MAGNETIC AND MÖSSBAUER STUDIES OF
SOME IRON COMPOUNDS

Being a Thesis submitted to the University
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by

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ABSTRACT

Some complexes of iron(II) with quadridentate Schiff bases e.g. \( \text{NN}^\prime\)-ethylenebis(salicylideneimine) and several of its ring-substituted derivatives, and \( \text{NN}^\prime\)-o-phenylenebis(salicylideneimine) have been prepared and shown from magnetic and Mössbauer investigations to be high-spin. These ligands take up planar configurations around bivalent metals, but the complexes are believed to have pentaco-ordinate structures.

The complexes form apparently pentaco-ordinate mononitrosyls by reaction with nitric oxide. The mononitrosyls are high-spin, with room temperature moments corresponding to three unpaired electrons. On cooling to 80°K, nitrosyl \( \text{NN}^\prime\)-ethylenebis(salicylideneiminato)iron and nitrosyl \( \text{NN}^\prime\)-o-phenylenebis(salicylideneiminato)iron change sharply to low-spin states at approximately 175°K and between 150-130°K respectively with a corresponding decrease in the N-O stretching frequency. The Mössbauer parameters change dramatically over the temperature range. Various reasons for spin-pairing, and the assignment of oxidation states to the iron and nitric oxide are discussed. Low temperature magnetic and infrared studies show that some change of the 5-nitro substituted nitrosyl to low-spin species has occurred at 80°K. The Mössbauer parameters remain constant from room to liquid nitrogen temperatures.

Another series of compounds, the tris(monothio-\( \beta \)-diketonato)iron(III) complexes, have been shown to provide further examples of spin-state isomerism. The complexes are predominantly high-spin at room temperature, with moments slightly reduced from the spin-only value. On cooling to 80°K, the complexes exhibit spin-pairing, the degree of which varies from compound to compound. Tris(pent-3-ene-4-thiono-2-onato)iron(III) changes abruptly from a high-to a low-spin state at approximately 150°K. Both spin-isomers, for each complex, are observed
in the Mössbauer spectra. The Mössbauer parameters for high- and low-spin iron(III) and the spectra are in qualitative agreement with the magnetic data. Determinations of magnetic moments by an n.m.r. method show that the complexes are predominantly high-spin in solution.

A complex of iron(II) with the bidentate Schiff base ligand, salicylaldimine, and the adducts formed by bis(salicylaldehydato)iron(II) with monodentate nitrogen-donor ligands have also been investigated.
ACKNOWLEDGMENTS

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INTRODUCTION
1. **HISTORICAL INTRODUCTION**

i) **SCHIFF BASE COMPLEXES OF IRON(II)**

Schiff bases are compounds containing an azomethine group -CH=N-, and they are usually formed by the condensation of a primary amine with an active carbonyl compound. For this study the quadridentate Schiff bases formed by the condensation of salicylaldehyde and substituted salicylaldehydes with ethylenediamine or \( \sigma \)-phenylenediamine are considered. These Schiff bases will be abbreviated to salen, \( \alpha \)-salen and salphen respectively. The quadridentate ligands force a planar configuration on the central metal atom. The bidentate ligand formed by the condensation of salicylaldehyde and ammonia, salicylaldimine, is also considered (Fig. 1).

The chemistry of Schiff base complexes particularly that of complexes with the first row transition metals, has been extensively studied since the original work of Schiff\(^1\) in 1869, the first comprehensive investigations being carried out by Pfeiffer and his co-workers\(^2\). Early in the study of Schiff base complexes it was noted that salen cobalt(II)\(^3,4\) and certain other similar cobalt(II) complexes\(^5\) were able to combine reversibly with atmospheric oxygen. The search for such synthetic oxygen-carriers has involved detailed studies on transition metal complexes of Schiff bases. The most successful metal ion has been cobalt(II). There has been a recent report that a manganese(II) complex\(^6\), \( \mathrm{NN} \)-trimethylenebis-(salicylideneiminato)manganese(II), is capable of reversible co-ordination with oxygen, nitrogen and carbon monoxide. However this compound has been found not to react with nitric oxide and the reported reactions with oxygen and nitrogen could not be repeated\(^7\).
Schiff-Base Ligands Derived from Salicylaldehyde

1. Quadridentate

SALEN or X-SALEN

2. Bidentate

Salicylaldimine

Fig. 1
Preparations of Schiff base complexes of iron(II) have not been very successful in the past mainly due to the susceptibility to aerial oxidation of iron(II) species in solution. The two main synthetic routes to metal(II)-Schiff base complexes have been:-

(1) Reaction of an aqueous solution of a metal salt (usually an acetate which liberates a weak acid on reaction) with a preformed Schiff base in an organic solvent.

(2) Reaction of a primary amine with a bis- or tris(salicylaldehydato) metal complex.

Hardt and Moeller found that bis(acetato)iron(II) can be prepared simply by the reaction of iron powder with acetic acid under nitrogen, the product being air-sensitive when dry. Larkworthy et al. and Calderazzo et al. have successfully synthesised salen iron(II) from bis(acetato)iron(II).

Many authors have used aqueous solutions of the more stable iron(II) salts, e.g. iron(II) chloride and iron(II) sulphate, in method (1). Although iron(II) compounds could have been obtained initially, most authors made no provision to exclude air and it is most probable that the products were oxidised.

Pfeiffer et al. suggested that Schiff base complexes of iron(II) could be made by method (1), and this has been verified as mentioned, but he investigated complexes of iron(III) only. Pfeiffer reacted aqueous iron(II) sulphate with salicylaldehyde and ethylenediamine in air and produced the red-brown oxo-bridged compound \( \mu \)-oxobis[NN'-ethylenbis-(salicylideneiminato)iron(III)](Fe salen)\(_2\). He also synthesised a number of other iron(III) derivatives e.g. salen iron(III) chloride, salen iron(III) acetate and salen iron(III) benzoate.
Salen iron(III) oxide and salen iron(III) chloride exhibit magnetic moments less than expected for a high-spin, d⁵ configuration. Mössbauer data and further magnetic measurements have been reported recently for salen and salphen iron(III) oxides and salen iron(III) chloride. The reduced moment has been attributed to antiferromagnetic interactions.

