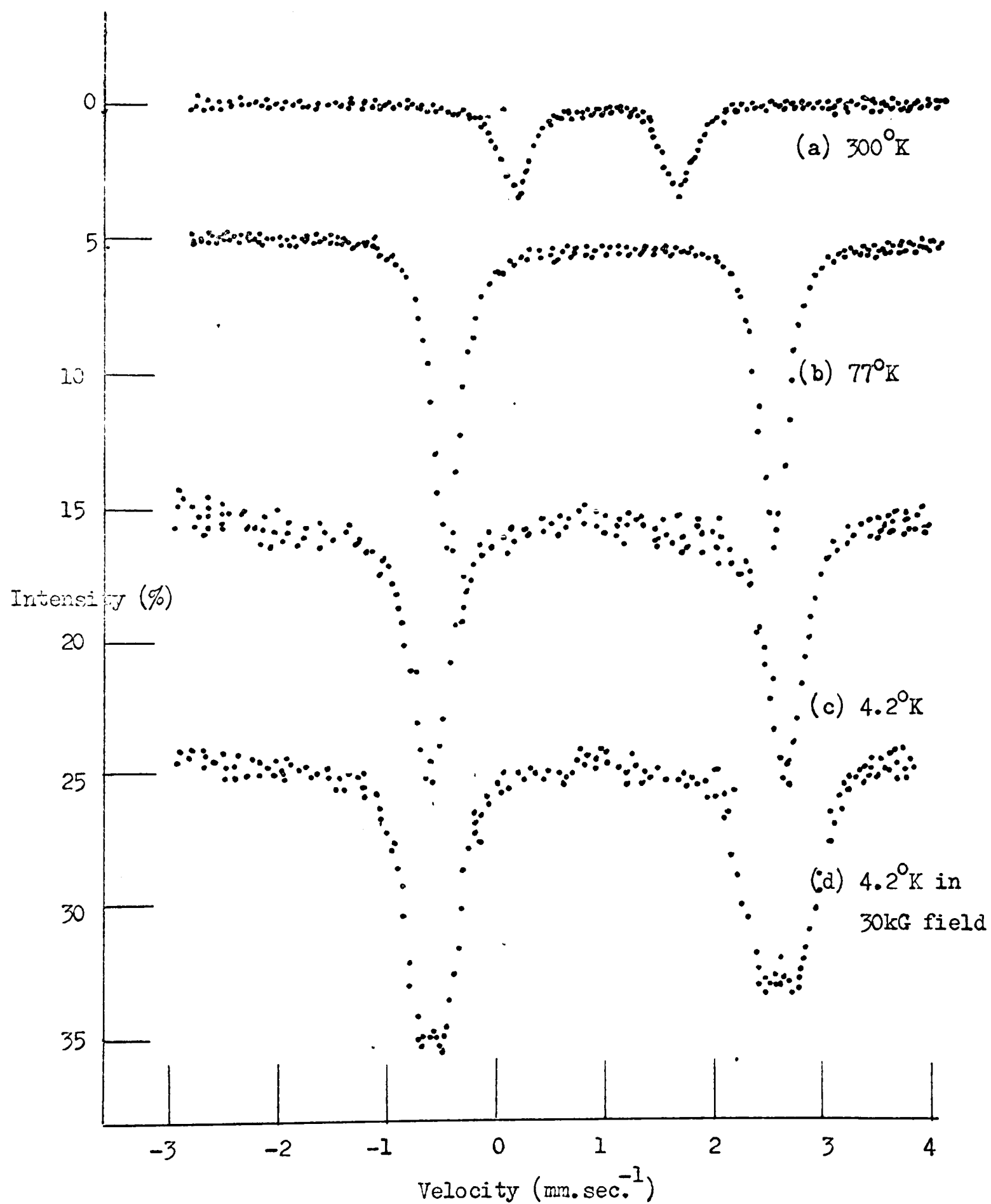
Mössbauer spectra of $\text{Fe}(\text{DTT})_3$ (a) at 77°K , (b) at 4.2°K , (c) at 1.3°K ,
 (d) at 4.2°K in 30kG field, (e) at 1.7°K in 30kG field.

Figure 4.6.

Epr spectrum of 10^{-3} M chloroform solution of Fe(TTD) (DTT) at 100°K .

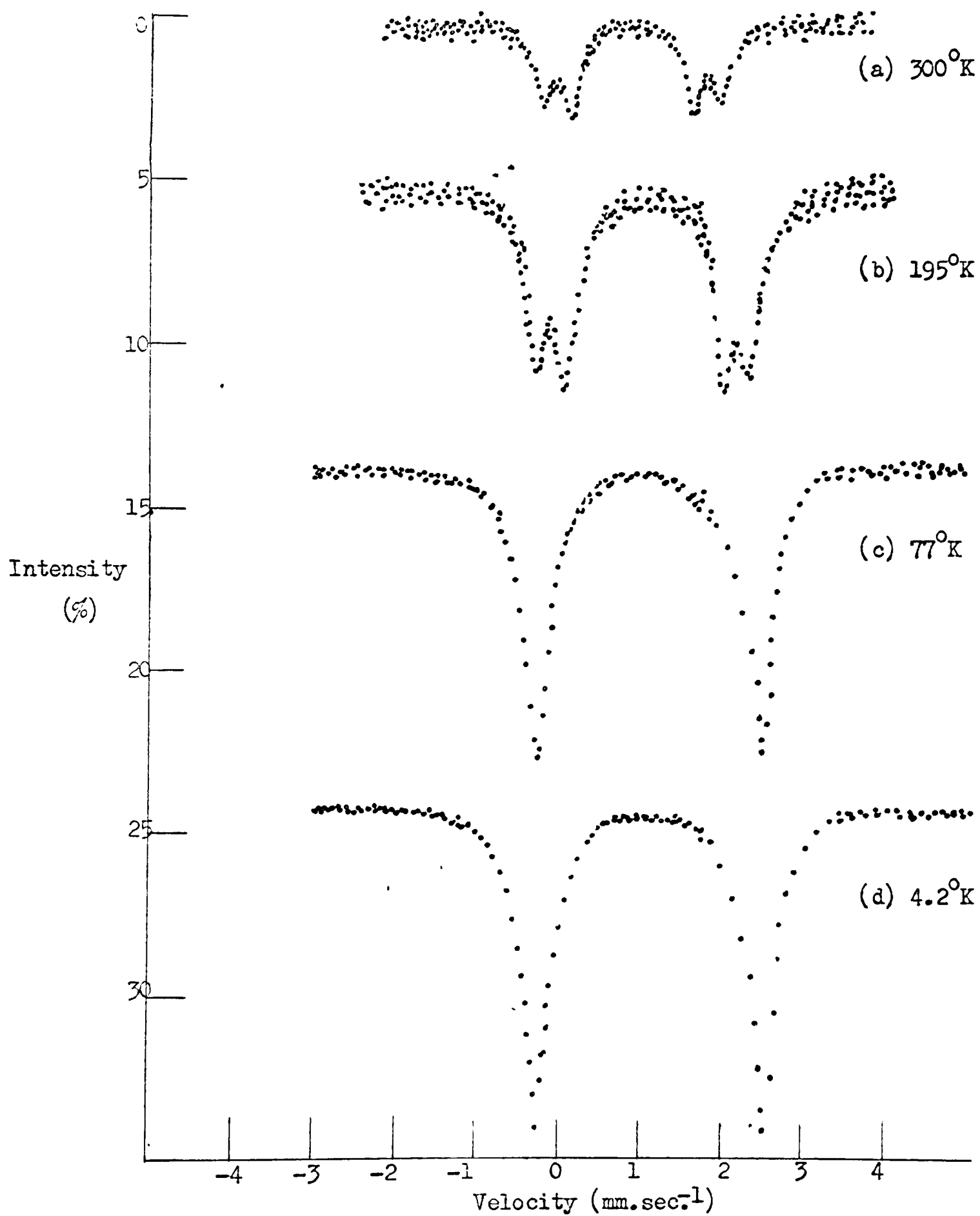
Figure 4.7.

Epr spectrum of 10^{-3} M solution of $\text{Fe}(\text{TTD})(\text{DTT})_2$ in chloroform, at 100°K .

Figure 4.8.

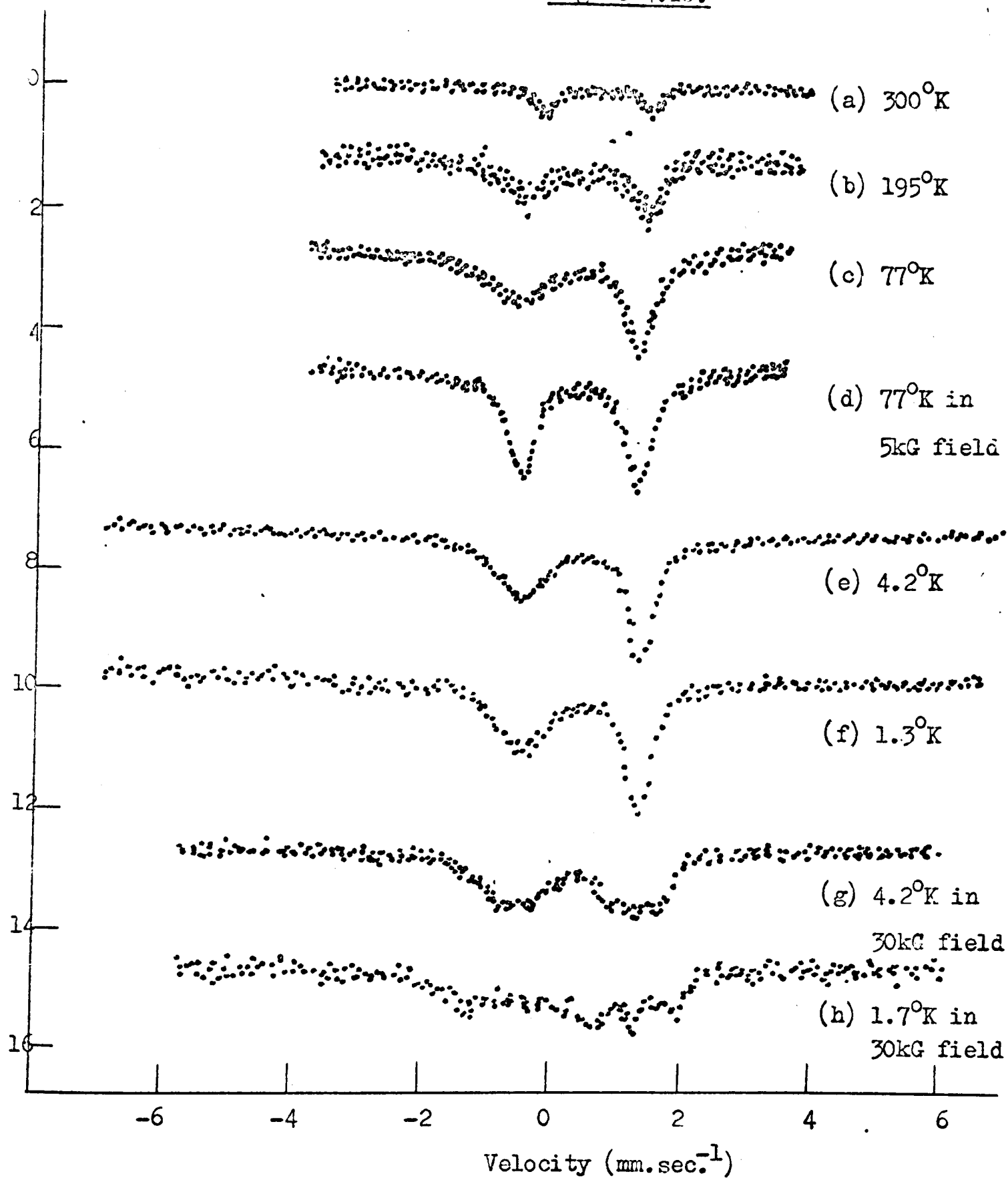
Mössbauer spectra of Fe(sacsac)₂Cl₄.

Figure 4.9.

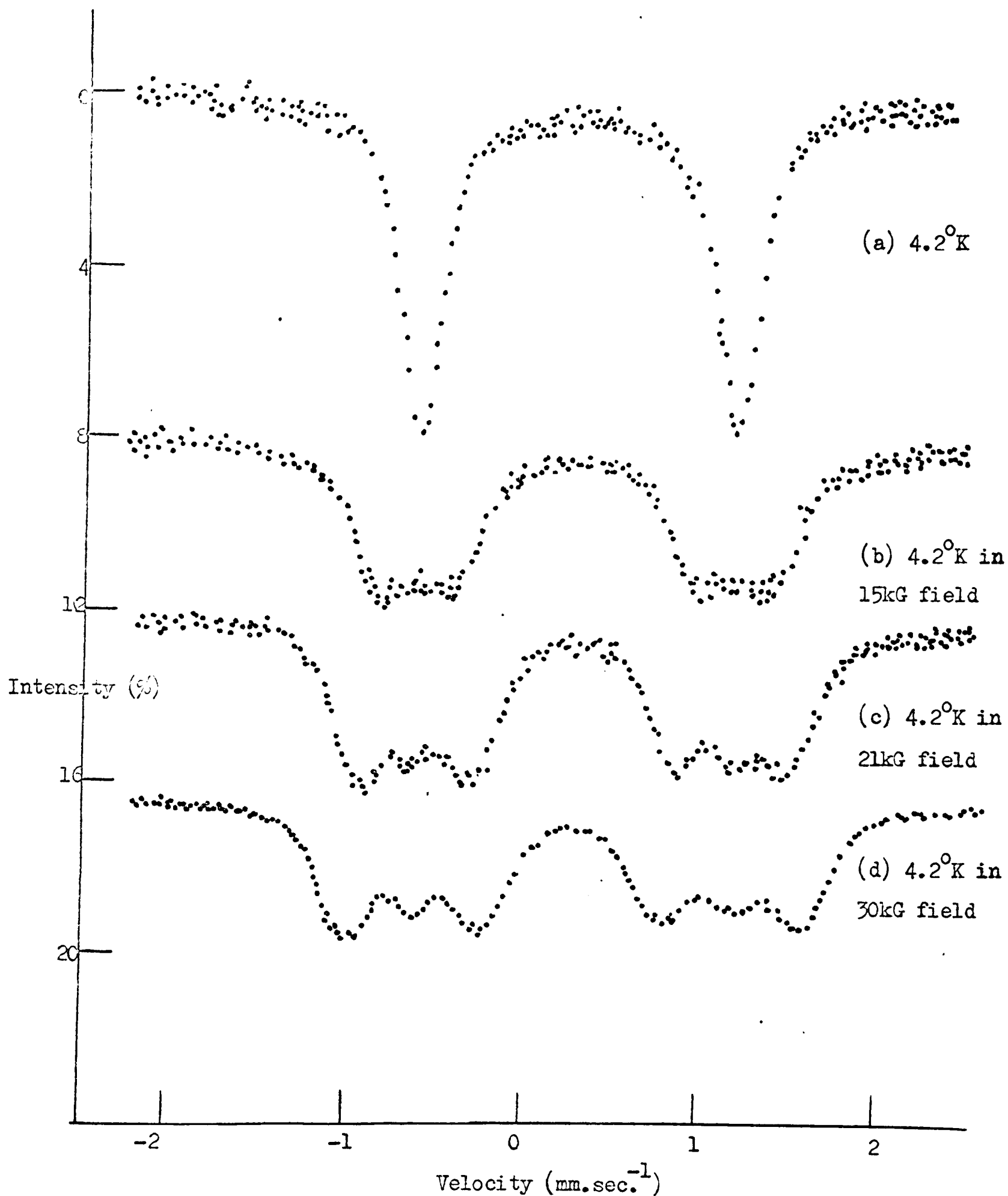


Mössbauer spectra of $(\text{Ph}_2\text{C}=\text{ES})_2\text{FeCl}_4$

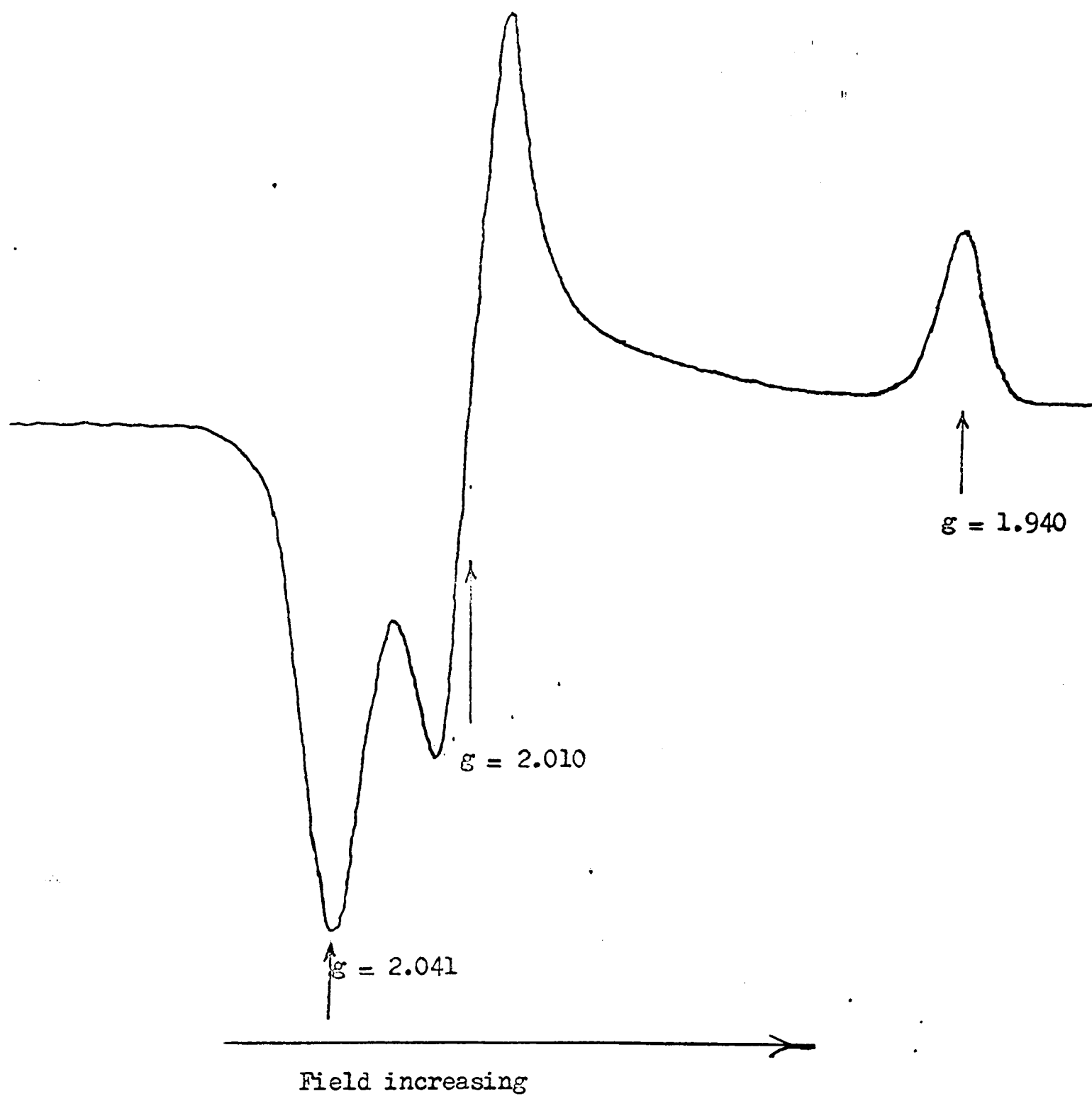
Figure 4.10.