A more recent study of salen iron(III) chloride has indicated that depending on the preparative details, both monomeric and dimeric forms can be isolated. The dimer has a low magnetic moment, \( \mu_{\text{eff}} = 5.30 \text{ BM} \), which has been attributed to antiferromagnetic interactions. Mössbauer data have been reported for the dimer and the structure has bridging Fe-O bonds similar to the Cu-O bridging bonds in the salen Cu(II) dimer (Fig. 2). In both structures the bridging M-O bonds are long and weak. The monomer has a normal magnetic moment for high-spin iron(III) of 5.9 BM and has an approximately square pyramidal structure, similar to that determined for salen zinc(II) monohydrate (Fig. 3). In both the dimer and monomer the Fe-Cl bond distance is 2.28 Å. Some confusion exists in the literature about the product obtained from recrystallisation of salen iron(III) chloride from nitromethane. The monomeric chloride described by Gerloch et al. and Bancroft et al. has the formula [Fe salen Cl]₂CH₃NO₂ whilst that described by Gerloch and Mabbs has the formula [Fe salen Cl]₂CH₃NO₂. A compound described by Buckley et al. has the formula [Fe salen Cl]₄CH₃NO₂ and they have suggested that it is dimeric, [Fe salen Cl]₂CH₃NO₂. The magnetic moment and Mössbauer data reported were similar to the data reported by Bancroft for [Fe salen Cl]₂.

Although no preparative details were reported, Calvin and Barkelew showed from magnetic susceptibility data that a number of iron(II)-Schiff base complexes were
Structures of Dimeric Schiff–Base Complexes

(Fe SalenCl)$_2$  

(Cu Salen)$_2$

Fig. 2

Structures of Monomeric Schiff–Base Complexes

Fe Salen Cl. MeNO$_2$  

Zn Salen. H$_2$O

Fig. 3
high-spin i.e. they contained four unpaired electrons. The results for salen iron(II), ethylenediamine, $\mu_{\text{eff}} = 5.09$ B.M., and 3-methoxy-salen iron(II), $\mu_{\text{eff}} = 5.0?$, B.M., were uncertain owing to the extreme difficulty in preventing atmospheric oxidation.

Marvel et al. attempted to prepare several iron(II) complexes of the salen type, including salen iron(II), salphen iron(II) and 5-nitrosalen iron(II). The method of preparation, the colour and analyses of the complexes (see Table 1) all lead to the conclusion that the complexes were oxidised. The authors commented on the unsatisfactory results and indicated that the products were probably oxidised. Crawford reported the visible and ultra-violet spectra of compounds purported to be salen iron(II) and salphen iron(II) but these are for similar reasons thought to be oxidised. Since analysis for the metal will not readily distinguish between say salen iron(II) and [Fe salen]$\text{O}$, its oxidation product, confusion is understandable. Poddar and Dey ascribed the low magnetic moments of the 3-carboxy-derivatives of salen and salphen iron(II) to partial spin-pairing, but their compounds were probably oxidised.

The first systematic study of genuine iron(II) Schiff base complexes of salen and its substituted derivatives was carried out by Larkworthy. Iron(II) complexes of salen, 5-methylsalen, 5-nitrosalen, 5-chlorosalen, 4-chlorosalen and 3-nitrosalen were prepared under nitrogen and found to be high-spin. The room temperature magnetic moments corresponded to four unpaired electrons. The moments were slightly low, $\mu_{\text{eff}} = 4.9$ B.M., probably due to distortion and delocalisation effects. This work demonstrated the need for anaerobic preparative conditions which had previously been overlooked and which had led to incorrect interpretations of magnetic and spectral data and Mössbauer data (see below).
Calderazzo et al. have prepared new iron(III)-organometallic derivatives from salen iron(II). Initially a solution of salen iron(II) was reduced with sodium in tetrahydrofuran to give \([\text{Fe salen}]^-\), which behaved as a strong nucleophile, and reacted with benzyl chloride to yield \(\text{C}_6\text{H}_5\text{CH}_2[\text{Fe(III) salen}]\). The phenyl derivative \(\text{C}_6\text{H}_5[\text{Fe(III) salen}]\) was prepared by a Grignard-type reaction of salen iron(III) iodide with phenyl magnesium bromide. Both reactions were carried out under nitrogen.

Calderazzo has recently prepared salen iron(II) by the displacement of carbon monoxide from iron pentacarbonyl by salen. Salen iron(II) was also prepared by the reaction of anhydrous bis(acetato)-iron(II) with salen. The acetate was obtained by reaction of iron pentacarbonyl with a mixture of acetic acid and acetic anhydride. The adduct, salen iron(II) pyridine, prepared by the reaction of salen iron(II) with pyridine, has a room temperature magnetic moment of 4.95 B.M. which indicates that the compound is a high-spin, \(d^6\) system. In order to demonstrate the ease of oxidation of salen iron(II), the complex was suspended in tetrahydrofuran and reacted with dry oxygen. The product was \(\mu\)-oxobis[N\(\equiv\)N'-ethylenebis(salicylideneiminato)-iron(III)]. Calderazzo and Larkworthy suggested that salen iron(II) could be planar, or highly distorted octahedral, or a dimer with long Fe-O bridging bonds (Fig. 4).

Berrett found that salen iron(II) prepared under nitrogen had Mössbauer parameters characteristic of high-spin iron(II), and in particular the large quadruple splitting (see Section 4iii) suggested a highly-distorted octahedral or even planar configuration for the complex in agreement with the magnetic data. One aim of the present work (see p. 92) was to confirm and extend this result. Berrett also found that \([\text{Fe salen}]_2\)O had Mössbauer spectra typical of iron(III), quite distinguishable from the spectra of salen iron(II). During the course of the
present work Stukan et al.\textsuperscript{15} and Kulgawczuk et al.\textsuperscript{31} reported Mössbauer spectra for salen iron(II) and related compounds which were typical of high-spin iron(III). To explain this anomalous result extensive back donation to the p-orbitals of the ligands was postulated\textsuperscript{15,31}. However, no precautions were taken to exclude air and it was apparent to us that oxidised products had again been investigated. Very recently, de Vries et al.\textsuperscript{32} have prepared a number of iron(II)-Schiff base and related complexes in vacuo by reaction of an aqueous iron(II) solution with a solution of ligand in alcohol, using degassed solvents. The colours of the complexes and Mössbauer data are identical with similar complexes reported in this study. De Vries\textsuperscript{32} noted that on oxidation the complexes absorbed 1/4 of an oxygen atom per iron atom and their colours changed. The Mössbauer data of the oxidised species were also found to be identical with the values of compounds believed to be iron(II) complexes by Stukan\textsuperscript{15}. De Vries\textsuperscript{32} confirmed our conclusion that no special effects need be invoked to rationalise the Mössbauer data.

Schiff base complexes of iron(II) with bidentate ligands have been little studied. Bidentate ligands, unlike quadridentate ligands, do not force a planar configuration on the metal atom. Poddar and Dey\textsuperscript{28} have prepared iron(II) complexes of 3-carboxy-salicylaldehyde condensed with aniline and anthranilic acid but they took no precautions to exclude air so that as with the derivatives of quadridentate ligands (p.15) the products were probably oxidised. Larkworthy\textsuperscript{9} has reported that the iron(II) complexes with N-phenyl- and N-methyl-salicylideneimine are high-spin.

De Vries\textsuperscript{32} has obtained Mössbauer data for bis(salicylideneiminato)-iron(II) which indicate that as for the iron(II) complexes of the quadridentate Schiff
Structures Proposed for NN'-ethylenebis(salicylideneimino)iron(II)

Planar Structure

![Planar Structure Diagram]

Dimeric Structure

![Dimeric Structure Diagram]

Structure of Bis(salicylaldehydeato)bis(adduct)metal(II) Complexes

![Complexes Diagram]

\[ M = \text{Fe(II), Co(II) or Ni(II)} \]

\[ X = \text{H or CH}_3 \]
bases, Stukan had investigated an oxidation product. ii) ADDUCTS OF BIS(SALICYLALDEHYDATO)IRON(II)

Adducts of bis(salicylaldehydato)iron(II) have rarely been reported in the literature. The 2:1 pyridine adduct was first obtained by Emmert and Jarczynski as blue-green prisms under nitrogen. Emmert and Seebode showed later that Fe(sal)$_2$py$_2$ (sal = salicylaldehydato; py = pyridine) was readily oxidised by air in methanolic or ethanolic solution. Nast and Rückemann, during their study of Fe(sal)$_2$pyNO, found the magnetic moment of the pyridine adduct to be 5.12 B.M. Smith has recently reported Mössbauer data and a similar magnetic moment (5.19 B.M.) for this adduct. He also commented that it decomposed slowly in air.

Tsumaki and Ohta have isolated 2:1 adducts of pyridine and β-picoline with bis(5-nitrosalicylaldehydato)iron(II), and 1:1 adducts with bis(5-bromosalicylaldehydato)iron(II). On heating under reduced pressure the base was removed.

Schwarzhans has reported proton magnetic resonance data on the 2:1 adducts of pyridine and picoline with cobalt(II), nickel(II) and iron(II) salicylaldehydato-complexes which were chosen because they have a simple ligand system in a pseudo-octahedral arrangement and are readily soluble in organic solvents. The co-ordinated pyridine and picoline readily exchange with excess ligand and this facilitated the assignment of the resonance peaks. Although no preparative details were presented, failure to prepare a 2:1 adduct of α-picoline with bis(salicylaldehydato)iron(II) was mentioned. The structure of the bis(salicylaldehydato)bis(adduct) metal(II) complexes was presented as octahedral with the base adducts in a trans position (Fig. 5).
As for the Schiff base complexes, conflicting Mössbauer data have been obtained by Stukan\textsuperscript{15} and de Vries\textsuperscript{32} for bis(salicylaldehydato)iron(II) probably the former's sample was oxidised.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Iron(II) Complex Colour (Ref. 9,10,32 and this work)</th>
<th>Oxidised Complex Colour (Ref. 26,27,32 and this work)</th>
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<tr>
<td>Salen</td>
<td>Chocolate-brown</td>
<td>Orange-red</td>
</tr>
<tr>
<td>Salphen</td>
<td>Green</td>
<td>Red-brown</td>
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2. NITRIC OXIDE COMPLEXES OF TRANSITION METALS

i) GENERAL PROPERTIES OF NITRIC OXIDE

Nitric oxide is a colourless, monomeric, paramagnetic gas and behaves as a stable free radical under normal conditions. It is moderately reactive and may be readily oxidised e.g. to nitrogen dioxide, the nitrosonium ion and nitric acid or reduced e.g. to nitrous oxide and hydroxylamine. The molecular orbital configuration of nitric oxide is

\[ (\sigma_1^2 \pi_2^2 \pi_2 \pi_2 \pi_2) \]

The extra electron occupies an antibonding \( \pi \) molecular orbital. The consequences of this extra electron are:

a) an intermediate bond order i.e. 2.5, which is substantiated by the observed bond distance, 1.1 Å. (The estimated values for double and triple bonds are 1.18 and 1.06 Å respectively.)

b) the easy removal of this electron to form the nitrosonium ion, NO\(^+\). The ionization potential of nitric oxide is lower than that of other diatomic molecules (nitric oxide 9.5 eV, nitrogen 14.5 eV). Many compounds containing the nitrosonium ion have been prepared, confirming the theoretical prediction of its existence. Nitrosonium bisulphate NO\(^+\)HSO\(_4^−\) is an important intermediate in the 'lead chamber' process for the manufacture of sulphuric acid. The removal of the electron from nitric oxide increases the strength of the N-O bond as apparent from infrared studies where the N-O stretching frequency increases from 1878 cm\(^{-1}\) in nitric oxide to 2300 cm\(^{-1}\) in NO\(^+\) salts.