Mössbauer spectra of tristetraphenylphosphonium trisdicyano-1,2-
dithiolene iron.

Figure 4.11.

Mössbauer spectra of $(\pi\text{-C}_{5\text{H}_5})_2\text{Fe(CO)SbF}_6$.

Figure 4.12.

Epr spectrum of 10^{-3} M acetone solution of $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2\text{SbF}_6$ at 100°K

4.5. Discussion.

(i) The 'persulphide' complexes

The Mössbauer spectra

The three complexes $\text{Fe}(\text{TTD})_2(\text{DTT})$, $\text{Fe}(\text{TTD})(\text{DTT})_2$ and $\text{Fe}(\text{DTT})_3$ all gave similar Mössbauer spectra with values of isomer shifts and quadrupole splittings about those expected for distorted low-spin ferric complexes. Relaxation effects are not seen, even at low temperatures, consistent with small iron - iron distances in these compounds. The intensity of the Mössbauer Effect for all three complexes was strongly temperature dependent; no effect was observed at room temperature for the compounds $\text{Fe}(\text{TTD})(\text{DTT})_2$ and $\text{Fe}(\text{DTT})_3$.

The isomer shift

The isomer shift for $\text{Fe}(\text{TTD})_2(\text{DTT})$ showed the dependence on temperature expected from the second order Doppler Effect.

The isomer shift of $\text{Fe}(\text{DTT})_3$ at 77°K is significantly greater than the shifts of the other two complexes (Table 4.1). This implies that the ability of the DTT ligand to accept electrons from the metal by back donation, and thus reduce the isomer shift by reducing the shielding of the s-electrons from the nucleus, is not as great as that of the TTD ligand. This may mainly be a consequence of the geometry of the complexes. Thus the S - Fe - S angle for the DTT ligand in $\text{Fe}(\text{TTD})(\text{DTT})_2$ is 76.0° ,

whereas for the TTD ligand the S - Fe - S angle is $92.6^{\circ(120)}$. A greater degree of metal - ligand overlap, and hence of electron delocalisation, is therefore possible for the latter ligand.

The quadrupole splitting

The quadrupole splittings observed for these complexes are large, reflecting the large distortions of the molecules from cubic symmetry. There is little significant difference in the values for the different compounds. The sign of the quadrupole splitting is not the same in each compound, however.

The application of a 30kG external magnetic field to the sample at 4.2°K enables the sign of the major component of the electric field gradient to be determined from the Mössbauer spectra. For $\text{Fe}(\text{DTT})_3$ this sign is positive; for the other compounds it is negative (see Figures 4.3, 4.4 and 4.5). In low-spin iron(III) complexes, when the distortions are large so that the ground state is almost a pure xy hole, a large negative electric field gradient is expected. The observations for $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ are therefore explicable. However, it is difficult to explain both the sign and the magnitude of the electric field gradient in $\text{Fe}(\text{DTT})_3$. For the low-spin iron(III) N,N dialkyldithiocarbamates, as for $\text{Fe}(\text{DTT})_3$, the sign of the major component of the electric field gradient is positive. In this case the positive sign is a consequence of a ground state which is a mixture of almost equal amounts of xz

and yz holes, with slightly less of xy. However, this ground state produces only a small quadrupole splitting, so that this ground state does not seem to explain satisfactorily the behaviour of the $\text{Fe}(\text{DTT})_3$ complex. The discrepancy may possibly be a consequence of the chloroform of crystallisation thought to be present in the coordination sphere⁽¹¹⁹⁾.

Magnetic hyperfine interactions

Magnetic hyperfine interactions are observed in the Mössbauer spectra of all three compounds, but only in large external magnetic fields at low temperatures. Values of the effective field at the iron nucleus, H_{eff} , at 4.2°K are estimated as:

$\text{Fe}(\text{TTD})_2(\text{DTT})$	-105kG
$\text{Fe}(\text{TTD})(\text{DTT})_2$	-90kG
$\text{Fe}(\text{DTT})_3$	-95kG

H_{eff} has been assumed to be negative. Poorly resolved spectra were observed at 1.7°K in a 30kG external field, except for $\text{Fe}(\text{DTT})_3$ for which H_{eff} increases by about 10kG over the small temperature range.

The values are of the order expected for low-spin ferric compounds, (see Chapter Six), but since there will be large contributions from the dipolar field, the contribution from the Fermi contact term will be much less than the empirically expected value of ~ -110kG, reflecting the strong covalent metal - ligand interactions in these complexes. The value of the hyperfine field and its relation

to the covalency of the complex is discussed in more detail in Chapter Six.

Electron paramagnetic resonance

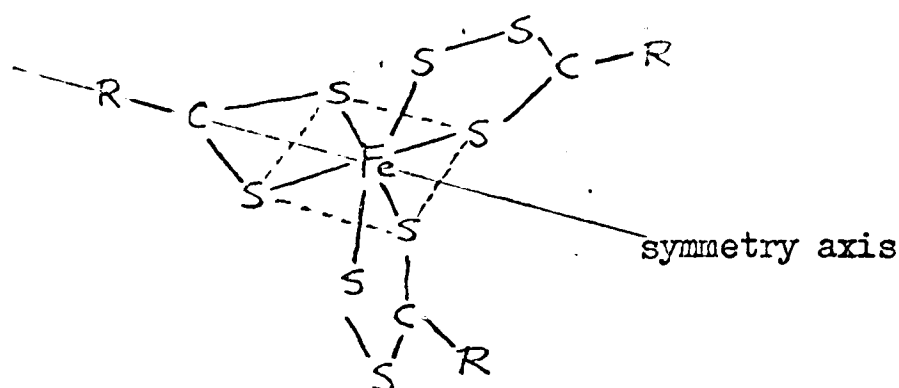
The epr spectra of $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ were measured in frozen chloroform solution at 100°K , and are illustrated in Figures 4.6 and 4.7. The g-values were found to be:

$$\text{Fe}(\text{TTD})_2(\text{DTT}) \quad g_1 = 2.036 \quad g_2 = g_3 = 2.088 \quad (\pm 0.005)$$

$$\text{Fe}(\text{TTD})(\text{DTT})_2 \quad g_1 = 2.018 \quad g_2 = 2.097 \quad g_3 = 2.156 \quad (\pm 0.005)$$

No epr spectrum could be detected for $\text{Fe}(\text{DTT})_3$.

The observation of three principal g-values for $\text{Fe}(\text{TTD})(\text{DTT})_2$ is expected, since the molecule has no symmetry. The observation of only two principal g-values for $\text{Fe}(\text{TTD})_2(\text{DTT})$ suggests that there is a symmetry axis and the structure could be:



The observed g-values can be used in the application of the method of Griffith⁽⁶⁰⁾ to a study of the ground state of the complexes. For $\text{Fe}(\text{TTD})_2(\text{DTT})$ no real solutions can be found for A, B and C that fit the experimental values, even when the orbital reduction

factor, k , is used to take account of covalency. The failure to find agreement exposes the limitations of the theory, and indicates that the assumption that the g -values are associated with the ground doublet alone is invalid. Presumably agreement could be found if spin-orbit coupling of higher states was taken into account. We can, however, obtain a more qualitative description of the ground state by this method. The best values of A , B and C are found to be $A = 0.030$, $B = 0.9995$, $C = 0$, with $k = 1$. These values satisfy the normalisation condition exactly and give for the g -values $g_z = 1.994$, $g_x = g_y = 2.083$. The calculated quadrupole splitting is in reasonable agreement with experiment, being $-2.5 \text{ mm} \cdot \text{sec}^{-1}$, the discrepancy is presumed to be a result of the neglect of the lattice contributions. The values of the coefficients of the ground state wave function correspond to a ground state that is almost a pure xy hole, separated by large energies from the next highest state, which is what we should predict from the quadrupole splitting data.

For $\text{Fe}(\text{TTD})(\text{DTT})_2$ the agreement is less good. The g -values can be fitted approximately with $A = 0.710$, $B = 0.014$ and $C = 0.727$, giving $g_z = 2.016$, $g_x = 2.064$ and $g_y = 2.120$ and corresponding to a ground state which is essentially a yz hole. The calculated quadrupole splitting is about zero. Considering the similarity of the compounds $\text{Fe}(\text{TTD})_2(\text{DTT})$ and $\text{Fe}(\text{TTD})(\text{DTT})_2$ and the similar nature of their Mössbauer spectra, we feel that the ground state of

the latter compound is better described by the coefficients $A = 0.030$, $B = 0.999$ and $C = 0.001$, corresponding to an xy hole as the ground state. The agreement with the Mössbauer spectra is good, the calculated quadrupole splitting being $-2.4 \text{ mm} \cdot \text{sec}^{-1}$, but the calculated g-values are in poor agreement with experiment with $g_z = 1.994$, $g_x = 2.081$ and $g_y = 2.084$.

(ii) The dithioacetylacetonatoiron complexes.

The isomer shift and quadrupole splitting of $\text{Fe}(\text{sacsac})_2\text{Cl}_4$ clearly indicate that the state of the iron atom in this complex is high-spin ferrous. The most marked feature of the Mössbauer spectrum of this complex is the strong temperature dependence of the quadrupole splitting which increases from $1.48 \text{ mm. sec.}^{-1}$ at 300°K to $3.29 \text{ mm. sec.}^{-1}$ at 4.2°K .

Ingalls⁽⁴¹⁾ has considered the temperature dependence of the quadrupole splitting for a high-spin ferrous ion in a distorted octahedral environment. The three t_{2g} orbitals are no longer degenerate and at finite temperatures will be populated to an extent that depends on the relative energy separations between them. At very high temperatures the levels will be equally populated and the quadrupole splitting will be zero. At temperatures small compared to the separation between the two lowest levels only the lowest level will be populated and the maximum quadrupole splitting will be observed. The temperature dependence of the quadrupole splitting is given by⁽⁴¹⁾:

$$\Delta E_{Q(T)} = \Delta E_{Q(0)} \frac{[1 + e^{-2T_1/T} + e^{-2T_2/T} - e^{-T_2/T} - e^{-T_1/T} - e^{-(T_1 + T_2)/T}]^{1/2}}{1 + e^{-T_1/T} + e^{-T_2/T}} \quad (62)$$

where $\Delta E_{Q(T)}$ is the quadrupole splitting at a temperature T , and T_1 , T_2 are the separations between the three t_{2g} levels.

A good fit to this curve is obtained for our data

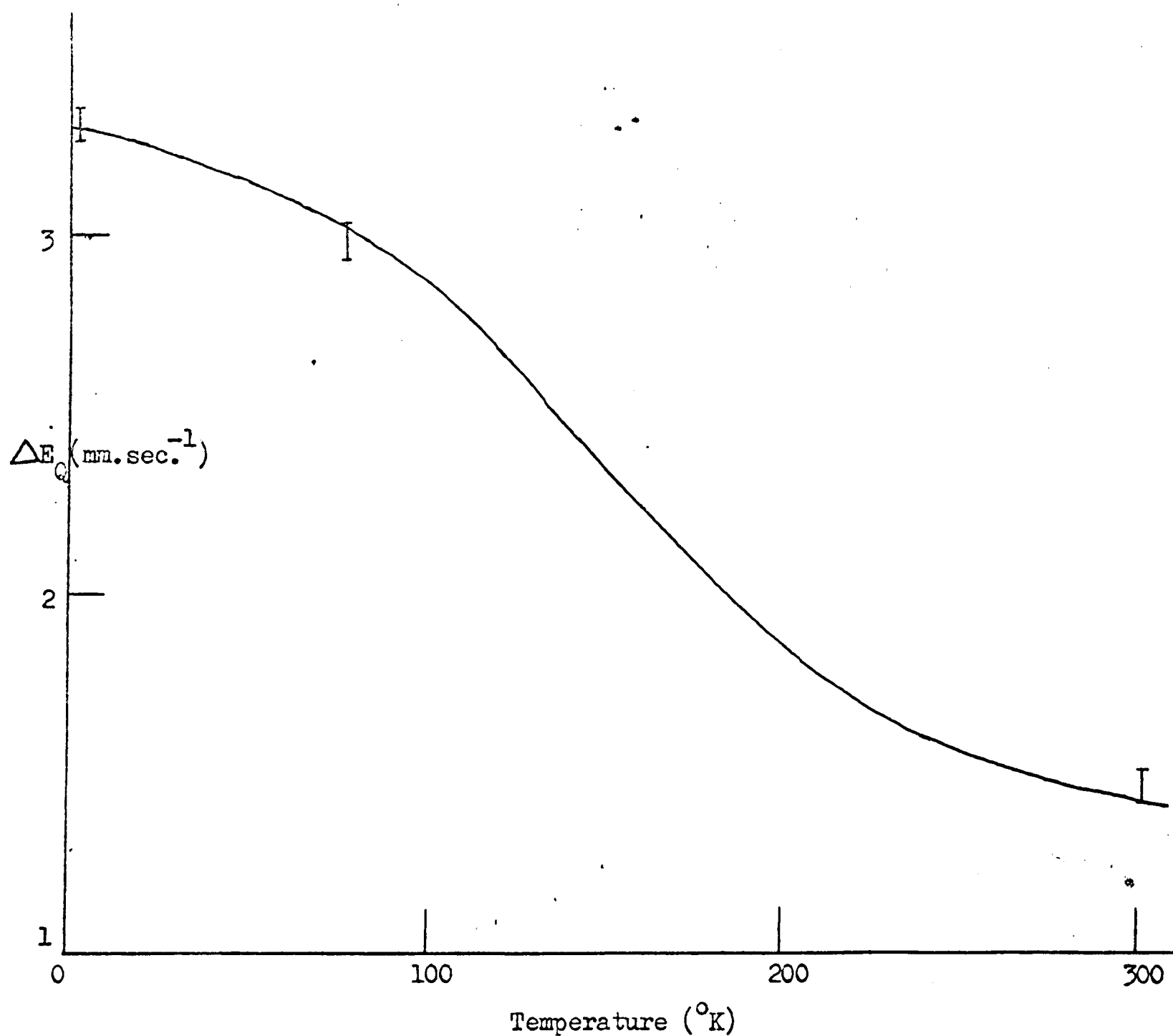
if T_1 is taken as 240°K and T_2 is taken as 480°K . The calculated curve and experimental points are shown in Figure 4.13. The values of T_1 and T_2 , however, are small compared to those found in other high-spin ferrous complexes.⁽⁴¹⁾⁽¹²⁹⁾

	T_1	T_2 (in $^\circ\text{K}$)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	800	1600
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	1000	2000
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	380	760
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	600	1200

If the proposed structure is correct (Figure 4.2), a large tetragonal distortion would be expected and correspondingly large values of T_1 and T_2 are expected.

The large variation of the quadrupole splitting with temperature is more satisfactorily explained if the high-spin ferrous ion is assumed to be in a tetrahedral environment. Edwards⁽¹³⁰⁾ has observed a large dependence on temperature of the quadrupole splitting of tetrahaloferrate ions, with the energy separations between the e orbitals being found to be $100 - 470 \text{ cm}^{-1}$ (i.e. $144 - 680^\circ\text{K}$). The formula of Ingalls for the temperature dependence of the quadrupole splitting of octahedral ferrous ions, (eq.(62)), is readily adapted to the case of tetrahedral ferrous ions, with the result:

$$\Delta E_{Q(T)} = \Delta E_{Q(0)} \frac{1 - e^{-\Delta/T}}{1 + e^{-\Delta/T}} \quad (63)$$

Figure 4.13.

Temperature dependence of the quadrupole splitting of $\text{Fe(sacsac)}_2\text{Cl}_4$.

The solid line is that calculated from the formula of Ingalls, for a tetragonally distorted octahedral complex with $T_1 = 240^\circ\text{K}$ and $T_2 = 480^\circ\text{K}$.

where Δ is the separation between the two e orbitals. From our measurements this separation is estimated as 315°K , in good agreement with the results of Edwards⁽¹³⁰⁾ for the FeCl_4^{2-} ion.

On the basis of these results it seems probable that the complex does not have the structure originally proposed but is in fact $(\text{sacsac}^+)_2\text{FeCl}_4^{2-}$. Further support for this conclusion was obtained by determining the sign of the quadrupole splitting. A 30kG field was applied to the specimen at 4.2°K . The left hand line of the quadrupole split pair split into two components and the right hand line split into three components (Figure 4.8). The sign of the major component of the electric field gradient is therefore negative, corresponding to a d_{z^2} orbital state as the ground state, as was found for other compounds containing the FeCl_4^{2-} ion⁽¹³⁰⁾.

X-ray structural investigations have since confirmed our assignment of the structure⁽¹³¹⁾⁽¹³²⁾.

The related complex $(\text{Ph}_2\text{C}_2\text{HS}_2)_2\text{FeCl}_4$ was also briefly investigated in an attempt to resolve some difficulties encountered during crystallographic studies. The spectrum shows two pairs of quadrupole split lines at temperatures of 300°K and 195°K , but only a single pair of lines is seen at 77°K and 4.2°K (Figure 4.9). The isomer shifts and quadrupole splittings suggest that the spectra arise from high-spin ferrous ions. The probable explanation is that at high temperatures the FeCl_4^{2-} ion in this complex can adopt one of two

orientations. At low temperatures all the iron atoms have identical environments, there being a phase change between 195°K and 77°K .

(iii) Tristetraphenylphosphonium trisdicyano-1,2-dithiolene iron.

Transition metal complexes of 1,2-dithiolenes have been the subject of much interest due to their electronic structures⁽¹³³⁾⁽¹³⁴⁾, and to the ease with which they undergo electron transfer reactions⁽¹³⁵⁾. Tristetraphenylphosphonium trisdicyano-1,2-dithiolene iron, $(\text{Ph}_4\text{P})_3(\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_3)$, was first prepared by McCleverty et al.⁽¹³⁶⁾, who investigated its magnetic, spectral and voltammetric properties. The magnetic moment was found to be $2.50 \mu_B$ at room temperature, decreasing to $2.28 \mu_B$ at 90°K . The epr spectrum of the solid, and of a dichloromethane solution of the complex, was investigated by Cotton and Gibson⁽¹²⁴⁾. Previous Mössbauer Effect measurements have only been made over a limited temperature range⁽¹³⁷⁾.