Although its electron affinity is not known, nitric oxide can gain an electron to form the NO\(^-\) ion. However, compounds formed between nitric oxide, sodium, potassium or barium originally formulated as Na\(^+\)NO\(^-\), K\(^+\)NO\(^-\) and Ba\(^2+\)(NO\(^-\))\(_2\) have now been shown to contain the hyponitrite ion \( N_2O_2^{2−}\).
ii) CO-ORDINATION OF NITRIC OXIDE IN COMPLEXES

The oxidation state of co-ordinated nitric oxide is difficult to assign unambiguously in many compounds. Lewis et al.\textsuperscript{39}, used the \textit{N-O} stretching frequency of a number of nitrosyl complexes to propose five possible forms of co-ordination for nitric oxide.

a) Sharing of an electron pair from neutral nitric oxide to give paramagnetic complexes.

\[
\text{M} \xleftarrow{\text{N}} \text{N} = 0
\]

In this case the \textit{N-O} stretching frequency should not be far removed from that of nitric oxide at 1878 cm\textsuperscript{-1}.

b) A one electron transfer from nitric oxide to the metal followed by sharing of two electrons from the nitrosonium ion NO\textsuperscript{+}. This can also be accompanied by back-bonding from the metal to the nitric oxide so that the system can be represented by the following resonance forms:

\[
\text{M} \xleftarrow{\text{N}} \text{N} = 0 \xleftrightarrow{\text{M}} = \text{N} = 0
\]

c) Transfer of an electron from the metal to the nitric oxide and sharing of two electrons from the NO\textsuperscript{-} ion.

\[
\text{M} \xleftarrow{\text{N}} \text{N} = 0 \xrightarrow{\text{M}}
\]

d) The nitrosyl group bonded in a bridging position.

\[
\text{M} \xleftarrow{\text{N}} \text{N} = 0 \xrightarrow{\text{M}}
\]

e) The nitrosyl group is not bonded to the metal atom in an end-on position with a linear M-N-O group but bonded at some angle.

\[
\text{N} \xleftarrow{\text{M}} \text{C}
\]

Lewis\textsuperscript{39} observed that on co-ordination the N-O stretching frequency was lowered, and proposed that
NO\textsuperscript{+} absorbed in the region 1580-1580 cm\textsuperscript{-1} whilst NO\textsuperscript{-} absorbed in the region 1580-1040 cm\textsuperscript{-1}. Gans\textsuperscript{40} and many other authors have criticised these assignments and have suggested that N=O stretching frequencies lying between 1700-1500 cm\textsuperscript{-1} may be assigned to NO\textsuperscript{-} and between 1940-1700 cm\textsuperscript{-1} to NO\textsuperscript{+}. Anomalies occur and it has been emphasised that each compound should be considered on its own merits. The possibility that the N=O stretching frequency may depend on the bond angle of the M-N=O group has also been considered extensively and will be considered in more detail later (section (viii)). Gray et al.\textsuperscript{41} have suggested that all compounds containing co-ordinated NO\textsuperscript{+} have a linear M-N=O grouping, and complexes containing NO\textsuperscript{2-} or NO\textsuperscript{-} are expected to have a bent M-N=O grouping. Symons et al.\textsuperscript{42} have suggested a N=O stretching frequency of \textasciitilde1900 cm\textsuperscript{-1} for a linear and \textasciitilde1650 cm\textsuperscript{-1} for a bent M-N=O grouping. It would appear from the recent literature that the criterion of the formal oxidation state of co-ordinated nitric oxide is the bond angle of the M-N=O group. A linear M-N=O grouping and a short M-N distance characterise NO\textsuperscript{+}, whereas NO\textsuperscript{-} is characterised by a bent M-N=O grouping with a rather long M-N distance\textsuperscript{43}.

The pentacyanonitrosyls, [M(CN)\textsubscript{5}NO]\textsuperscript{2-} (M=V, Cr, Fe, Co; n=2,3 or 5) provide an interesting class of complexes. Examples of co-ordinated nitric oxide of class a) NO\textsuperscript{+}, b) NO\textsuperscript{-} and c) NO\textsuperscript{2-} are shown in Table 2. Gray\textsuperscript{41} has proposed a molecular orbital scheme for pentacyanonitrosyls on which the electronic configurations of the outer orbitals in Table 2 are based. In this scheme the \(d_x\) and \(d_y\) d-levels are separated by a \(\pi^*\)NO antibonding level, producing the relative order:

\[d_{xz',yz} < d_{xy} < \pi^*\text{NO} < d_{x^2-y^2} < d_{z^2}\]

Conflicting data on the ground state electronic configurations for several pentacyanonitrosyls appear in the literature. E.s.r.\textsuperscript{44} measurements of [Fe(CN)\textsubscript{5}NO]\textsuperscript{3-} have been interpreted by assigning the unpaired electron to a \(\pi^*\)NO orbital confirming the accepted Fe(II) NO\textsuperscript{+}.
structure for this complex. Symons\textsuperscript{42} and Danon et al.\textsuperscript{45} have proposed a different molecular orbital scheme from e.s.r. data placing the energy levels in the order:

\[ d_{xz}, yz < d_{xy} < d_{z^2} < d_{x^2-y^2} \]

and assigned the unpaired electron of \([Fe(CN)_{5}NO]^{3-}\) predominantly to the \(d_{z^2}\) orbital. The e.s.r. data\textsuperscript{46} of \([Cr(CN)_{5}NO]^{3-}\) have been explained by the electronic configuration \((d_{xz}, yz)^{2} (d_{xy})^{1}\) although considerable back donation is said to occur, with 50% \(\pi^*\) NO character in the lowest lying d-orbitals (see Table 3). An alternative electron configuration \((d_{xz})^{2} (d_{z^2})^{2} (d_{xy})^{1}\) has been proposed for \([Cr(CN)_{5}NO]^{3-}\) also based on e.s.r. data\textsuperscript{42}. To explain this configuration it was proposed that the nitric oxide group made an angle of about 45° with the z-axis. It was postulated that the major factor governing the M-N-O bond angle was the number of electrons in the \(d_{z^2}\) level. If the level was empty as in \([Fe(CN)_{5}NO]^{2-}\) and \([Mn(CN)_{5}NO]^{2-}\) the bond would be linear, if half-filled as in \([Fe(CN)_{5}NO]^{3-}\) the angle would be small and if filled as in \([Cr(CN)_{5}NO]^{3-}, CoNO[S_{2}CN(CH_{3})_{2}]_{2}\) and \(FeNO[S_{2}CN(CH_{3})_{2}]_{2}\) the angle would be about 45° with the z-axis. Manoharan and Gray\textsuperscript{46} have correlated the decrease in N-O stretching frequency in a series of pentacyanonitrosyls with the increase of M-\(\pi^*\)NO intramolecular transfer of electron density. Table 3 shows the increase of \(\pi^*\)NO character of the \((d_{xz}, yz)\) level.