The Mössbauer spectrum

Intensity, line widths and relative line intensities

The intensity of the Mössbauer Effect increased about eightfold on cooling from 300°K to 77°K , indicating a low effective Debye temperature for the compound.

At all temperatures, in zero external magnetic field, the spectrum consisted of a quadrupole split pair of lines. The temperature dependence of the relative line intensities provides some insight into the relaxation properties of the compound.

At 300°K the intensities and widths of both lines are approximately equal (Figure 4.10). On decreasing the temperature

the left hand line broadens as the electron spin relaxation rate becomes slow compared to the lifetime of the ^{57}Fe , $I = 3/2$, excited state. The temperature dependence of the line widths and intensities can be understood in terms of the relative magnitudes of the spin-lattice relaxation time T_1 , and the spin-spin relaxation time T_2 .

At room temperature the spin-lattice relaxation time is short. However, it is temperature dependent, and at 195°K and below it has become long (i.e. $> 10^{-7}$ sec.). The spin-spin relaxation time, which is temperature independent, must be of the order of 10^{-7} sec. Since well resolved magnetic hyperfine interactions are not observed in zero field, even at very low temperatures. Thus at high temperatures T_1 dominates the relaxation process. At low temperatures T_2 is dominant.

The effect of a small external magnetic field on the Mössbauer spectrum of this compound at 77°K is of interest. It is seen (Figure 4.10) that the application of a 5kG field causes the left hand line to become narrower and more intense. The effect of the field is to increase the relaxation rate. A possible explanation for this phenomenon is found in some work of Orbach⁽¹³⁸⁾. It was shown that the relaxation rate $1/T_1$ is given by:

$$\frac{1}{T_1} \propto \frac{H^2 + \mu H_{\text{hyp}}^2 + \frac{1}{2}\mu' H_{\text{dip}}^2}{H^2 + H_{\text{hyp}}^2 + \frac{1}{2}H_{\text{dip}}^2} \quad (64)$$

where H is the external field, H_{hyp} is the hyperfine field, and H_{dip}

is the dipolar field. μ and μ' are terms dependent on the orbit lattice parameters. μ' is also dependent on temperature and concentration. Generally $\mu < 1$ and $\mu' = 2$, so that if H_{dip} is small compared to H_{hyp} it is evident that the effect of an applied magnetic field is to increase the spin-lattice relaxation rate.

The isomer shift

The shift of the centre of the quadrupole split pair of lines increases from $0.29 \text{ mm. sec.}^{-1}$ at 300°K to $0.41 \text{ mm. sec.}^{-1}$ at 77°K , which is about the increase expected from the second order Doppler Effect. The magnitude of the shift is comparable with the values observed in the iron(III) N,N dialkyldithiocarbamates, and is again a consequence of electron donation from the ligand orbitals into the metal d-orbitals, with little contribution from back donation from the metal orbitals into empty ligand π -orbitals.

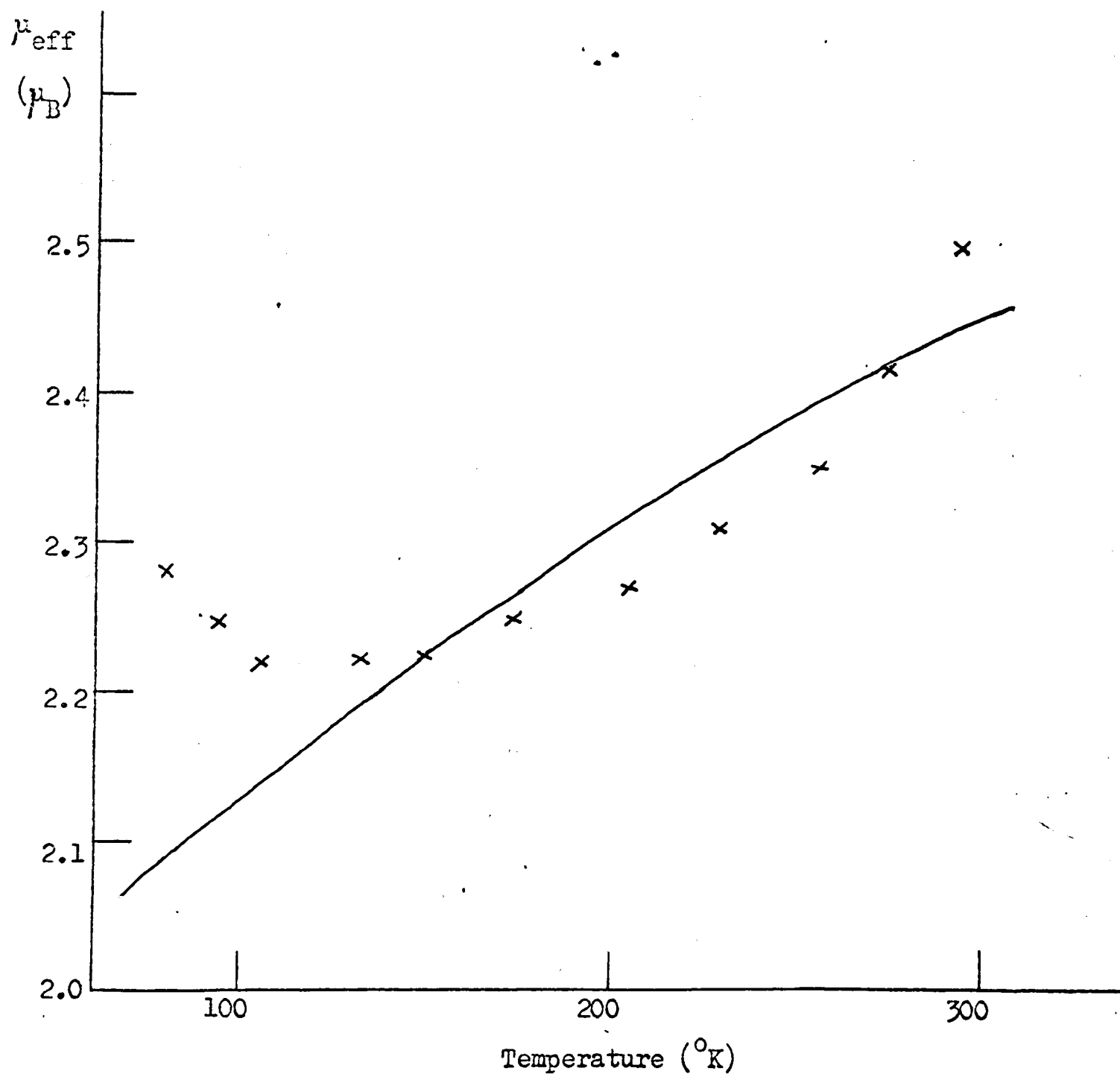
The quadrupole splitting

There is a small but significant increase in the quadrupole splitting on cooling the sample from 300°K to 77°K . This is paralleled by a decrease in the magnetic moment over the same temperature range. The observations may be explained qualitatively as follows. The degeneracy of the 2T_2 state is lifted by the combined effects of spin - orbit coupling and the ligand field. The resultant electric field gradient will be temperature dependent and will be largest at low temperatures. The magnetic moment will

similarly be temperature dependent, but will be largest at high temperatures.

We can attempt to put the correlation between the temperature dependence of the magnetic moment and of the quadrupole splitting on a more quantitative basis. Figgis⁽¹³⁹⁾ has calculated the effective magnetic moment arising from the 2T_2 terms of a transition metal complex, where the degeneracy has been lifted by both an axial ligand field component and by spin orbit coupling. The results are expressed in terms of the parameters δ/λ' and k , where δ is the separation between the orbital levels of the 2T_2 term created by the axial ligand field component in the absence of spin-orbit coupling, λ' is the spin-orbit coupling constant for the complexed species and k is the orbital reduction factor. The best agreement that can be obtained between this theory and the experimental data⁽¹³⁶⁾ is when we take δ/λ' as unity, $k = 1$, and $\lambda' = 400 \text{ cm}^{-1}$. The calculated curve and the experimental points are shown in Figure 4.14. The agreement is unremarkable and is especially poor at the lower end of the temperature scale.

Using a similar empirical approach we can attempt to fit the quadrupole splitting data to the theory of Golding⁽¹⁰¹⁾ (see page 97). Good agreement is found in this case between theory and experiment when δ/λ is taken as 0.42, (λ is the one electron spin-orbit coupling constant), and λ' is taken as 300 cm^{-1} . The

Figure 4.14.

Temperature dependence of the magnetic moment of $(\text{Ph}_4\text{P})_3(\text{FeS}_6\text{C}_6(\text{CN})_6)$.

The solid line is calculated after Figgis, assuming $\delta/\lambda' = 1$ and $\lambda' = 400\text{cm}^{-1}$.

theoretical curve and experimental points are shown in Figure 4.15.

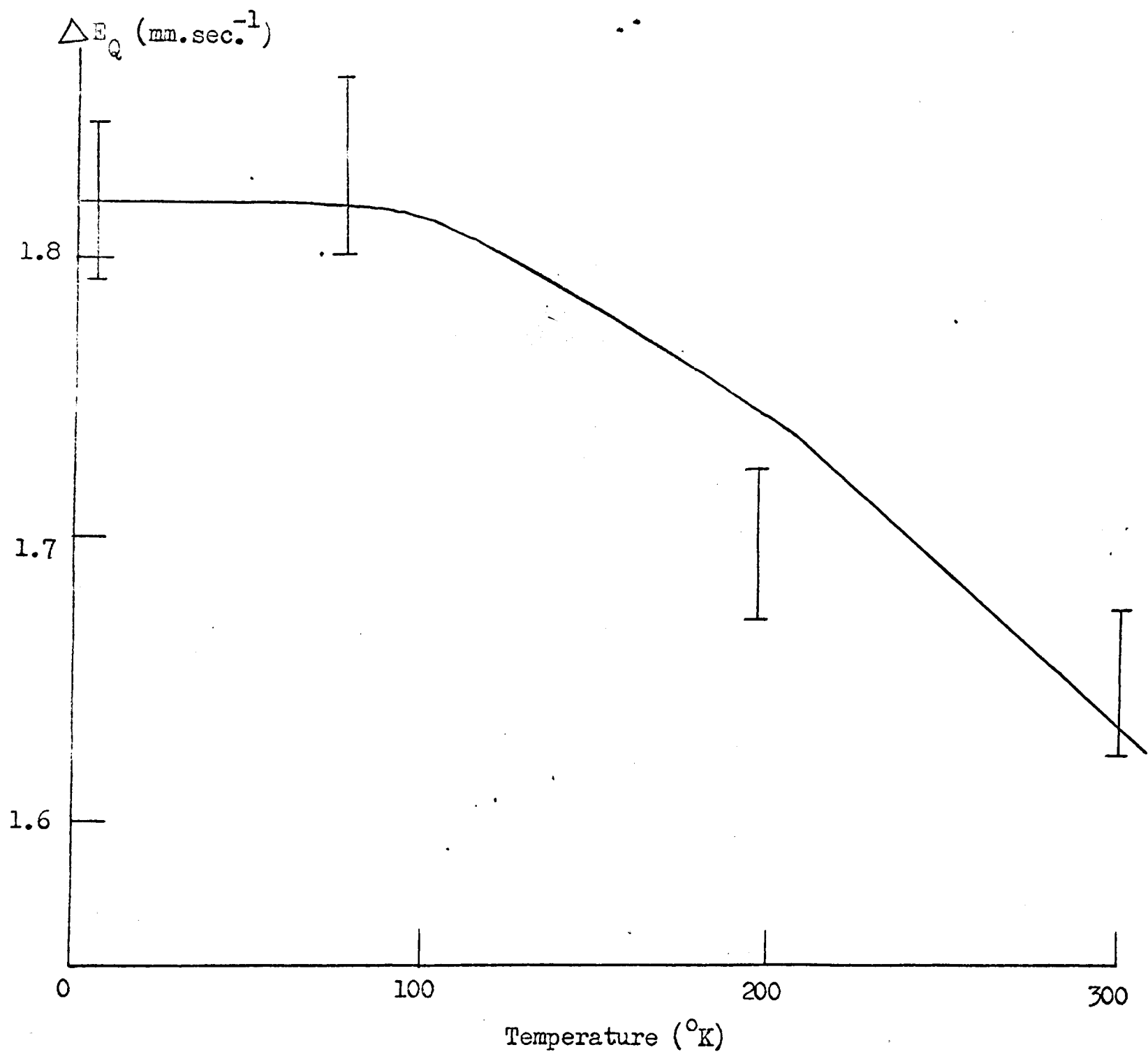
Assuming λ to be 435 cm^{-1} we should predict

to be much smaller from the quadrupole splitting data alone, than from the magnetic data alone. The limitations of the theory become apparent when it is realised that δ/λ' can be estimated, in the case of a good fit, only to within ± 0.5 or $\pm 25\%$. Similarly, the temperature dependence of the quadrupole splitting does not vary greatly over quite a wide range of δ/λ .

Magnetic hyperfine interactions

The broadening of the left hand line of the quadrupole split pair as the temperature is lowered, (Figure 4.10), suggests that this line arises from the $|\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$ transition. Confirmation of this is obtained when an external magnetic field is applied to the sample at 4.2°K and 1.6°K . The left hand line splits into two components and the right hand line splits into three. The sign of the major component of the electric field gradient is therefore negative. The splitting of the line due to the $|\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$ transition, in the magnetic field, is greater than that of the line due to the $|\pm 1/2\rangle \rightarrow |\pm 1/2\rangle$ transition. The direction of magnetisation is therefore parallel to the direction of the major component of the electric field gradient, which accounts for the poorly resolved spectra observed in magnetic fields.

Despite the poor resolution it is possible to

Figure 4.15.

Temperature dependence of the quadrupole splitting of $(\text{Ph}_4\text{P})_3(\text{FeS}_3\text{C}_6(\text{CN})_6)$.

The solid line is calculated after Golding, assuming $S/\lambda = 0.42$ and $\lambda = 300 \text{ cm}^{-1}$.

estimate values for the effective field at the iron nucleus. Taking the internal field to be negative, values for H_{eff} of -70kG and -95kG are obtained at 4.2°K and 1.6°K respectively. These values fit the relation:

$$H_{\text{eff}} = H_n B_s (\mu H/kT) - H$$

for $S = 1/2$, i.e. when:

$$B_{\frac{1}{2}} (\mu H/kT) = \tanh (\mu H/kT).$$

The value of the saturation hyperfine field H_n is estimated as -110kG.

The orbital ground state

The hyperfine interaction between the nucleus and its surrounding electrons in the presence of an external magnetic field H , is described by the Hamiltonian:

$$\mathcal{H} = g_n \beta_n H \cdot I + A_{\parallel} S_{\parallel} I_{\parallel} + A_{\perp} S_{\perp} I_{\perp} + \mathcal{H}_Q$$

where $A_{\parallel}$ and $A_{\perp}$ are the components of the magnetic hyperfine interaction tensor parallel and perpendicular to the principal axis of the ligand field. The hyperfine interactions are given by:

$$\begin{aligned} A_{\parallel} &= 2g_n \beta_n (-K - 4/7) \langle r^{-3} \rangle \\ A_{\perp} &= 2g_n \beta_n (-K + 2/7) \langle r^{-3} \rangle \end{aligned} \quad (65)$$

Since the direction of magnetisation for our polycrystalline sample is parallel to the direction of the major component of the electric field gradient, $A_{\parallel} > A_{\perp}$. From eqs.(65), therefore, we expect the sign of the major component of the electric field gradient to be negative as is indeed observed. Thus lattice contributions to the

electric field gradient are not important in determining its sign.

The negative sign corresponds to a d_{xy} hole as the orbital ground state.

The same conclusion as to the nature of the orbital ground state is reached from a consideration of the epr data of Cotton and Gibson⁽¹²⁴⁾. The observed g-values are:

$$g_1 = 1.986 \quad g_2 = 2.114 \quad \text{and} \quad g_3 = 2.225$$

These values can be fitted to eqs.(41)(42)(43) when $A = 0.059$,

$B = 0.998$ and $C = 0.019$ with $k = 1$. The values of V/λ and Δ/λ

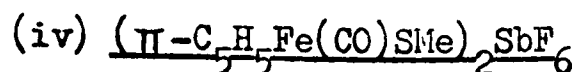
obtained on solution of the secular equations(53) are 9.35 and 13.90

respectively, reflecting the large distortion from cubic symmetry.

The calculated quadrupole splitting is $-2.4 \text{ mm. sec.}^{-1}$, in good

agreement with experiment, since we have neglected lattice contributions which will probably be of the opposite sign⁽⁴¹⁾. The orbital ground

state thus corresponds to a d_{xy} hole, well separated from higher states.



A large number of organometallic compounds containing bridging thiol groups are known⁽¹⁴⁰⁾. A polarographic study of a number of these compounds indicated that in many cases stable species were formed on their oxidation⁽¹⁴¹⁾. In particular $(\pi-C_5H_5Fe(CO)SMe)_2$ is readily oxidised; it can be oxidised by Ag^+ . The oxidised species can be isolated as the hexafluoroantimonate salt, $(\pi-C_5H_5Fe(CO)SMe)_2SbF_6$ ⁽¹²⁶⁾. Previous studies of this compound have shown it to be paramagnetic with a magnetic moment of $2.3 \mu_B$ at 296°K. Its solution epr spectrum showed an average g-value of 1.998⁽¹²⁶⁾. The compound appeared to us to be a promising model for a number of reasons. It contains two iron atoms linked by sulphur bridging groups. It has a spin of $\frac{1}{2}$, and the iron atoms may be considered to be in the Fe(II) and Fe(III) oxidation states, which are the oxidation states postulated as occurring in the reduced non-haem iron proteins⁽¹³⁾. Finally, like the reduced non-haem iron proteins, its epr spectrum has an average g-value less than the free electron value. We have therefore carried out epr and Mössbauer spectroscopic studies of this complex.

The Mössbauer spectrum

The spectrum observed in zero field, at all temperatures, consisted of a single pair of quadrupole split lines (Figure 4.11). Both iron atoms are therefore in identical environments.

The unpaired electron is shared equally by both iron atoms, the rate at which it hops between the iron atoms must be faster than 1.5×10^{-7} sec., the lifetime of the ^{57}Fe excited state.

The isomer shift

The isomer shift shows the temperature dependence expected from the second order Doppler Effect. The value of the isomer shift at 77°K is $0.27 \text{ mm. sec.}^{-1}$ which may be compared with the value of $0.45 \text{ mm. sec.}^{-1}$ found for $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2$ ⁽¹⁴²⁾. The removal of one d-electron decreases the shielding of the s-electrons from the nucleus and results in a decrease in the isomer shift.