The assignment of NO\textsuperscript{-} in \([Co(CN)_{5}NO]^{3-}\) rests on the electronic configuration and the observed low N-O stretching frequency (Table 2). The stretching frequency is similar to that for amine oxides \((R_{3}N^{+}\rightarrow\overset{\text{O}}{\overset{\text{O}}{\text{O}}}, N-O\) stretching frequency in the range 950 to 1350 cm\(^{-1}\) depending on \(R_{-}\) where the N-O bond order is close to unity. Such a low bond order could be explained from the following resonance forms:

\[
\begin{align*}
\text{Co} & \leftarrow \overset{\text{O}}{\overset{\text{O}}{\text{O}}} \\
\text{Co} & \rightarrow \overset{\text{N}}{\overset{\text{N}}{\text{O}}} 
\end{align*}
\]
### TABLE 2

<table>
<thead>
<tr>
<th>Formal Structure</th>
<th>Compound</th>
<th>ν(N-O) cm⁻¹</th>
<th>μeff B.M.</th>
<th>Occupation of outer orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>d⁵NO⁺</td>
<td>[Mn(CN)₅NO]²⁻</td>
<td>1885</td>
<td>1.76</td>
<td>(dₓz,ᵧz)⁴/₅ (dₓᵧ)¹/₅</td>
</tr>
<tr>
<td></td>
<td>[Cr(CN)₅NO]³⁻</td>
<td>1645</td>
<td>1.87</td>
<td>&quot;</td>
</tr>
<tr>
<td>d⁶NO⁺</td>
<td>[Fe(CN)₅NO]²⁻</td>
<td>1939</td>
<td>1.63</td>
<td>(dₓz,ᵧz)⁴/₅ (dₓᵧ)²</td>
</tr>
<tr>
<td></td>
<td>[Mn(CN)₅NO]³⁻</td>
<td>1730</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>[Cr(CN)₅NO]²⁻</td>
<td>1515</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>[V (CN)₅NO]⁵⁻</td>
<td>1575</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>d⁶NO⁻</td>
<td>[Fe(CN)₅NO]³⁻</td>
<td>1120</td>
<td>1.5</td>
<td>(dₓz,ᵧz)⁴/₅ (dₓᵧ)²</td>
</tr>
<tr>
<td>d⁶NO⁻</td>
<td>[Co(CN)₅NO]³⁻</td>
<td>1120</td>
<td>1.5</td>
<td>(dₓz,ᵧz)⁴/₅ (dₓᵧ)²</td>
</tr>
</tbody>
</table>

### TABLE 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(N-O) cm⁻¹</th>
<th>% πₓN⁰ character in dₓz,ᵧz M.O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(CN)₅NO]²⁻</td>
<td>1939</td>
<td>24.8</td>
</tr>
<tr>
<td>[Mn(CN)₅NO]²⁻</td>
<td>1885</td>
<td>31.8</td>
</tr>
<tr>
<td>[Mn(CN)₅NO]³⁻</td>
<td>1725</td>
<td>42.2</td>
</tr>
<tr>
<td>[Cr(CN)₅NO]³⁻</td>
<td>1645</td>
<td>50.2</td>
</tr>
<tr>
<td>[V (CN)₅NO]⁵⁻</td>
<td>1575</td>
<td>73.7</td>
</tr>
</tbody>
</table>
Since the complex is diamagnetic, it should have a bent Co-N-O grouping but no structural data are yet available.

The existence of bridged nitrosyls, class d), is not yet certain. It has been suggested that several cyclopentadienyl complexes \((\text{C}_5\text{H}_5)_2\text{Mn}_2\text{(NO)}_3\)\(^{47}\), \([(\text{C}_5\text{H}_5)_2\text{Mn(CO)NO}]_2\)\(^{48}\), and \([(\text{C}_5\text{H}_5)_2\text{Cr(NO)}]_2\)\(^{49}\) contain bridging nitric oxide groups. This class of nitrosyl has been assigned a N-O stretching frequency of ~1500 cm\(^{-1}\).

Although several examples of class e) have been proposed, only one has been experimentally verified. An X-ray examination showed nitrosylbis(NN-dimethyldithiocarbamato)cobalt, \(\text{CoNO}[(\text{S}_2\text{CN(\text{CH}_3})_2]_2\), to have a square-pyramidal structure, the cobalt atom slightly raised above the plane. The N-O bond axis is inclined at an angle of 139° to the pyramidal axis. It has been assumed by many authors that the N-O bond of isomorphous iron nitrosyls of substituted dithiocarbamates was bonded in a similar manner. X-ray diffraction studies have shown a square-pyramidal structure in which the Fe-N-O grouping of nitrosyl (NN-dimethyl\(^{50,51}\) and NN-diethyldithiocarbamato\(^{52}\))iron is almost linear. There is now some doubt concerning the data of the cobalt compound.

The nitrosyls of iron and related systems will now be discussed in more detail.

iii) **SIMPLE NITROSYLS OF IRON**

The black, unstable iron tetranitrosyl, \(\text{Fe(NO)}_4\), was prepared by heating iron pentacarbonyl with nitric oxide under pressure. The infrared spectrum showed two N-O stretching frequencies in the NO\(^+\) region and one at 1140 cm\(^{-1}\) assigned to NO\(^-\). The structure suggested was tetrahedral with three nitric oxide groups co-ordinated as NO\(^+\) and one co-ordinated as NO\(^-\). (\(^\text{**\text{For compounds and data with no reference see ref. 53}}\))
In metal complexes, nitric oxide co-ordinating as NO\(^+\) shares three electrons, whereas carbon monoxide shares only two. Thus replacement of three carbonyl groups by two nitric oxide groups may take place in iron carbonyls, whilst maintaining the effective atomic number rule. Many nitrosyl carbonyl and related compounds have been prepared conveniently in this manner.