The quadrupole splitting

The quadrupole splitting shows little dependence on temperature, consistent with large separations of excited states above the orbital ground state.

In several previous examples we have seen that the application of a large magnetic field to a sample at low temperatures can enable the sign of the quadrupole splitting to be determined. When a 30kG field is applied to a sample of $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2\text{SbF}_6$ at 4.2°K , both lines of the quadrupole split pair are split into three components. This is because the asymmetry parameter, η , is close to unity. Then, since:

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad \text{and}$$

$$\eta = 1 = \frac{V_{xx} - V_{yy}}{V_{zz}},$$

$V_{xx} = 0$ and $V_{zz} = -V_{yy}$, and we are unable to distinguish a major component of the electric field gradient.

Magnetic hyperfine interactions

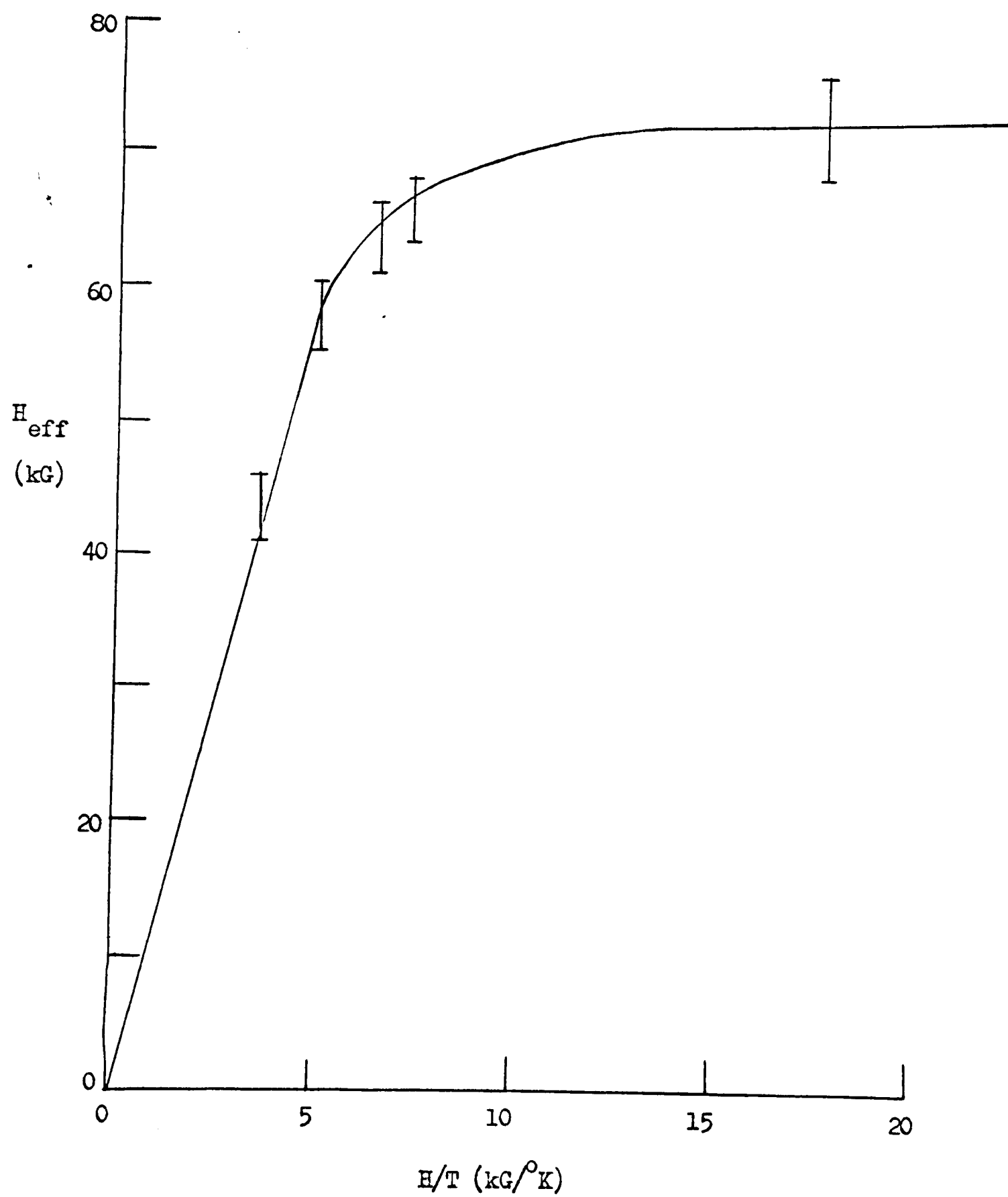
Values for the effective field at the iron nucleus, H_{eff} , can be estimated from the Mössbauer spectra observed in external magnetic fields. The splitting observed for this complex at 4.2°K in a 30kG external field is equivalent to 36kG⁽¹⁴¹⁾. The values of H_{eff} obtained are plotted against H/T in Figure 4.16. H_{eff} has been assumed to be negative. We have also assumed that there is a linear relation between the splitting and the value of the hyperfine field. The saturation value of the hyperfine field, H_n , is estimated from Figure 4.16 to be $-72 \pm 5\text{kG}$. This value is very small, almost half the value expected for a low-spin ferric ion in a non-cubic environment, and is presumably a consequence of the unpaired electron being distributed over both iron atoms.

Electron paramagnetic resonance

The epr spectrum of a 10^{-3} M acetone solution of the complex was measured at 100°K and is illustrated in Figure 4.12. The g -values were found to be:

$$g_1 = 1.940, \quad g_2 = 2.010, \quad g_3 = 2.041 \quad (\pm 0.005)$$

These g -values can be used in the application of two different models, in an attempt to describe the nature of the orbital ground state of the complex.

Figure 4.16.

Plot of H_{eff} against H/T for $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SMe})_2\text{SbF}_6$.

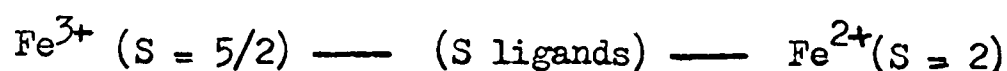
Firstly, we shall consider the g -values as though they arose simply from a single low-spin ferric ion. Then, using the method of Griffith⁽⁶⁰⁾ that we have previously used for low-spin ferric complexes, we find that the ground state wave functions may be characterised by the coefficients:

$$A = 0.810 \quad B = 0.586 \quad C = 0.007$$

giving energy separations for the one hole orbitals as $\Delta = 0.031\lambda$ and $V = 7 \times 10^{-5} \lambda$, and corresponding to extremely small distortions from cubic symmetry. Agreement is also found for the condition that:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} = \frac{-6AC}{A^2 - 2B^2 + C^2} = 1.$$

Secondly, we shall apply a treatment developed by Gibson et al.⁽¹⁴⁾ for describing the epr spectrum of reduced spinach ferredoxin. The two iron atoms are considered to interact through the ligands and the complex is described by:



Antiferromagnetic exchange couples the spins to give a total spin S of $1/2$ for the ground state.

If a spin S_1 with g -value g_1 is coupled with a spin S_2 with g -value g_2 , the effective g -value of the coupled state with spin S is given by:

$$g = \frac{g_1 + g_2}{2} + \frac{(g_1 - g_2)}{2S(S + 1)} (S_1(S_1 + 1) - S_2(S_2 + 1)) \quad (66)$$

For anisotropic g -values eq.(66) holds for the separate components of g , if the principal axes of g_1 and g_2 are the same.

For $S_1 = 5/2$, $S_2 = 2$ and $S = 1/2$:

$$g = (7g_1 - 4g_2)/3 \quad (67)$$

Gibson et al. then choose an orbital energy level scheme in order to fit the g -values in detail. Following them we shall assume an isotropic g -value for the high-spin ferric ion and take g_1 as 2.019. For the high-spin ferrous ion the scheme shown in Figure 4.17 may be used for which the g -values are:

$$g_z = g_e$$

$$g_x = g_e + 3\lambda/2 (E_{yz} - E_z^2)$$

$$g_y = g_e - 3\lambda/2 (E_{xz} - E_z^2)$$

where g_e is the free electron value, λ is the spin orbit coupling constant and E_i is the energy of the i th state.

Letting $g_1 = g_e + \Delta g_1$ we then have:

$$g_x = g_e + \frac{7\Delta g_1}{3} - 2\lambda/(E_{yz} - E_z^2)$$

$$g_y = g_e + \frac{7\Delta g_1}{3} - 2\lambda/(E_{zx} - E_z^2)$$

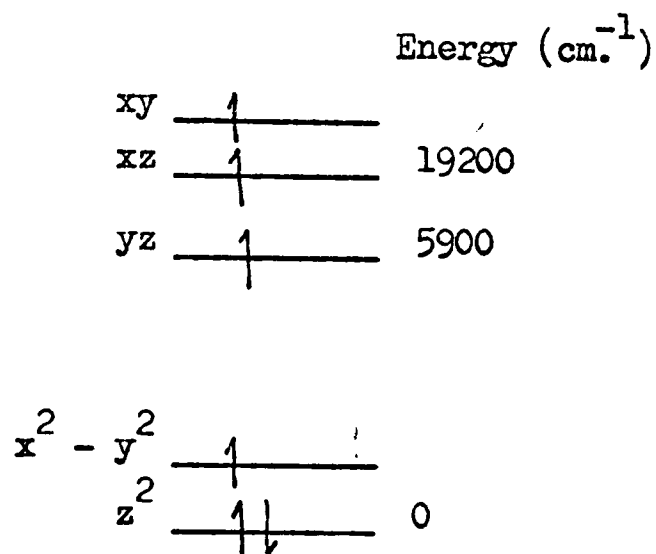
$$g_z = g_e + \frac{7\Delta g_1}{3} :$$

We take $g_x = 1.940$, $g_y = 2.010$ and $g_z = 2.041$. (Note that this corresponds to a different choice of axes than in the previous case.)

Solving the equations gives the energies of E_{yz} and E_{xz} relative to

E_z 2. Taking λ as 300cm^{-1} the orbital separations are found to be as shown in Figure 4.17

Figure 4.17.



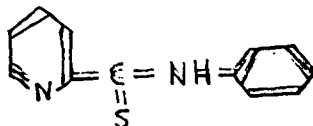
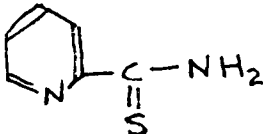
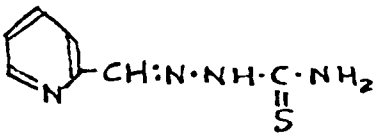
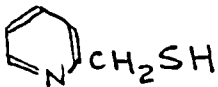
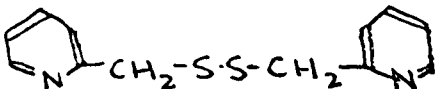
Orbital separations in $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})^-$ estimated by the method
of Gibson et al.

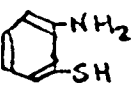
CHAPTER FIVE. SOME COMPLEXES OF IRON WITH 2-SUBSTITUTED PYRIDINES.

5.1. Introduction.

In the study of complexes of iron with sulphur ligands it would be useful if we could assess how a variation in the nature of the sulphur ligand atom affects the physical and chemical properties of the complexes. We have attempted to pursue this idea by preparing complexes of iron with 2-substituted pyridines as ligands. The 2-substituent is varied to give a wide range of sulphur ligand atom, while the nitrogen atom of the pyridine remains constant as the other ligand atom of a bidentate chelate. We report in this chapter the preparation and investigation of complexes of a number of 2-substituted pyridines. The ligands investigated are listed in Table 5.1.

Table 5.1.

<u>Ligand</u>	<u>Formula</u>	<u>Abbreviation used</u>
Thiopicolinic acid anilide		TPCA
Thiopicolinamide		TPC
Pyridine-2-aldehyde thio-semicarbazone		PTSC
2-Mercaptomethylpyridine		MMP
Di-2,2'-picolyldisulphide		DPD

The complex formed between ferrous ion and o-aminobenzenethiol, , ABT, was also investigated, to compare its behaviour with that of the complex of MMP.

Of the above ligands TPCA, TPC, PTSC, and ABT have been investigated previously as forming complexes with iron, but the complexes formed have often not been isolated, or have been inadequately characterised. MMP has been used to form complexes with a number of transition metals, but its reactions with iron salts have not been described before.⁽¹⁴⁴⁾

5.2. Experimental.

The starting materials used in the following preparations were obtained as follows: 2-cyanopyridine and pyridine-2-aldehyde, Aldrich Chemical Co.; o-aminobenzenethiol, picolylchloride hydrochloride and thiosemicarbazide, Koch Light, Ltd.; aniline, α -picoline, pyridine, triethylamine, AnalaR ferrous sulphate heptahydrate and AnalaR ferric chloride sexahydrate, British Drug Houses; tetrahydrofuran and thiourea, Harrington Bros. All chemicals were normal commercial purity unless otherwise stated. Ferrous perchlorate hexahydrate was prepared by the literature method⁽¹⁴⁵⁾, recrystallised from air free water and stored under nitrogen.

Ligand preparations

Thiopicolinic acid anilide⁽¹⁴⁶⁾

α -Picoline (90g), sulphur (45g) and aniline (45g)

were refluxed together for 48hrs. The mixture was then steam distilled to remove excess aniline and α -picoline. The residue was extracted twice with warm KOH solution (300ml. 3N). Acidification gave the crude product, which was recrystallised from methanol.
m.p. 52°C (lit.⁽¹⁴⁶⁾ 52°C).

Thiopicolinamide⁽¹⁴⁷⁾

2-Cyanopyridine was dissolved in an equal weight of pyridine. An equimolar amount of triethylamine was added. Dry H₂S was passed in a steady stream for 3hrs. The solution was then poured into water to precipitate the product, which was filtered off and recrystallised from ethanol.

m.p. 135°C (lit.⁽¹⁴⁷⁾ 135 - 137°C)

Pyridine-2-aldehydethiosemicarbazone⁽¹⁴⁸⁾

A fine suspension of sodium acetate (4g) and thiosemicarbazide (10g) in ethanol (100ml), was slowly treated with water until it was all dissolved. Pyridine-2-aldehyde (10g) was added and the solution heated for 30 mins. on a water bath. The product separated out as long needles that were filtered off, washed with ethanol and dried in air.

m.p. 209°C (lit.⁽¹⁴⁸⁾ 210°C)

2-Mercaptomethylpyridine

2-Picolylchloride hydrochloride (33g) in ethanol (100ml) was treated with thiourea (16g). The mixture was refluxed for

1 hr. The S-alkylthiuronium salt which was formed, was filtered off, and refluxed with NaOH solution (200ml.20%) for 1 hr. After cooling, the solution was neutralised with CO_2 and the product extracted with ether. Distillation of the ethereal extract in vacuo yielded the product as a colourless liquid.

b.p. 40°C / 0.8 mm. (lit.⁽¹⁴⁹⁾ 89°C / 10mm.)

Di-2,2'-picolyldisulphide

Attempts to prepare this compound by the literature method of oxidation of the thiol with iodine⁽¹⁴⁹⁾ gave a yellow crystalline product of composition $(\text{Py}.\text{CH}_2\text{SH})\text{I}$. An alternative method was developed.

2-Mercaptomethylpyridine was dissolved in dilute ammonia solution and treated with 5% $\text{K}_3\text{Fe}(\text{CN})_6$ solution until the solution was yellow in colour. The oil obtained was extracted with ether. After drying over anhydrous Na_2SO_4 , excess ether was evaporated off, and the remaining oil was purified by low temperature crystallisation from ether/petroleum ether.

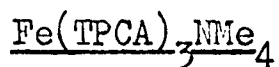
m.p. 39°C (lit.⁽¹⁴⁹⁾ 38.5°C)

Reactions of the ligands

Complexes of thiopicolinic acid anilide (TPCA)

Bahr and Scholtz⁽¹⁵⁰⁾ reported the preparation of two iron(II) complexes of thiopicolinic acid anilide, tetramethylammonium tris(thiopicolinic acid anilido)iron(II), $\text{Fe}(\text{TPCA})_3\text{NMe}_4$, and bis(thiopicolinic acid anilido)iron(II), $\text{Fe}(\text{TPCA})_2$. It seemed possible

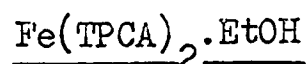
that the ligand could also function as a neutral ligand and we have prepared the novel complex tris(thiopicolinic acid anilide)iron(II) perchlorate, $\text{Fe}(\text{TPCA})_3(\text{ClO}_4)_2$.



Thiopicolinic acid anilide (7g) was dissolved in dilute NaOH solution (150ml. 3%). $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2g) suspended in water (10ml) was added. A solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2g) in water (50ml) containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5g) and a little concentrated hydrochloric acid was also prepared. Both solutions were warmed and the iron(II) solution was added to the alkaline ligand solution. After cooling for 30 min. the solution was filtered through a sintered glass funnel and then heated to boiling. A solution of $\text{Me}_4\text{N.OH}$ (30ml. 3N) was slowly added with stirring. The solution was allowed to cool while being stirred. Dark blue crystals of the product were deposited and dried in vacuo.

Analysis: Found C = 61.7% H = 5.36 % N = 12.2%. Calc. C = 62.1% H = 5.49%

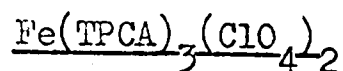
N = 12.6%.



$\text{Fe}(\text{TPCA})_3\text{NMe}_4$ (3.3g) was dissolved in 50% ethanol (100ml). Dilute sulphuric acid (50ml. 0.1N) was added. The solution turned green and was decanted from the slimy precipitate which was washed with ethanol and then boiled with ethanol until crystalline. The dark green crystals contain ethanol of crystallisation⁽¹⁵⁰⁾.

Analysis: Found C = 58.3% H = 4.11% N = 10.5%. Calc. C = 58.8% H = 4.57%

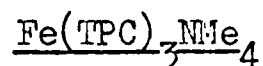
N = 10.6%.



$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.9g) in acetone (20ml) was added to a solution of thiopicolinic acid anilide (3.6g) in acetone (30ml). Addition of ether to the green solution precipitated the product, which was washed several times with ether and dried in vacuo. Analysis: Found C = 47.7% H = 3.35% N = 9.40%. Calc. C = 48.1% H = 3.35% N = 9.36%

Complexes of thiopicolinamide (TPC)

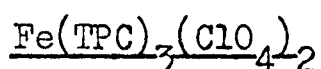
Sutton⁽¹⁵¹⁾ has investigated the transition metal complexes of this ligand and has reported the preparation of tris(thiopicolinamide)iron(III) perchlorate, $\text{Fe}(\text{TPC})_3(\text{ClO}_4)_3$. All our attempts to prepare this complex were totally unsuccessful. It was possible, however, to carry out reactions analogous to those above and the novel complexes $\text{Fe}(\text{TPC})_3\text{NMe}_4$ and $\text{Fe}(\text{TPC})_3(\text{ClO}_4)_2$ were obtained.



Thiopicolinamide (5g) was dissolved with KOH (7g) in the minimum quantity of cold ethanol. $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.6g) in ethanol was added. $\text{Me}_4\text{N.OH}$ (8.2g) in ethanol (20ml) was added and the solution was filtered. Addition of ether precipitated a dark blue solid which was filtered off, washed with a little ethanol and ether and dried in vacuo. The product is much less stable than $\text{Fe}(\text{TPCA})_3\text{NMe}_4$ especially when moist. It may be purified by repeatedly dissolving in ethanol and precipitating with ether.

Analysis: Found C = 48.0% H = 5.28% N = 17.5% Calc. C = 48.5% H = 5.56%

N = 18.0%



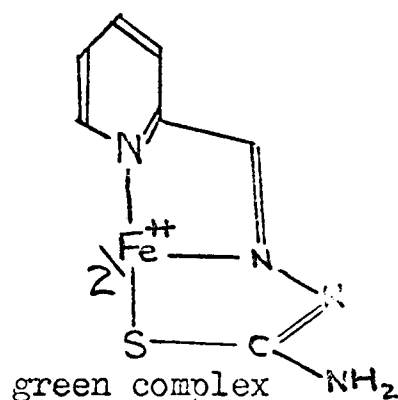
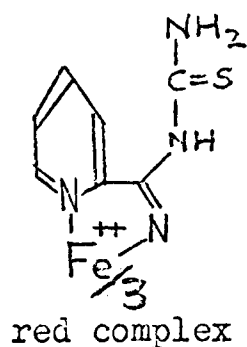
$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.9g) in acetone (20ml) was added to a solution of thiopicolinamide (2.1g) in ether (50ml). The product is immediately precipitated as a green solid and is filtered off, washed with acetone and ether and dried in vacuo.

Analysis: Found C = 32.8% H = 2.91% N = 12.1% Cl = 10.6% Calc.

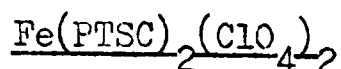
C = 32.3% H = 2.76% N = 12.5% Cl = 10.6%.

Complexes of pyridine-2-aldehydethiosemicarbazone (PTSC)

The complexing ability of pyridine-2-aldehydethiosemicarbazone has been investigated to some extent by Hemmerich, Prijs and Erlenmeyer⁽¹⁴⁸⁾, who reported that it formed red and green complexes with iron(II). The complexes were not isolated but were ascribed the formulae shown:

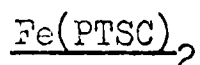


We have isolated a red and a green complex. The complexes are bis(pyridine-2-aldehydethiosemicarbazono)iron(II) perchlorate, $\text{Fe}(\text{PTSC})_2(\text{ClO}_4)_2$, and bis(pyridine-2-aldehydethiosemicarbazono)iron(II), $\text{Fe}(\text{PTSC})_2$, respectively.



$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.71g) in tetrahydrofuran (10ml) was added to a solution of the ligand (0.72g) in tetrahydrofuran (25ml). The solution became dark red in colour. Addition of ether while stirring the solution precipitated a dark red solid, which was recrystallised from acetone/dichloromethane and dried in vacuo.

Analysis: Found C = 26.9% H = 3.11% N = 18.3% Calc. C = 27.3% H = 2.76%
N = 18.2%.



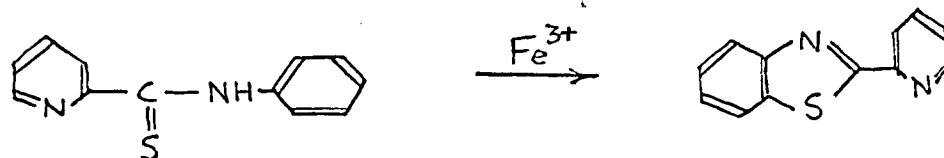
$\text{Fe(PTSC)}_2(\text{ClO}_4)_2$ was dissolved in 50% ethanol. Dilute sodium hydroxide solution (2N) was added with stirring until the solution became dark green in colour. The product was extracted into dichloromethane. The extract was dried over CaCl_2 and the dichloromethane removed to leave a dark green solid which was recrystallised from dichloromethane/ether and dried in vacuo.

Analysis: Found C = 39.7% H = 3.61% N = 26.3% Calc. C = 40.2% H = 3.87%
N = 27.0%

Reaction of iron(III) with TPCA, TPC, and PTSC

Attempts to form iron(III) complexes with the ligands thiopicolinic acid anilide, thiopicolinamide and pyridine-2-aldehydethioscmicarbazone, were unsuccessful. In alkaline solution the complexes Fe(TPCA)_3^- , Fe(TPC)_3^- and Fe(PTSC)_2 were obtained. In neutral or acid aqueous solution, or in organic solvents, complex

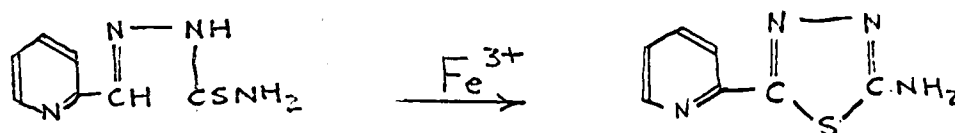
reactions appeared to occur. In the first case it is probable that oxidation of the ligand to 2,2'-pyridylbenzothiazole occurred:



since ferric ion is known to oxidise thioanilides to thiazoles⁽¹⁵²⁾.

The product may complex with ferric or ferrous ions present in solution, but no detailed investigation of this reaction was carried out, since it was beyond the scope of this work.

Ferric ion is also known to oxidise thioamides⁽¹⁵³⁾ and thiosemicarbazones⁽¹⁵⁴⁾ to thiadiazoles, and these reactions presumably account for the failure to obtain iron(III) complexes of these ligands. For PTSC the reaction is probably:



giving 2-pyridyl-1,3,4-thiadiazole.

Complexes of o-aminobenzenethiol (ABT)

It was decided to investigate the reactions of ferrous and ferric ions with ABT before studying the similar ligand 2-mercaptomethylpyridine, since previous workers have investigated the transition metal complexes of the former ligand quite thoroughly⁽¹⁵⁵⁾⁽¹⁵⁶⁾. Larkworthy, Murphy and Phillips⁽¹⁵⁵⁾ have previously prepared and characterised bis(o-aminobenzenethiolato)iron(II), Fe(ABT)₂.

Fe(ABT)₂

The procedure of Larkworthy⁽¹⁵⁵⁾ was found to be

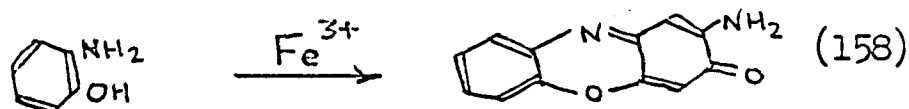
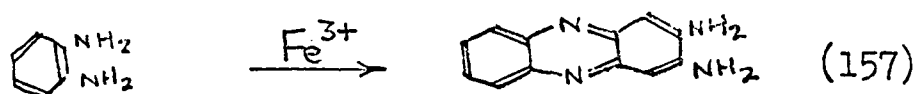
unsatisfactory in preparing this complex and an alternative method was developed. The complex is extremely air sensitive, so air must be rigorously excluded during and after the preparation, which was carried out in a glove bag under nitrogen.

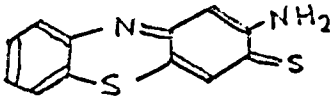
$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.8g) in degassed ethanol (10ml) was treated with 2 ml. o-aminobenzenethiol. Degassed water (30ml) was added to the solution immediately. The yellow precipitate was filtered off and washed with degassed water, ethanol and ether. It was dried in a stream of nitrogen and stored in a sealed tube under nitrogen.

Analysis: Found C = 47.6% H = 4.04% N = 9.3% Calc. C = 47.2% H = 3.93%
N = 9.2%.

The reaction of iron(III) with o-aminobenzenethiol

The reaction of ferric salts with o-aminobenzene-thiol in aqueous solution results in the formation of $\text{Fe}(\text{ABT})_2$ and some disulphide, which precipitates out. The $\text{Fe}(\text{ABT})_2$ complex is rapidly oxidised in the air. When the reaction is carried out in ethanolic solution an intense red colour develops. This is probably due to a reaction analogous to those known for o-phenylenediamine and o-aminophenol:



giving in this case a phenothiazine, , which may be susceptible to further oxidation.

Complexes of 2-mercaptomethylpyridine (MMP)

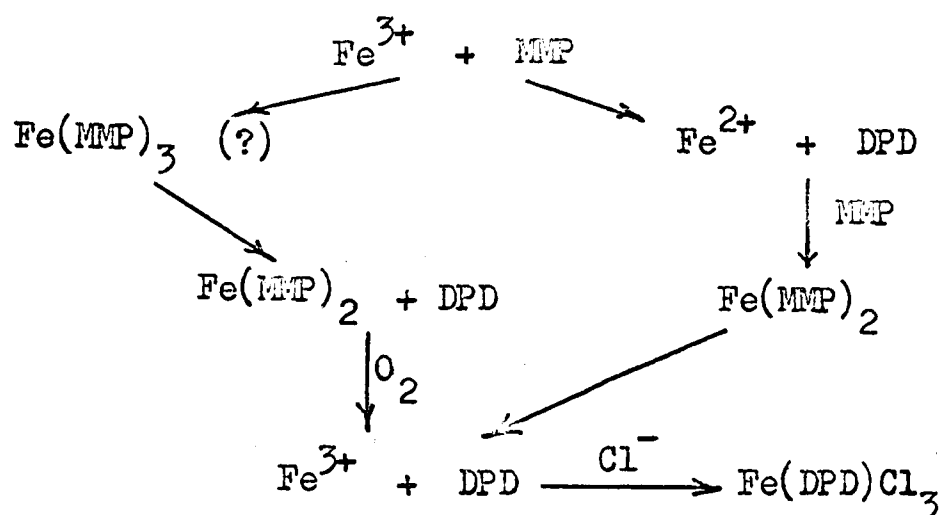
The novel complex bis(2-mercaptomethylpyridino)-iron(II), $\text{Fe}(\text{MMP})_2$ was prepared in an analogous way to $\text{Fe}(\text{ABT})_2$.

$\text{Fe}(\text{MMP})_2$

$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.8g) in degassed ethanol (10ml) was treated, under nitrogen, with a solution of 2-mercaptomethylpyridine (1.3g) in degassed ethanol (10ml). The yellow brown precipitate was filtered off, washed with air free ethanol and ether and dried in a stream of nitrogen. It was stored under nitrogen. The complex is extremely air sensitive and may decompose explosively in air.

Analysis: Found C = 46.5% H = 3.40% N = 8.8% Calc. C = 47.2% H = 3.93%
N = 9.2%

The reaction between ferric ion and 2-mercaptomethylpyridine is complex. In the absence of air $\text{Fe}(\text{MMP})_2$ and di-2,2'-picolyldisulphide are formed. In the presence of air further reactions occur. If $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is used the final product is $\text{Fe}(\text{DPD})\text{Cl}_3$ (see next section). The reactions occurring may be explained by the scheme:



Complexes of di-2,2'-picolyldisulphide

No reaction occurs between ferrous ion and this ligand. An iron(III) complex is formed, however. The complex is the novel disulphide complex $\text{Fe}(\text{DPD})\text{Cl}_3$.

$\text{Fe}(\text{DPD})\text{Cl}_3$

Equimolar quantities of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and di-2,2'-picolyldisulphide were dissolved in ethanol. The solutions were mixed and shaken vigorously for 10min. Brown crystals of the product were deposited. They were filtered off, washed with ethanol and dried in vacuo.

Analysis: Found C = 35.2% H = 3.23% N = 6.3% Cl = 25.7% Calc. C = 35.1%

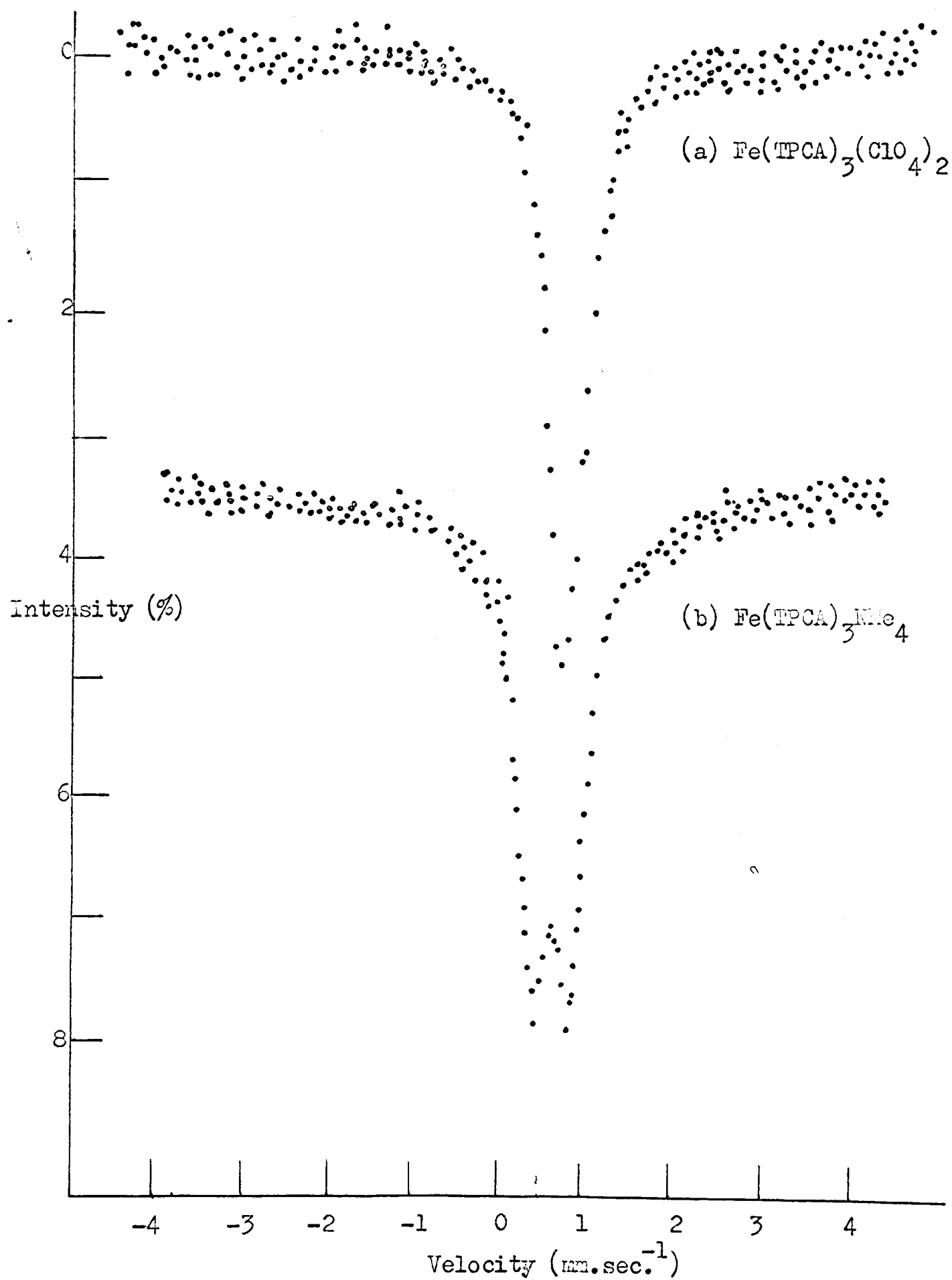
H = 2.92% N = 6.8% Cl = 25.9%

5.3. Results.

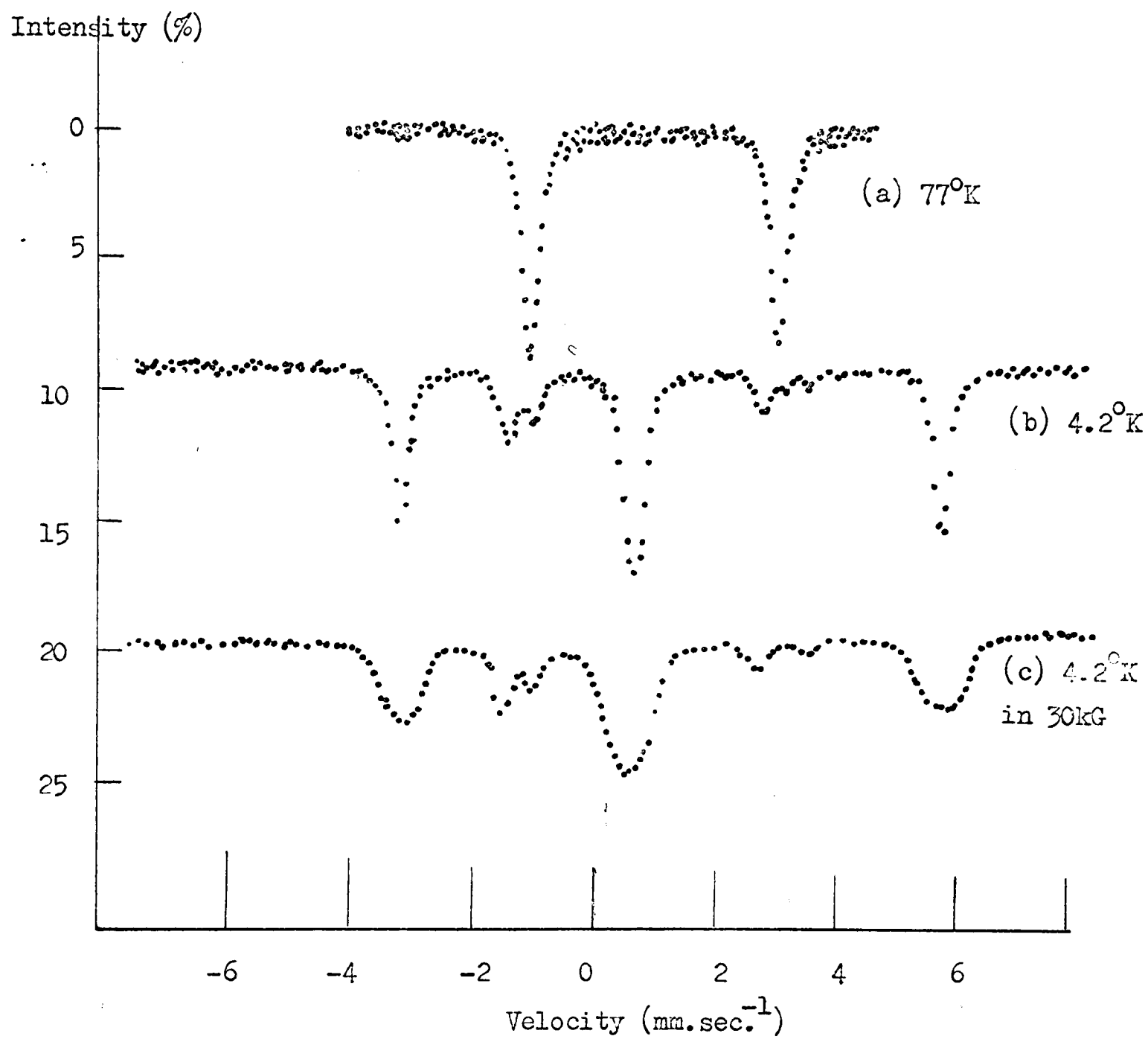
The Mössbauer parameters obtained for the complexes described above are given in Table 5.2. Some of the more interesting spectra are shown in Figures 5.1 - 5.4.