Two distinct classes of iron nitrosyl halides have been prepared. Compounds of the general series, Fe(NO)\(_3\)\(X\) (\(X = \text{Cl, Br and I}\)), have been shown to be monomeric, diamagnetic and unstable. The nitric oxide is assumed to be co-ordinated as NO\(^+\). However, dinitrosyl halides, [Fe(NO)\(_2\)]\(_2\) \(X = \text{Cl, Br and I}\), are dimeric, stable and diamagnetic, the odd electrons on the metal atoms forming a metal-metal bond. The Fe-N-O grouping has been shown to be slightly bent in [Fe(NO)\(_2\)]\(_2\).\(^{56}\).

Many complexes of the general series Fe(NO)\(_2\)\(XL\) (\(X = \text{Cl, Br and I; L = phosphine or a related ligand}\)) have been prepared from the nitrosyl halides.

Related to the nitrosyl halides are some sulphur-containing iron nitrosyls. The best known are Roussin's Red and Black salts. A series of dark red, diamagnetic esters of the general formula [Fe(NO)\(_2\)SR]\(_2\) (\(R = \text{CH}_3\), \(\text{C}_2\text{H}_5\) and \(\text{C}_6\text{H}_5\)) have been prepared from the red salt, K\(_2\)[Fe(NO)\(_2\)S]\(_2\). X-ray examination of [Fe(NO)\(_2\)SeEt]\(_2\) has shown that the Fe-N-O groupings are slightly bent.\(^{55}\) Related selenium and tellurium derivatives, [Fe(NO)\(_2\)MR]\(_2\) (\(M = \text{Se or Te}\)) are also known. Roussin's Black salts are diamagnetic and contain the monomeric anion, [Fe\(_4\)(NO)\(_7\)S\(_3\)]\(^-\). X-ray examination of the caesium salt has shown the Fe-N-O groupings to be approximately linear although a formal Fe(III) NO\(^-\) structure was proposed.\(^{56}\).
The thiocyanate \([\text{Fe(NO)}_2\text{SCN}]_2\) can be prepared by treating \([\text{Fe(NO)}_2\text{Br}]_2\) with AgSCN in tetrahydrofuran. Numerous isocyanides of the general series \(\text{Fe(NO)}_2(\text{CNR})_2\) have been reported.

Table 4 lists the N-O stretching frequencies of some of the compounds mentioned in this section.

**TABLE 4**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{N-O})) cm(^{-1})</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe(NO)}_4)</td>
<td>1810, 1730, 1140</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>(\text{Fe(NO)}_2(\text{CO})_2)</td>
<td>1810, 1767</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>(\text{Fe(NO)}_2(\text{PPh}_3)_2)</td>
<td>1756, 1740, 1728</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>(\text{Fe(NO)}_2\text{I})</td>
<td>1809, 1771</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>([\text{Fe(NO)}_2\text{I}]_2)</td>
<td>1818, 1771, M-N-O = 161°</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>(\text{K}_2[\text{Fe(NO)}_2\text{S}]_2)</td>
<td>1716</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>([\text{Fe(NO)}_2\text{SeEt}]_2)</td>
<td>1773, 1742, M-N-O = 167°</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>([\text{Fe(NO)}_2\text{SeEt}]_2)</td>
<td>1769, 1747</td>
<td>NO(^+)</td>
</tr>
<tr>
<td>((\text{NH}<em>4)[\text{Fe}(</em>{7}\text{NO})_7\text{S}_3]\cdot\text{H}_2\text{O})</td>
<td>1800, 1741, 1729, M-N-O = 180°</td>
<td>NO(^-)</td>
</tr>
<tr>
<td></td>
<td>1706, 1600</td>
<td></td>
</tr>
<tr>
<td>([\text{Fe(NO)}_2\text{SCN}]_2)</td>
<td>1818, 1750</td>
<td>NO(^+)</td>
</tr>
</tbody>
</table>
iv) PENTACYANONITROSYLS OF IRON

The well known red-brown, diamagnetic complex sodium nitroprusside, Na$_2$[Fe(CN)$_5$NO], has a linear Fe-N-O grouping. The N-O stretching frequency at 1939 cm$^{-1}$ is in the region for NO$^+$ and the nitroprusside ion has the formal structure Fe(II) NO$^+$. Nitric oxide has been shown by many authors to be a powerful $\pi$-bonding ligand. Infrared studies (Table 3) suggested that the amount of $\pi$-bonding varied in the pentacyanonitrosyls [M(CN)$_5$NO]$^{2-}$ (M=V, Cr, Mn or Fe). The decrease in the N-O stretching frequency was concomitant with the increase of M-N $\pi$-bonding. Gans et al. have suggested from a study of the M-N stretching frequencies of a series of pentacyanonitrosyls that nitric oxide is a powerful $\pi$-bonding ligand, more powerful than carbon monoxide or the cyanide ion. The N-O stretching frequency was thought to be influenced more by $\sigma$-bonding than by $\pi$-bonding. Mössbauer studies have substantially confirmed the existence of Fe-NO back-bonding in sodium nitroprusside.

The electronic configuration of the outer orbitals of [Fe(CN)$_5$NO]$^{2-}$ i.e., $(d_{xz}, yz)^4 (d_{xy})^2$ has already been mentioned (Table 2) and confirmed by Mössbauer studies from which the molecular orbital $(d_{xz}, yz)$ was calculated to have 24.5% $\pi^*\text{NO}$ character. This agreed well with 24.8% $\pi^*\text{NO}$ character calculated by Manoharan and Gray.

The reduced species of the nitroprusside ion [Fe(CN)$_5$NO]$^{3-}$ has been mentioned (p.23) and the conflicting e.s.r. data presented. Mössbauer studies have suggested that the electronic configuration for [Fe(CN)$_5$NO]$^{3-}$ is $(d_{xz}, yz){}^4 (d_{xy})^2 (\pi^*\text{NO})^1$ in agreement with the assignment by Gray and Hockings.