Table 5.2.Mössbauer data for some iron complexes of 2-substituted pyridines.

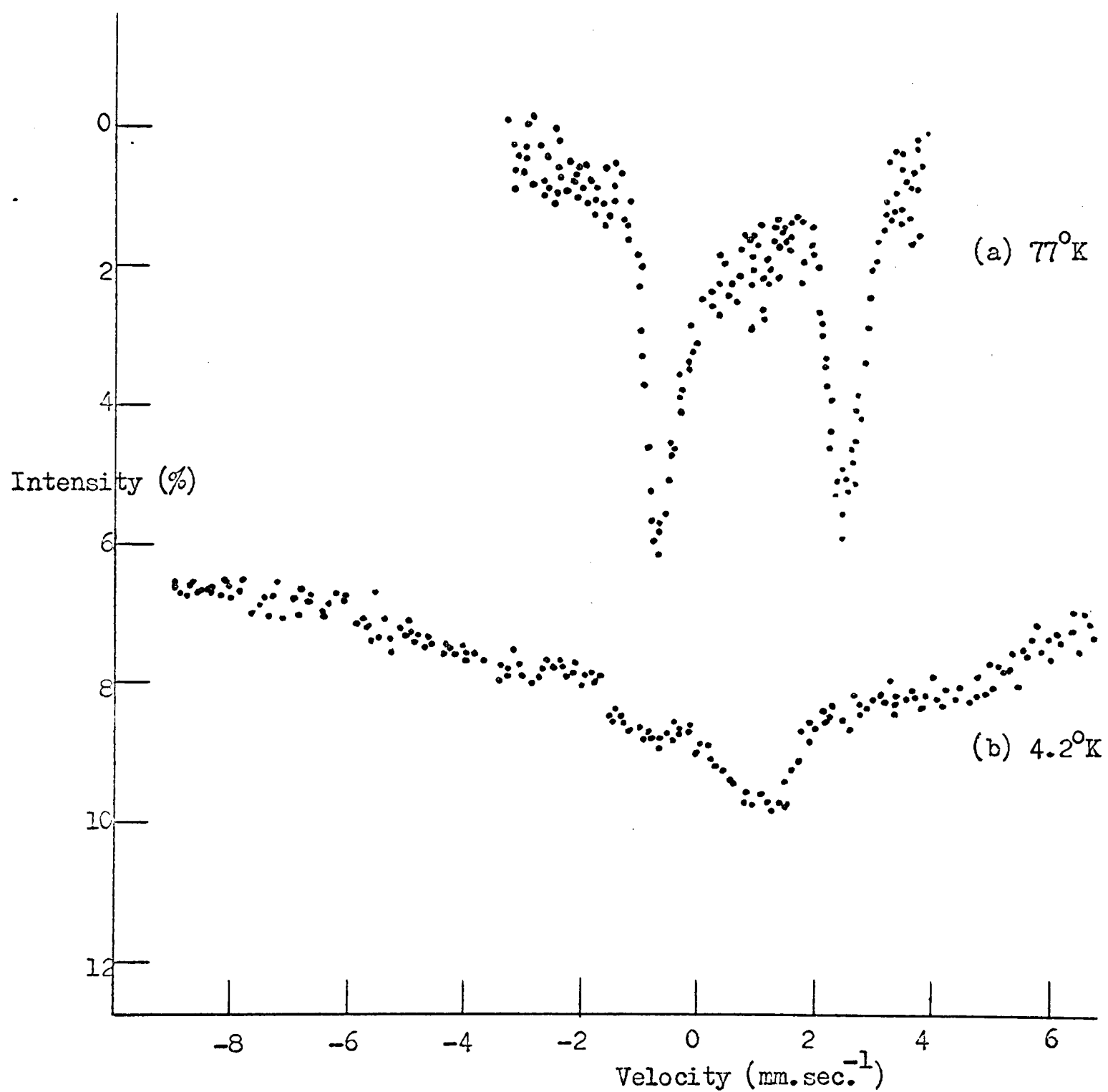
<u>Complex</u>	<u>Temperature(°K)</u>	<u>δ (mm.sec.⁻¹)</u>	<u>ΔE_Q (mm.sec.⁻¹)</u>
Fe(TPCA) ₃ NMe ₄	300	0.28	0.50
	77	0.32	0.44
Fe(TPCA) ₂	300	0.19	2.20
	77	0.26	2.28
Fe(TPCA) ₃ (ClO ₄) ₂	300	0.37	0.00
	77	0.44	0.00
Fe(TPC) ₃ NMe ₄	300	0.23	0.62
	77	0.31	0.64
Fe(TPC) ₃ (ClO ₄) ₂	300	0.32	0.36
	77	0.43	0.42
Fe(PTSC) ₂ (ClO ₄) ₂	300	0.27	0.40
	77	0.32	0.40
Fe(PTSC) ₂	300	0.25	0.56
	77	0.32	0.58
Fe(ABT) ₂	77	0.90	4.06
Fe(MMP) ₂	77	0.91	3.14
Fe(DPD)Cl ₃	300	0.22	1.25
	77	0.32	1.28
	4.2	0.33	1.29

Figure 5.1.

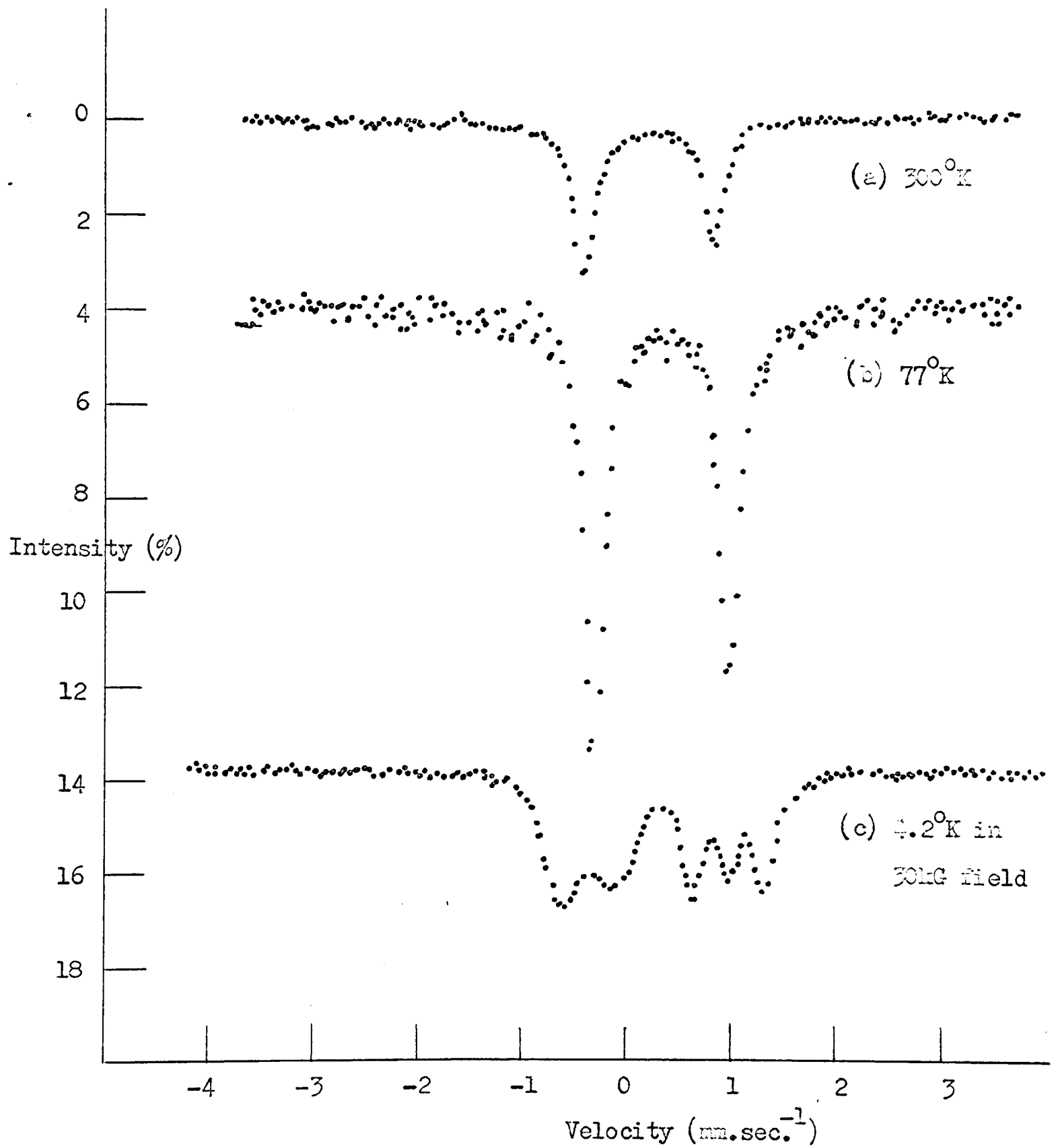
Mössbauer spectra of some low-spin iron(II) complexes at 77°K

Figure 5.2.

Mössbauer spectra of Fe(ABT)₂

Figure 5.3.

Mössbauer spectra of Fe(MP)₂.

Figure 5.4.

Mössbauer spectra of Fe(DPD)Cl₅.

5.4. Discussion.

The most noticeable characteristic of the series of complexes of 2-substituted pyridines described above, is that with one exception, no iron(III) complexes have been able to be prepared. The reasons for this are described in the experimental section. The dominant feature of the preparative chemistry of these complexes is the ease with which the ligand is oxidised by ferric ion, and with substituted pyridines, oxidative cyclisation to more exotic heterocyclic compounds occurs. The exception to the above is the complex formed between ferric chloride and di-2,2'-picolyldisulphide. This is, to our knowledge, the first disulphide complex of iron that has been characterised. Disulphide complexes of other metals are not well known, the best characterised example being $\text{CuCl} \cdot \text{Et}_2\text{S}_2$, which has a polymeric structure containing bridging chloride and disulphide groups⁽¹⁵⁹⁾.

The discussion of the complexes of 2-substituted pyridines may conveniently be divided into three sections, the low-spin ferrous complexes, the high-spin ferrous complexes, and the low-spin ferric complex.

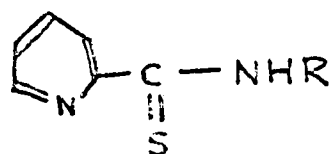
(i) The low-spin ferrous complexes

The Mössbauer parameters of all the complexes of TPCA, TPC and PTSC clearly show that they are low-spin. Since all known four coordinate complexes of iron(II) are high-spin complexes,

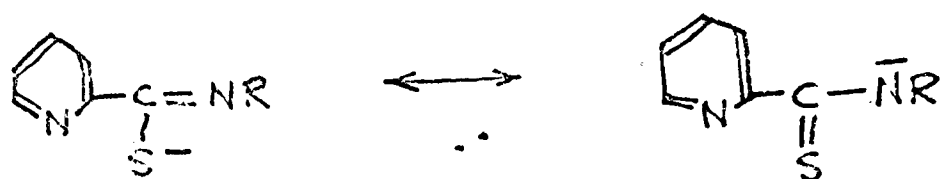
none of these complexes can be four coordinate. In $\text{Fe}(\text{PTSC})_2(\text{ClO}_4)_2$, therefore, it is probable that pyridine-2-aldehydethiosemicarbazide acts as a tridentate ligand, and not as a bidentate ligand as proposed by Hemmerich, Prijs and Erlenmeyer⁽¹⁴⁸⁾. $\text{Fe}(\text{TPCA})_2$ shows a large quadrupole splitting, of the order expected for a high-spin ferrous complex. The isomer shift of $0.26 \text{ mm. sec.}^{-1}$ at 77°K , however, is that expected for a low-spin ferrous complex, which implies that the complex cannot be four coordinate as its empirical formula would suggest. The ethanol of crystallisation and another molecule of the complex presumably complete the coordination sphere.

Thiopicolic acid anilide and thiopicolinamide are bidentate ligands. Coordination is assumed to occur via the pyridine nitrogen atom and the thioamide sulphur atom. This assumption is justified for the case of TPCA since here the alternative of coordination via the amide nitrogen atom is sterically impossible due to the phenyl substituent. The chemical and physical properties of the TPC and TPCA complexes are very similar suggesting that the mode of coordination of the TPC ligand is the same as that of TPCA.

The complexes $\text{Fe}(\text{TPCA})_3\text{NMe}_4$ and $\text{Fe}(\text{TPC})_3\text{NMe}_4$ have lower isomer shifts than $\text{Fe}(\text{TPCA})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{TPC})_3(\text{ClO}_4)_2$. The ligand in the latter case is the neutral species,



whereas in the former case it is negatively charged:

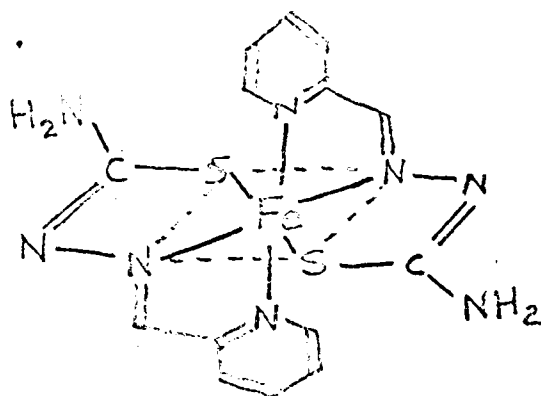


The lower isomer shift can be associated with the greater σ -donor power of the negatively charged ligand. The formation of σ -bonds with partial metal 4s character increases the s-electron density at the nucleus. The concentration of electron density between the metal and the ligand should also lead to an increase in the electric field gradient, and indeed larger quadrupole splittings are observed for $\text{Fe}(\text{TPCA})_3\text{NMe}_4$ and $\text{Fe}(\text{TPC})_3\text{NMe}_4$ than for $\text{Fe}(\text{TPCA})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{TPC})_3(\text{ClO}_4)_2$.

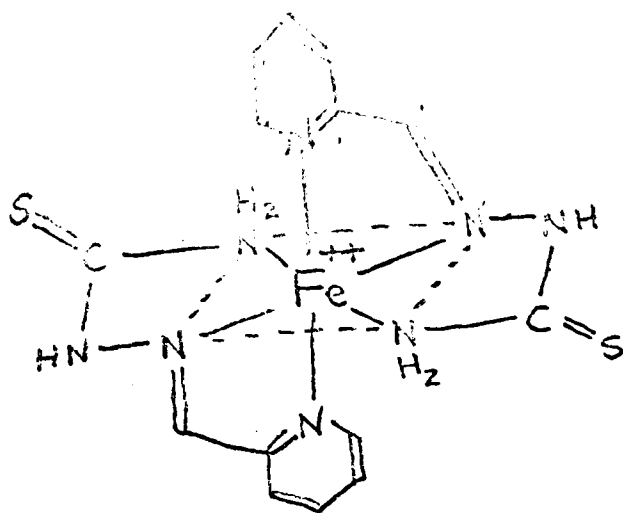
An alternative explanation for the differences in isomer shifts can be proposed. The negatively charged ligand may be a better π -acceptor than the neutral ligand. Then the delocalisation of the d-electrons from the metal on to the ligand would lead to a decreased shielding of the s-electrons from the iron nucleus and to a lower isomer shift. However, the delocalisation of the d-electrons would lead to a reduction in the value of $\langle r^{-3} \rangle_{3d}$ and to a smaller quadrupole splitting (see eq.(13)) which is not observed.

The thiopicolinamide complexes have isomer shifts lower than the analogous thiopicolinic acid anilide complexes, which is consistent with the greater electron withdrawing power of the phenyl substituent, making TPCA a weaker σ -donor than TPC.

The same dependence of isomer shift and quadrupole splitting on the charge of the ligand is not observed for the PTSC complexes. The lack of correlation in this case may be due to significant structural differences. Thus, whereas it is probable that in $\text{Fe}(\text{PTSC})_2$ the ligand is coordinated via two nitrogen atoms and the sulphur atom:



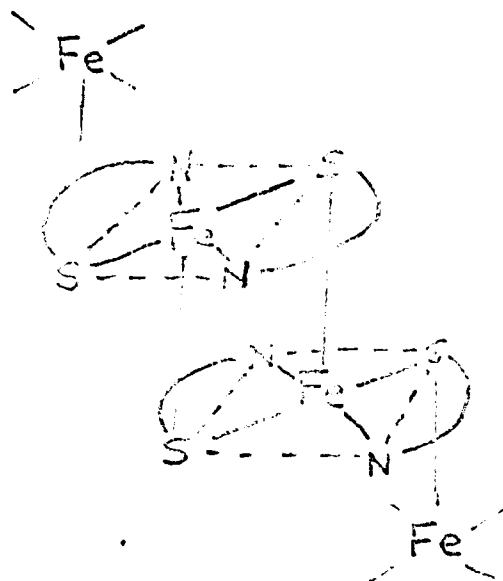
it is possible that $\text{Fe}(\text{PTSC})_2(\text{ClO}_4)_2$ is coordinated by six nitrogen atoms from the two PTSC ligands:



(ii) The high-spin ferrous complexes

The Mössbauer parameters for $\text{Fe}(\text{ABT})_2$ and $\text{Fe}(\text{MMP})_2$ confirm that these complexes are high-spin. The isomer shifts are 0.90 and 0.91 mm.sec.⁻¹ respectively at 77°K, and are at the lower end of the range observed for high-spin ferrous complexes. It has been observed by other workers that the isomer shifts of four coordinate high-spin ferrous complexes are lower than those of six coordinate high-spin ferrous complexes with the same ligands⁽¹³⁰⁾.

The quadrupole splittings are large for both complexes, indeed the splitting of 4.06 mm.sec.⁻¹ observed for $\text{Fe}(\text{ABT})_2$ at 77°K is the largest quadrupole splitting observed to date for an iron compound. It is presumably a consequence principally, of a large contribution to the electric field gradient from the valence electrons. Were the complex purely square planar, however, this contribution would be cancelled out to some extent by a lattice contribution to the electric field gradient of opposite sign⁽¹⁶⁰⁾. It therefore seems likely that the complex has a polymeric structure with bridging sulphur atoms, as is known to occur in other square planar iron-sulphur complexes.⁽¹⁶¹⁾ Larkworthy, Murphy and Phillips⁽¹⁵⁵⁾ have found that the absorption spectrum of the complex in the solid state is consistent with this structure, which is illustrated below:



The same workers have also investigated the magnetic susceptibility of $\text{Fe}(\text{AST})_2$, and find that it is antiferromagnetic with a Neel point at 138°K . Our Mössbauer measurements are not entirely consistent with this result. At 77°K the Mössbauer spectrum is a simple quadrupole split pair of lines, (Figure 5.2(a)), indicating the absence of antiferromagnetism at this temperature. At 4.2°K the spectrum shown in Figure 5.2(b) is obtained. The spectrum now clearly shows the existence of a magnetic field at the iron nucleus. In order to confirm that the sample was antiferromagnetic, the spectrum was measured in an external field of 30kG at 4.2°K . The spectrum then observed is shown in Figure 5.2(c). The only effect of the external field is to broaden the lines. For an antiferromagnet there is no net moment with which the external field can interact. The internal field at the iron nucleus is increased in half the iron atoms and decreased in the others, depending on the orientation of the

atomic spin. The lines are broadened due to the distribution of internal fields, but the position of the lines remains the same.

$\text{Fe}(\text{MCP})_2$ shows a similar spectrum to $\text{Fe}(\text{ABT})_2$ at 77°K (Figure 5.3(a)), with a large quadrupole splitting. On lowering the temperature to 4.2°K, the spectrum broadens and gives the appearance of a spectrum expected for a slowly relaxing paramagnet, (Figure 5.3(b)). This is most unusual for a high-spin ferrous complex, and the only similar example is found in the spectrum of oxygenated haemoglobin⁽³⁰⁾. The effect of an axial field and spin-orbit coupling upon the $^5\text{T}_2$ state of the high-spin ferrous ion, is to remove the degeneracy of the state and to leave a state with effective spin S of zero as the lowest state. Magnetic hyperfine interactions are not therefore expected to be observed in ferrous complexes. The spectrum of oxygenated haemoglobin is explained as being due to the occurrence of a small hyperfine field at the iron nucleus due to the paramagnetic oxygen molecule. This explanation obviously cannot be extended to the complex $\text{Fe}(\text{MCP})_2$. By analogy with $\text{Fe}(\text{ABT})_2$, the spectrum may be a consequence of a small hyperfine field arising at the iron nucleus due to weak antiferromagnetism between $\text{Fe}(\text{MCP})_2$ moieties that are bridged by sulphur atoms.

(iii) The low-spin ferric complex.

The analytical results for this compound confirm that its empirical formula is $\text{Fe}(\text{DPD})\text{Cl}_3$. The solubility properties of the complex suggest that it is ionic; thus it is soluble in solvents of high dielectric constant, such as water, alcohol and dimethylacetamide, but it is insoluble in non-polar solvents, such as benzene and ether. When an aqueous solution of the complex is treated with silver nitrate solution all the chlorine in the complex is precipitated as silver chloride.

The magnetic susceptibility of the complex was measured by the Gouy method at 293°K , on a Newport Instruments Gouy balance calibrated with $\text{HgCo}(\text{NCS})_4$. The magnetic susceptibility was found to be $1415 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$. The magnetic moment is therefore $1.73 \mu_B$ (diamagnetic correction = $-169 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}(162)$).

The Mössbauer parameters confirm that the complex contains low-spin iron(III) (see Table 5.2). The values of the quadrupole splitting and the effective field at the iron nucleus (Figure 5.4) are those expected for a low-spin ferric complex in a distorted octahedral environment. The isomer shift shows the temperature dependence expected from the second order Doppler Effect. The quadrupole splitting is virtually temperature independent, indicating the absence of nearby excited levels.

The epr spectrum of a 10^{-3} M solution of the complex

in dimethylacetamide was measured at 100°K , and is illustrated in Figure 5.5. The g-values were found to be:

$$g_1 = 1.956 \quad g_2 = 2.011 \quad g_3 = 2.042 \quad (-0.005)$$

The spectrum showed very broad lines, but no hyperfine splittings were resolved. Addition of sodium dithionite to the solution caused it to develop an intense reddish colour. The appearance of this coloration was accompanied by the disappearance of the epr signal.

The g-values are close to those observed for $(\pi\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2\text{SbF}_6$ (see page 175) and correspond to almost cubic symmetry. The Mössbauer spectrum shows, however, that in the solid state the symmetry of the iron atom is far from cubic. It seems probable that some dissociation of the complex occurs on dissolution in the polar solvent.

By comparison with $\text{CuCl}\cdot\text{Et}_2\text{S}_2$ a possible structure for the complex in the solid state is:

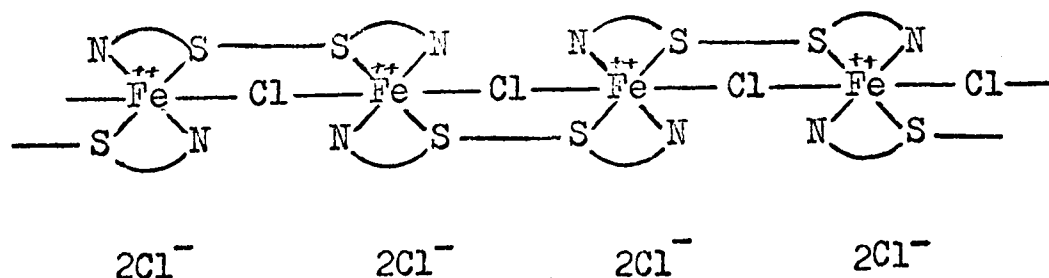
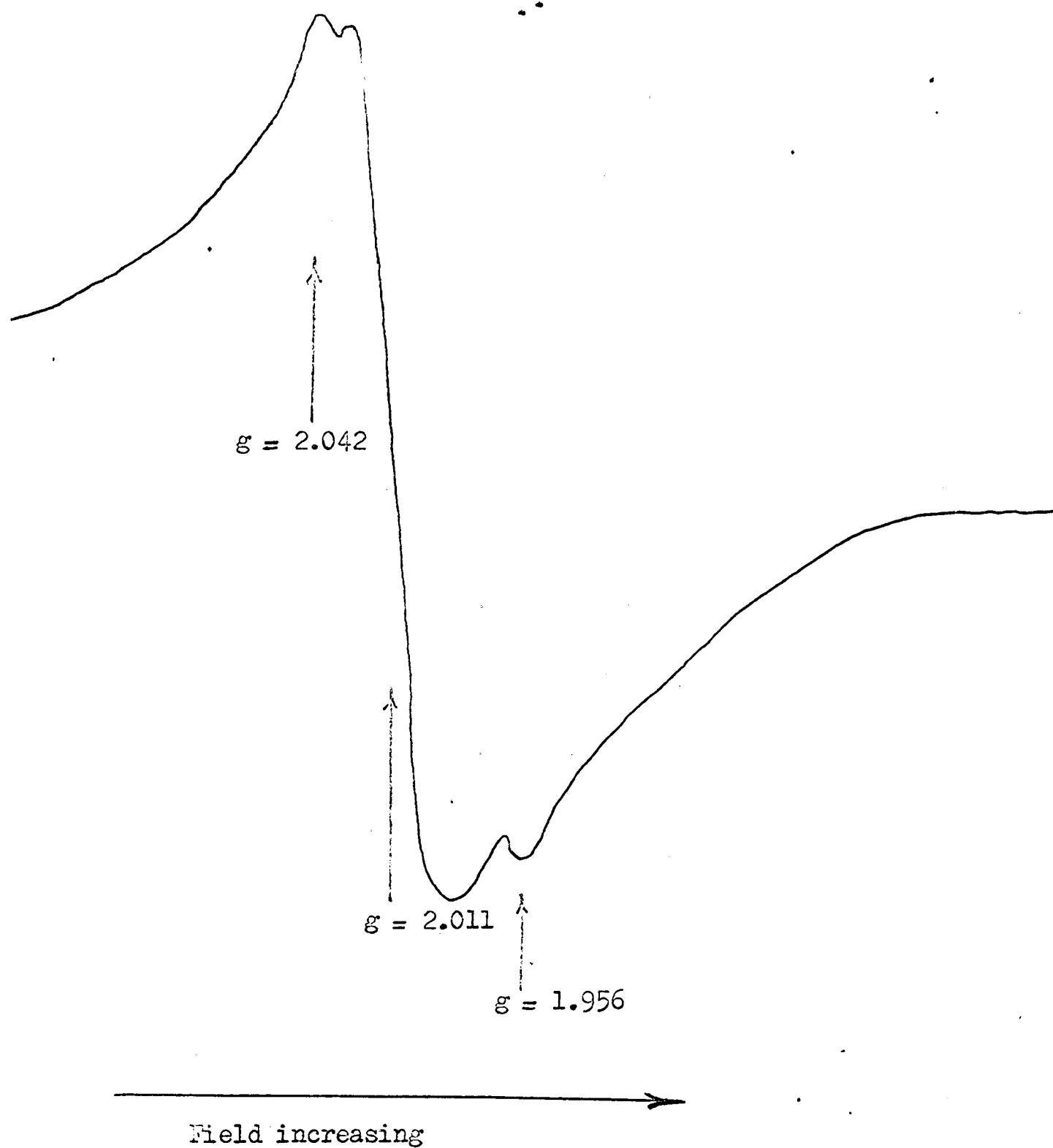


Figure 5.5.

EPR spectrum of 10^{-3} M DMA solution of $\text{Fe}(\text{DPD})\text{Cl}_3$ at 100°K .

Antiferromagnetic interactions between the iron atoms, via the bridging chloride groups, could account for the low value observed for the magnetic moment. The polymeric structure is expected to break down in solution as for $\text{CuCl} \cdot \text{Et}_2\text{S}_2$ ⁽¹⁵⁹⁾. Further investigations of this novel complex are merited before its structure and properties are fully understood.

CHAPTER SIX. CONCLUSIONS.

In the previous chapters we have accumulated and discussed a considerable amount of information on a variety of iron-sulphur complexes. In this chapter we attempt to summarise some of the more important aspects of the data that we have obtained from the Mössbauer and epr spectroscopic studies. The information obtained has been of two kinds, that concerning the molecular structure of the complexes and that concerning their electronic structures.

6.1. Molecular structure.

In the diagnosis of molecular structure both Mössbauer spectroscopy and epr have a limited value. Their use as fingerprinting techniques is restricted, since only a few transitions are observed. We have, however, been able to draw some conclusions about the symmetry and molecular structure of some of the complexes studied. For example, epr measurements have shown the complex $\text{Fe}(\text{TID})_2(\text{DTT})$ to have axial symmetry, whereas the related complex $\text{Fe}(\text{TID})(\text{DTT})_2$ has orthorhombic or lower symmetry. From Mössbauer Effect investigations we have shown that the originally proposed structure for $\text{Fe}(\text{sacsac})_2\text{Cl}_4$ was incorrect, and that the probable structure is $(\text{FeCl}_4^{2-})(\text{sacsac}^+)_2$. The assignment of spin state by Mössbauer spectroscopy may also enable conclusions to be drawn about the molecular structure. Thus since the complex $\text{Fe}(\text{PTSC})_2(\text{ClO}_4)_2$

contains low-spin ferrous ions it must be six coordinate.

Further information may be obtained from the Mössbauer spectrum when the time scale of the experiment is considered. The lifetime of the ^{57}Fe excited state is 1.5×10^{-7} sec. The appearance of a single spectrum for the iron(III)N,N dialkyl-dithiocarbamates reveals that the rate of change of spin state is faster than $1.5 \times 10^7 \text{ sec}^{-1}$. The single pair of quadrupole split lines observed for the complex $(\eta\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2\text{SbF}_6$ is a consequence of the unpaired electron being shared equally by both iron atoms, at least over the lifetime of the ^{57}Fe excited state. On the other hand, the appearance of two pairs of quadrupole split lines in the Mössbauer spectrum of $(\text{Ph}_2\text{C}_3\text{HS}_2)_2\text{FeCl}_4$ indicates that two types of iron atom are present in this complex.

6.2. Electronic structure of molecules.

The paucity of the information obtainable from Mössbauer spectroscopy and epr about molecular structure is in contrast to the wealth of information that can be acquired concerning the electronic structure of molecules. Since the electrons in the orbitals of highest energy are those essentially associated with the metal, both the physical techniques used are able to provide data associated with the properties of these electrons. Mössbauer spectroscopy also has the advantage that it yields information on complexes which are not suitable for studies by magnetic resonance methods, which require

the presence of unpaired spin density.

We shall consider the main parameters obtained from the Mössbauer spectrum in turn, to see the kinds of chemically important information that can be derived.

Intensities and line widths

The temperature dependence of the Mössbauer spectrum enables approximate estimates of effective Debye temperatures to be made. It has been found that iron-sulphur complexes generally show low values for Θ_D . More important, however, is the information that can be obtained in favourable cases from an investigation of the temperature dependence of the relative line intensities. Thus the temperature dependence of the Mössbauer spectrum of tristetraphenylphosphonium trisdicyano-1,2-dithiolene iron has been interpreted in terms of the relative magnitudes of the spin-lattice and spin-spin relaxation times. Similarly, the appearance of line broadening in the spectra of the iron(III) N,N dialkyldithiocarbamates has been related to the size of the alkyl substituent and consequent separation of the iron nuclei, which affects the spin-spin relaxation times.

The isomer shift

The isomer shift provides a measure of the s-electron density at the nucleus of the absorber. For all the complexes we have studied, except the iron(III) N,N dialkyldithiocarbamates, the isomer shift showed the temperature dependence

expected from the second order Doppler Effect. The discrepancy observed for the iron(III) N,N dialkyldithiocarbamates can be explained as being due to the spin equilibrium.

Isomer shift values have been discussed by many authors⁽³⁶⁾⁽³⁷⁾⁽³⁸⁾, and related to chemical bonding parameters such as electronegativity, ionicity and the nephelauxetic series. The difficulties encountered in attempting to find extended agreement in these correlations have been mentioned in Chapter Two.

The isomer shift of the free ion will be modified by bonding with ligands. The ways in which the s-electron density at the nucleus can be affected by metal-ligand bonding are threefold: (i) an increase of 4s electron density may occur as a result of the partial occupation of the iron 4s orbitals by ligand electrons; (ii) donation of electrons from the ligand into the metal 3d orbitals will increase the 3d electron density and increase the shielding of the s-electrons from the nucleus; (iii) delocalisation of metal d-electrons on to the ligands, by π -bonding of the metal d-orbitals with empty ligand orbitals, will decrease the shielding of s-electrons from the nucleus. Mechanisms (i) and (iii) result in a decrease of the isomer shift, (ii) increases the isomer shift. The difficulty in interpreting isomer shift values in terms of subtle changes of metal-ligand bonding can readily be recognised.

The only high-spin ferric complex that we have studied, iron(III) pyrrolidylthiocarbamate, has an isomer shift at

300°K of 0.40 mm.sec.⁻¹, which is appreciably lower than the isomer shifts observed for other high-spin ferric complexes, e.g. FeF₃, 0.75 mm.sec.⁻¹; Fe₂(SO₄)₃·7H₂O, 0.67 mm.sec.⁻¹; Fe₂O₃, 0.63 mm.sec.⁻¹; FeCl₃·6H₂O, 0.60 mm.sec.⁻¹(36). Here the correlation between decreasing isomer shift, decreasing electronegativity, increasing polarisability and increasing tendency to form covalent bonds, is very satisfactory, and may be explained in terms of increasing occupancy of the iron 4s orbitals by electrons from the ligands.

For the low-spin ferric complexes the agreement is less satisfying. Both mechanisms (ii) and (iii) above are now operating. The shifts observed for the low-spin FeS₆ compounds are considerably higher than those observed in many other low-spin ferric complexes, e.g. K₃Fe(CN)₆, -0.16 mm.sec.⁻¹, (Fe(ophen)₂(CN)₂)NO₃, 0.10 mm.sec.⁻¹(163). We conclude that for these complexes the deshielding effects of π -back bonding are outweighed by the covalency effects between the filled ligand orbitals and the metal d-orbitals.

For low-spin ferrous complexes the variations in isomer shift provide almost the only information about the electronic structures of the complexes. The value of this information is illustrated by the data obtained and discussed in Chapter Five.

The isomer shift provides information which is unique to the Mössbauer experiment. It is unfortunate that full investigations of the relationship of the isomer shift to other

chemical bonding properties have yet to be carried out satisfactorily.

The quadrupole splitting

The quadrupole splitting is closely related to the symmetry of the complex and can, as mentioned earlier, assist in the diagnosis of molecular structure. The magnitude of the quadrupole splitting is difficult to interpret satisfactorily, since it is so intimately associated with the electronic structure as well as with the crystal and molecular structure. We have found only approximate agreement between the observed quadrupole splittings of iron(III) N,N dimethyldithiocarbamate, the 'persulphide' complexes, and of $(\text{Ph}_4\text{P})_3(\text{FeS}_6\text{C}_6(\text{CN}))$, and with the quadrupole splittings calculated on the basis of orbital separations deduced from the results of measurements of magnetic hyperfine interactions and epr. To attempt the reverse, and calculate orbital separations from the observed quadrupole splittings is not generally possible.

However, the determination of the sign of the quadrupole splitting and of its temperature dependence, can provide knowledge of the nature of the orbital ground state, and of its separation from higher states. Thus we have shown that for $(\text{FeCl}_4^{2-})(\text{sacsac}^+)_2$ the d_z^2 orbital is the lowest lying orbital, and that it is separated by 315 K from the $d_{x^2-y^2}$ orbital. For the other complexes investigated the results are less straightforward. For nitrosyliron bis(N,N diethyldithiocarbamate) contributions

from the lattice and from covalency are important in determining the sign of the quadrupole splitting. We must then resort to the complex procedure of calculating the Mössbauer spectrum.

In the low-spin ferric complexes the use of epr measurements in conjunction with the Mössbauer data enables the nature of the orbital ground state to be ascertained. We have not always found total agreement between the epr and the Mössbauer data. The theory that we have used to explain the epr spectra assumes that the 2T_2 state is well separated from higher states. This is certainly not the case for the iron(III) N,N dialkyldithiocarbamates. Further, the theory neglects spin-orbit coupling with excited states. This approximation may not be valid in iron-sulphur complexes. A refinement of the theory introduces the orbital reduction factor, k , to take account of covalency. We have found that taking k as less than one does not improve the agreement between theory and experiment to any great extent. Strictly, different values for k should be taken in each of the equations (41), (42) and (43), but this makes solution of the equations impossible. Despite the limitations of the theory we have been able to obtain realistic semi-quantitative descriptions of the ground states of the low-spin ferric complexes.