Formation of the reduced species [Fe(CN)$_5$NO]$^{4-}$ has been claimed from the reaction of hydroxylamine hydrochloride with [Fe(CN)$_5$NO]$^{2-}$. In the absence of any physical data it is difficult to assign any formal oxidation state to the nitric oxide. It has been suggested it may be a derivative
of the hyponitrite ion \([(\text{CN})_5\text{Fe-ON=NO-Fe(CN)}_5]^8-\) or it may be a member of the series \([\text{Fe(CN)}_5\text{NO}]^{2-}\) \(-\text{NO}^+\), \([\text{Fe(CN)}_5\text{NO}]^{3-}\) \(-\text{NO}^+\), \([\text{Fe(CN)}_5\text{NO}]^{4-}\) \(-\text{NO}^+\). There is polarographic evidence for the latter suggestion.

v) **BROWN RING COMPOUNDS**

The earliest known nitrosyls were obtained from the direct reaction of ferrous salts with nitric oxide. The reaction

\[
[\text{Fe(H}_2\text{O)}_6]^2+ + \text{NO} \rightleftharpoons [\text{Fe(H}_2\text{O)}_5\text{NO}]^{2+} + \text{H}_2\text{O}
\]

is reversible and the product unstable. Manchot et al. determined a 1:1 ratio for the absorption of nitric oxide by ferrous solutions and succeeded in isolating several complexes including \(\text{2FeSO}_4\cdot\text{NO}\cdot\text{13H}_2\text{O}\) and \([\text{Fe(H}_2\text{O)}_5\text{NO}]\text{SeO}_4\). These black, unstable complexes liberated nitric oxide when exposed to the atmosphere. Infrared and solution magnetic susceptibility studies by Lewis et al. suggested that the brown ring compounds \([\text{Fe(H}_2\text{O)}_5\text{NO}]^{2+}\) and \([\text{Fe(NH}_3)_5\text{NO}]^{2+}\) had the formal structure \(\text{Fe(I)}\) \(-\text{NO}^+\). The room temperature magnetic moments were independent of concentration and corresponded to three unpaired electrons, a high-spin \(\text{d}^7\) configuration. The N-O stretching frequencies occurred in the region expected for \(\text{NO}^+\) (see Table 5).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu\text{NO cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(H}_2\text{O)}_5\text{NO}]\text{SO}_4)</td>
<td>1765</td>
</tr>
<tr>
<td>([\text{Fe(H}_2\text{O)}_5\text{NO}]\text{Cl}_2)</td>
<td>1795</td>
</tr>
<tr>
<td>([\text{Fe(NH}_3)_5\text{NO}]\text{SO}_4)</td>
<td>1754</td>
</tr>
<tr>
<td>([\text{Fe(NH}_3)_5\text{NO}]\text{Cl}_2)</td>
<td>1745</td>
</tr>
</tbody>
</table>

The **brown colour** of the complexes has been attributed to charge-transfer bands associated with the Fe-N-O system.
The Mössbauer data$^{60}$ of $[\text{Fe(H}_2\text{O)}_5\text{NO}^{2+}$ have been interpreted in terms of a high-spin, $d^7$, Fe(I) complex with an outer orbital electronic configuration $(d_{xz}, yz)^{6} (d_{xy})^{1} (d_{dz^2})^{1} (d_{2z-y^2})^{1}$. It was also suggested that the complexes could be formulated as Fe(II) NO$^+$ with a rather weak antiferromagnetic coupling between the $S=2$ state of Fe(II) and the $S=\frac{1}{2}$ state of nitric oxide.

Recent Mössbauer and infrared studies$^{69}$ have assigned a Fe(III) NO$^-$ structure to the complex $[\text{Fe(NH}_3)_5\text{NO}]\text{Cl}_2$. The N-O stretching frequency of the freshly prepared compound was $\sim$1600 cm$^{-1}$ compared to $\sim$1750 cm$^{-1}$ for an old sample. It was suggested that the magnetic susceptibility of the freshly prepared compound may confirm the oxidation state of the iron atom.

vi) MONONITROSYL IRON COMPLEXES OF DITHIOCARBAMATE, DITHIOLENE AND SALEN LIGANDS

The mononitrosyls of alkyl- and aryl-substituted dithiocarbamates of transition metals have been well studied, particularly iron and cobalt complexes. Cambi et al.$^{70}$ reported the preparation of many complexes of the general formula $\text{MNO(S}_2\text{CNR}_2)_2$ ($\text{M}=\text{Co}$ or Fe; $\text{R}=\text{alkyl}$ or aryl). The iron complexes were air-stable when dry with room temperature magnetic moments corresponding to one unpaired electron$^{71}$. The N-O stretching frequencies for the NN-dimethyl-, NN-diethyl-$^{39}$, NN-di-isopropyl- and NN-diphenyl-derivatives$^{72}$ were about 1680 cm$^{-1}$ corresponding to nitric oxide co-ordinated as NO$^+$. Symons$^{42}$ has suggested a bent Fe-N-O grouping from the low N-O stretching frequency. The formal oxidation state, Fe(I), has been proposed for these complexes by many authors. E.s.r. and Mössbauer data have confirmed the formal structure Fe(I) NO$^+$, but have differed on the location of the unpaired electron. Gray et al.$^{73}$ assigned the unpaired electron to the $d_{xz} - y^2$ orbital. Later, the electronic configuration for the outer orbitals, $(d_{xz}, yz)^{6} (d_{xy})^{2} (d_{z^2})^{1}$ was suggested from
Mössbauer data have also been interpreted by assigning the unpaired electron to a \( \pi^* \) NO orbital. The different interpretations of the independent Mössbauer studies are confusing as the data are so similar.

The structure of the mononitrosyl cobalt complex, \( \text{CoNO}\left[S_2\text{CN(CH}_3\text{)}_2\right]_2 \), has been given previously (p. 26). The Fe-N-O grouping in \( \text{FeNO}\left[S_2\text{CN(CH}_3\text{)}_2\right]_2 \) and \( \text{FeNO}\left[S_2\text{CN(C}_2\text{H}_5\text{)}_2\right]_2 \) is almost linear (174°) which has been mentioned (p. 26). Recent X-ray diffraction studies on \( \text{FeNO}\left[S_2\text{CN(CH}_3\text{)}_2\right]_2 \) have shown the Fe-N-O bond angle to be 174° at room temperature and 170° on cooling to -190°K. Detailed structural information could not be obtained owing to the high amplitude of thermal vibration of the nitrosyl oxygen atom.

A mononitrosyl iron complex of a selenium derivative of dithiocarbamate, \( \text{FeNO}\left[\text{Se}_2\text{CN(C}_2\text{H}_5\text{)}_2\right]_2 \), has been reported but not isolated. The N-O stretching frequency is identical to the corresponding thio complex.