Iron(III) N,N dimethyldithiocarbamate possesses almost cubic symmetry, with a ground state consisting of equal amounts of $|xz\rangle$ and $|yz\rangle$ with slightly less of $|xy\rangle$. The

temperature dependence of the quadrupole splitting deviates from that expected for this ground state, due to the population of the nearby excited 6A_1 state.

The remaining low-spin ferric complexes that we have investigated are grossly distorted from cubic symmetry.

$\text{Fe}(\text{TTD})_2(\text{DTT})$, $\text{Fe}(\text{TTD})(\text{DTT})_2$ and $(\text{Ph}_4\text{P})_3(\text{FeS}_6\text{C}_6(\text{CN})_6)$ have ground states that are almost pure xy holes, separated by large energies from the next highest state. The quadrupole splitting is expected to be virtually temperature independent, although this is not found to be the case for the latter complex.

Magnetic hyperfine interactions

The magnetic hyperfine interactions observed in Mössbauer spectroscopy are capable of providing valuable chemical information, although many previous workers in this field have neglected to investigate them, presumably due to the experimental difficulties.

The measurement of Mössbauer spectra at low temperatures and in external magnetic fields has enabled us to observe magnetic hyperfine interactions in a number of complexes. We have also been able to establish the nature of the interaction causing the effective field at the nucleus, and have found examples of ferromagnetic, ($((\text{C}_2\text{H}_5)_2\text{NCS})_2\text{FeCl}$), antiferromagnetic, ($\text{Fe}(\text{ABT})_2$), and paramagnetic, (e.g. $((\text{CH}_2)_4\text{NCS})_3\text{Fe}$), complexes.

The magnetic hyperfine interaction spectrum enables the sign of the major component of the electric field gradient to be established. Information on the ground state of a complex has also been obtained by investigating the field and temperature dependence of the magnetic hyperfine interactions. Thus, for iron(III) pyrrolidyl dithiocarbamate, we have shown the zero field splitting to be large and negative, and have estimated its value (4D) as -9.3°K , in good agreement with the measured value of $-8.4\text{ cm}^{-1}(164)$.

The magnetic susceptibility of a complex may also be studied by the Mössbauer Effect. We have found that the dependence of the effective field at the nucleus, H_{eff} , upon H/T for nitrosyliron bis(N,N diethyldithiocarbamate), follows the Brillouin function for $S = 1/2$, thus providing the first low temperature susceptibility data for this complex, and confirming the assignment of the spin state.

The value of the effective field at the nucleus can also provide information. We have discussed the contributions to H_n , the saturation hyperfine field, in Chapter Two. The largest contribution usually arises from the Fermi contact term, H_s , and is a measure of the spin density at the nucleus. Calculated unrestricted Hartree-Fock values for H_s for Fe^{3+} ($S = 5/2$) and Fe^{2+} ($S = 2$) ions are -650kG and -550kG respectively. These values result from the polarisation of s-electrons by the unpaired d-electrons, so that we expect a single unpaired d-electron to give rise to a contribution of about -130kG to the hyperfine field. When the iron atom is placed in

a ligand field, interactions between the ion and the ligands result in the d-electrons becoming delocalised on to the ligands to some extent. The hyperfine field will decrease as the polarisation of the s-electrons by the unpaired d-electrons decreases, and we may expect a correlation between the magnitude of the hyperfine field and the covalency of the metal-ligand interaction. Some experimental values for the hyperfine fields of some high-spin ferric compounds are given in Table 6.1. The values are in good agreement with the calculated value.

Table 6.1.

<u>Compound</u>	<u>H_n (kG)</u>	<u>Coordination</u>	<u>Reference</u>
FeF_3	-622	6F^-	165
$\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$	-584	$6\text{H}_2\text{O}$	166
Fe_2O_3	-540	6O^{2-}	167
FeCl_3	-487	6Cl^-	168

The correlation between the magnitude of H_n and covalency appears excellent, although it is limited by the few measurements that have been made on high-spin ferric complexes. The value of H_n for iron(III) pyrrolidylthiocarbamate is -470 kG reflecting the covalency of the iron-sulphur bond in this complex.

The correlation can be extended to other complexes

in different spin states, but now H_n may contain contributions from H_L the orbital term and H_d the dipolar term.

From the Mössbauer spectra of nitrosyliron bis(N,N diethyldithiocarbamate) H_n has been estimated as -110kG. The contribution from the orbital term will be negligible since $g \approx 2$ ⁽¹¹²⁾. The dipolar field produced by a single electron is given by:

$$H_d = -\sqrt{3}q \quad (68)$$

The perpendicular component of H_d is given by:

$$H_{d\perp} = -\frac{1}{2}\sqrt{3}q \quad (69)$$

and for this complex has a value of -16kG. The value of H_s is therefore -94kG, appreciably reduced by covalency from the expected value of ~ -130 kG.

For bis(N,N diethyldithiocarbamate)iron(III) chloride, which has three unpaired electrons, the relationship (68) is no longer valid. The dipolar field can, however, be estimated if the ordering of the 3d orbitals is known. Wickmann⁽¹⁰⁷⁾ give the electronic configuration of this complex as:

$$(3d_{x^2-y^2})^2(3d_{xz})^1(3d_{yz})^1(3d_z)^1(3d_{xy})^0$$

Martin and White⁽⁷³⁾ suggest that the ordering of the energies of the 3d orbitals is:

$$3d_{xy} < 3d_{xz}, 3d_{yz} < 3d_z^2 < 3d_{x^2-y^2}$$

It can be seen from Table 2.1 that both these electronic configurations would give rise to a zero electric field gradient and the large

quadrupole splitting must then originate from lattice contributions, which seems very unlikely. The magnitude and sign of the quadrupole splitting can be accounted for if the electronic configuration is postulated as being:

$$(3d_x^2 - y^2)^2 (3d_{xy})^1 (3d_{xz})^1 (3d_{yz})^1 (3d_z^2)^0$$

or:

$$(3d_{xy})^2 (3d_x^2 - y^2)^1 (3d_{xz})^1 (3d_{yz})^1 (3d_z^2)^0$$

Then, for the electrons localised on the metal:

$$q = \frac{8}{7} \langle r^{-3} \rangle$$

In this case the dipolar field, which is given by:

$$H_d = \frac{1}{7} \beta \langle (L_z^2 - 2)(S_z) \rangle \quad (70)$$

is zero. H_L is again negligible since $g \approx 2^{(110)}$. H_S for bis(N,N diethyldithiocarbamato)iron(III) chloride is therefore -340kG. It is somewhat surprising that in this $S = 3/2$ complex, the contribution to the Fermicontact term per unpaired electron is larger, at -113kG, than in the $S = 5/2$ complex iron(III)pyrrolidylthiocarbamate, where it is -94kG.

The low-spin ferric complexes that we have investigated are of two kinds, those which have nearly cubic symmetry, such as the low-spin iron(III) N,N dialkyldithiocarbamates, and those which are highly distorted from cubic symmetry, such as the 'persulphide' complexes and tristetraphenylphosphonium tris-dicyano-1,2-dithiolene iron. The g-values in both cases lie near to

the free electron value, a situation which can arise either from a nearly cubic environment, or from a highly distorted environment when the electron (or hole) is isolated on the energy scale. In the former case, small quadrupole splittings are observed; in the latter case large quadrupole splittings are observed. The values of H_n observed are of the order of 300kG and -100kG respectively. The difference in the magnitudes of H_n is due to the orbital contribution to the hyperfine field, H_L . H_L is given by:

$$H_L = 2\beta \langle r^{-3} \rangle \langle L \rangle \quad (71)$$

For cubic symmetry $\langle L \rangle \neq 0$, so that H_L is not negligible. H_d will be small and H_s may be taken as -100kG. H_L is then -200kG or 400kG, depending on the sign of H_n . Unfortunately we have not been able to establish the sign of H_n for these complexes.

For the remaining low-spin ferric complexes

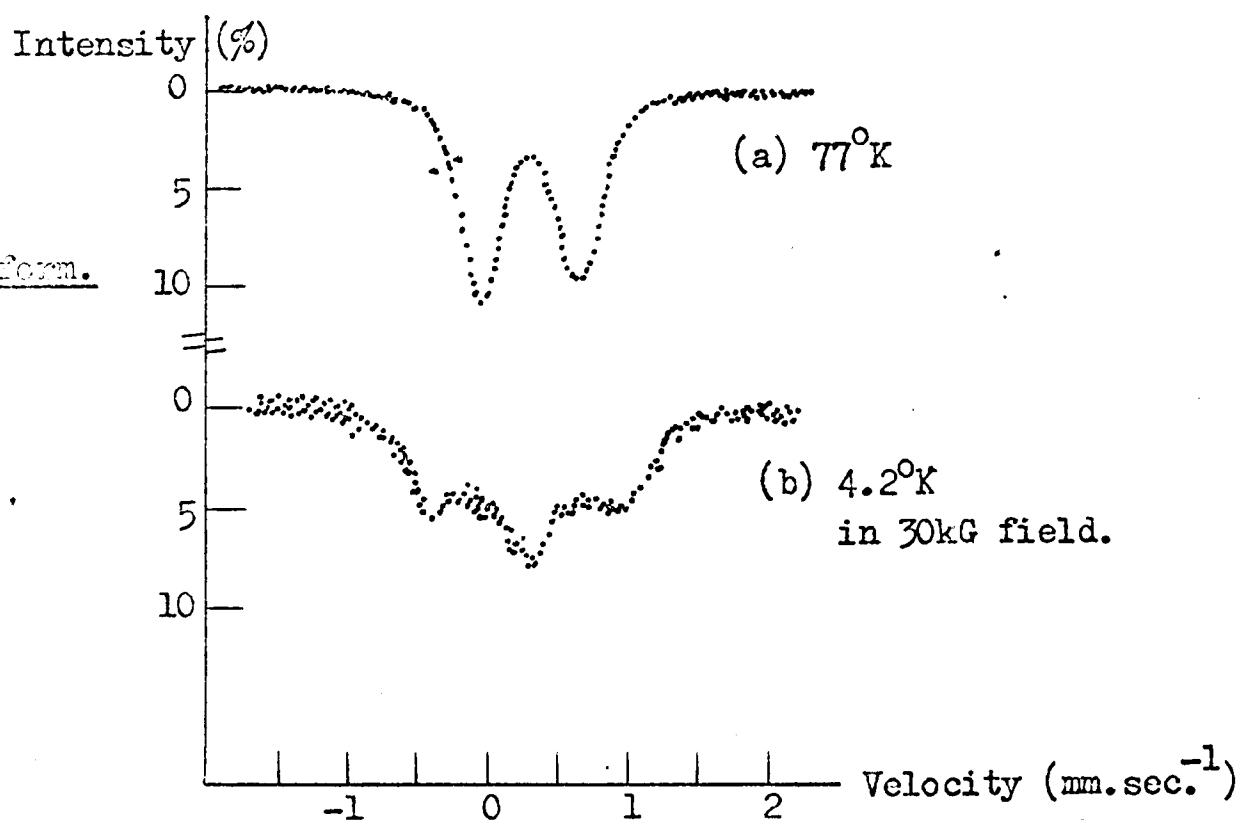
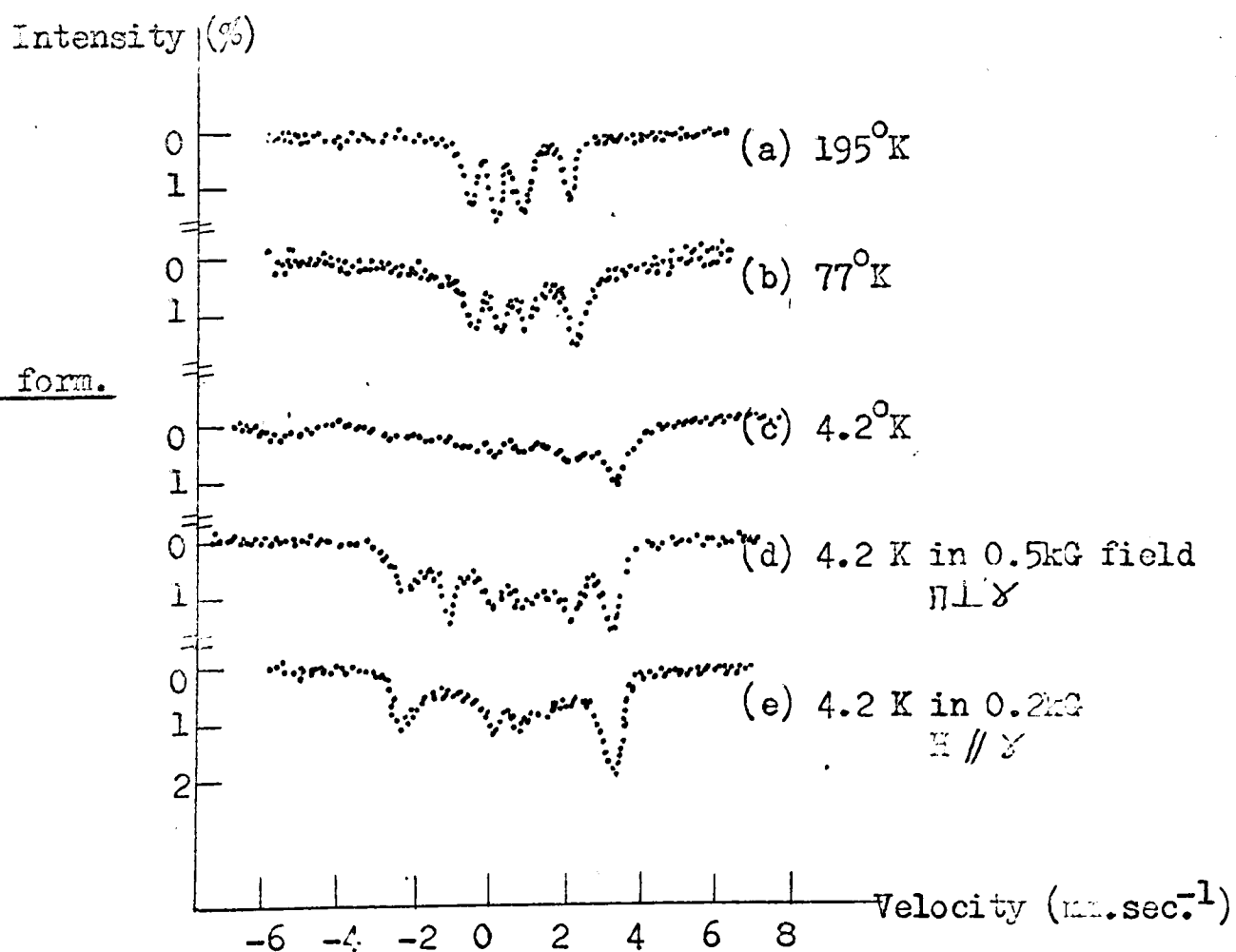
$\langle L \rangle \approx 0$, so that only the dipolar and Fermi contact contributions to H_n are significant. For tristetraphenylphosphonium trisdicyano-1,2-dithiolene iron $H_n = -110$ kG. H_d is estimated as -33kG, giving H_s as -77kG. Reliable estimates of H_s cannot be obtained for the other complexes but it is evident that they are of the same order of magnitude. These values are much smaller than expected for a single unpaired d-electron and reflect the strong covalent iron-sulphur interactions in these complexes.

6.3. Iron-sulphur complexes and the non-haem iron proteins.

In conclusion, we shall briefly consider the relevance of some of our results to the study of the non-haem iron proteins. The structure, function and physical properties of the ferredoxins were considered in Chapter One. The Mössbauer spectra of a representative example, Euglena ferredoxin, will now be considered in more detail. The spectra are shown in Figures 6.1 and 6.2, and may be interpreted as follows⁽¹³⁾.

In the oxidised state the Mössbauer spectrum consists of a quadrupole split pair of lines (Figure 6.1(a)). At 77°K the values of the isomer shift and quadrupole splitting are 0.22 mm. sec⁻¹ and 0.65 mm.sec.⁻¹ respectively. The quadrupole splitting is independent of temperature over the range 1.3°K - 77°K. The application of a 30kG magnetic field to the sample at 4.2°K produces a splitting of 30kG (Figure 6.1(b)) indicating that the iron atoms are in a non-magnetic state. The major component of the electric field gradient is positive in sign.

The spectrum of the reduced form is more complex, (Figure 6.2). At low temperatures in zero field and in small magnetic fields all the iron atoms give the same Mössbauer spectrum, indicating that the single unpaired electron is shared equally by the two iron centre of the molecule. The effective magnetic field, H_n , at the nuclei is 180kG, about half that expected for a typical low-spin

Figures 6.1 & 6.2.6.1. Oxidised form.6.2. Reduced form.

ferric ion in a cubic environment, and could be a result of the unpaired electron being shared equally by the two iron atoms. The component of the electric field gradient in the direction of the magnetic field is negative. At high temperatures the spectrum collapses to give two quadrupole doublets, which are believed to be a consequence of the unpaired electron jumping between the iron atoms at a rate slower than $1.5 \times 10^7 \text{ sec}^{-1}$.

None of the complexes that we have studied, that have been proposed as models for the non-haem iron proteins, show Mössbauer spectra similar to those of Figure 6.2. The spectra of $^{57}\text{iron(III) N,N dimethyldithiocarbamate}$ diluted in cobalt(III) N,N dimethyldithiocarbamate (Figure 3.18) are most similar. The relaxation times are of the same order and the spectra also show a similar field dependence. The hyperfine field is, however, about twice as large as in reduced Euglena ferredoxin.

$(\text{Ph}_4\text{P})_3(\text{FeS}_6\text{C}(\text{CN})_6)$ and the 'persulphide' complexes show larger quadrupole splittings and have values for the effective magnetic field at the nucleus of about -100kG . Their suitability as model compounds for the interpretation of the Mössbauer spectra of the ferredoxins is therefore limited.

The proposal that the single unpaired electron being equally shared by both iron atoms, gives rise to a value of H_n half that expected for a single low-spin ferric ion, is similar to

the explanation that we have put forward to explain the small value of H_n observed in $(\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)SMe})_2\text{SbF}_6$ in Chapter Four. In the latter case, however, the environment of the iron atoms is non-cubic.

Our results are certainly consistent with the interpretation of the Mössbauer spectrum of reduced Euglena ferredoxin, and may help throw light on further investigations of the non-haem iron proteins. Obviously there is considerable scope for further studies in the field of iron-sulphur complexes and their use as model complexes.

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