The dinitrosyl complex, \( \text{Fe(NO)}_2\left[S_2\text{CN(C}_2\text{H}_5\text{)}_2\right]_2 \), has been reported and found to be essentially diamagnetic at room temperature \( (\mu_{\text{eff}} = 0.8 \text{ B.M.}) \). Infrared studies showed two bands in the region expected for NO\(^+\) (1820 s, 1842 sh) from which it was concluded that the nitric oxide groups were cis.

Five co-ordinate mononitrosyl-1,2-dithiolene complexes of the general formula \( [\text{MNO}(S_2\text{C}_2\text{R}_n)_2]^2^- \) \( (\text{M} = \text{Co or Fe}; \text{R} = \text{CN, CF}_3 \text{ or C}_6\text{H}_5; \text{n} = -2, -1, 0) \) have been prepared. These complexes have very similar physical and structural data to the nitrosylbis(dialkyl-dithiocarbamate)iron complexes. The N-O stretching frequencies fall within the range generally associated with NO\(^+\); the dianionic ions absorb between 1620 to 1650 cm\(^{-1}\), the anionic ions between 1770 to 1870 cm\(^{-1}\) and the neutral
complexes absorb at \(1800 \text{ cm}^{-1}\). X-ray diffraction studies have shown the dianionic complex \((\text{NH}_4)_2[\text{FeNO}\{\text{S}_2\text{C}_2(\text{CN})_2\}]_2\) to have a slightly bent Fe-N-O grouping (168°). However, as with \(\text{FeNO}[\text{S}_2\text{CN}](\text{CH}_3)_2]_2\), thermal motion of the nitrosyl oxygen atom reduced the experimental accuracy. It was suggested that all the dianionic species had bent Fe-N-O groupings and the neutral and anionic species linear groupings. The dianionic and neutral species were found to be paramagnetic with room temperature magnetic moments corresponding to one unpaired electron. The compounds were considered to have square-pyramidal structures and from e.s.r. and magnetic results the following molecular orbital scheme was proposed for mononitrosyl-1,2-dithiolene iron complexes:

\[
d_{xz,yz} < d_{x^2-y^2} < L < \pi^\text{NO} < d_{xy} < d_z^2
\]

\(L\) was primarily a sulphur ligand orbital in character.

The following electronic configurations of the outer orbitals and formal structures of the complexes were proposed:

**Dianionic**

\[
\begin{align*}
\text{Dianionic} & \quad (d_{xz,yz})^4 \quad (d_{x^2-y^2})^2 \quad L^2 \quad (\pi^\text{NO})^1 \\
& \quad [\text{Fe(II)NO}^\ast (-\text{S}_4)^{4\text{-}}]^2\text{-}
\end{align*}
\]

**Anionic**

\[
\begin{align*}
\text{Anionic} & \quad (d_{xz,yz})^4 \quad (d_{x^2-y^2})^2 \quad L^2 \\
& \quad [\text{Fe(II)NO}^\ast (-\text{S}_4)^{4\text{-}}]^1\text{-}
\end{align*}
\]

**Neutral**

\[
\begin{align*}
\text{Neutral} & \quad (d_{xz,yz})^4 \quad (d_{x^2-y^2})^2 \quad L^1 \\
& \quad [\text{Fe(II)NO}^\ast (-\text{S}_4)^{3\text{-}}]^0
\end{align*}
\]

It was pointed out that the assumption of pure molecular orbitals was an oversimplification and the assignment of the formal oxidation state Fe(II) was to be used cautiously. Mössbauer data of these complexes have been explained using the electronic configurations above. The similarity of e.s.r. data of mononitrosyl-1,2-dithiolene iron complexes with those of nitrosylbis(dithiocarbamato) iron complexes have been interpreted by assigning the
unpaired electron of both groups of complexes to the \( d_{2}^{*} \) orbital \(^{74} \).

Neutral paramagnetic complexes of the general formula \([\text{FeNO}(S_{2}C_{2}Ar_{2})_{2}] \) (\( Ar = C_{6}H_{5}^{-} \) and various substituted \( C_{6}H_{5}^{-} \)) have recently been reported \(^{82} \). These complexes have room temperature magnetic moments corresponding to one unpaired electron and N-O stretching frequencies at \( \sim 1800 \text{ cm}^{-1} \).

Closely related to the dithiocarbamate and dithiolene mononitrosyl complexes are the mononitrosyls of quadridentate Schiff base -cobalt and -iron complexes studied by Larkworthy and his co-workers \(^{83,84} \). Rallo and Silverstroni \(^{85} \) found that nitric oxide reacted and irreversibly with salen cobalt(II). Larkworthy \(^{83} \) isolated a number of mononitrosyls of salen- and substituted salen- cobalt(II) and found the compounds to be stable when dry. A five co-ordinate, square pyramidal structure was proposed for these complexes based on the similarity of their physical properties with those of \( \text{CoNO}[S_{2}CN(CH_{3})_{2}J_{2} \). The complexes were shown to be monomeric and had fractional magnetic moments arising from temperature independent paramagnetism. The N-O stretching frequency occurred in the range for co-ordinated NO\(^{+} \) and was observed to increase with the electron-withdrawing power of the substituents. The complexes were originally considered to have the configuration \( \text{Co(I)NO}^{+} \), but were reformulated \(^{84} \) as \( \text{Co(III)NO}^{-} \), based on the N-O stretching frequency range for NO\(^{-} \) proposed by Gans \(^{40} \). Larkworthy \(^{84} \) has prepared a similar series of apparently five co-ordinate mononitrosyls of iron from the reaction of nitric oxide with salen- and substituted salen-iron(II) complexes. Their N-O stretching frequencies occurred from 1670 to 1790 cm\(^{-1} \), within the range proposed for NO\(^{-} \). These complexes have been assigned the formal structure \( \text{Fe(III)NO}^{-} \) and
electronic configuration \((d_{xz, yz})^4 (d_{xy})^1 (\pi^*_{NO})^2\) like that in the cobalt mononitrosyls. There was no apparent relationships between the electronic effects of the substituents and the N-0 stretching frequencies. The mononitrosyl salen iron complexes have room temperature magnetic moments corresponding to three unpaired electrons and are the only examples of stable high-spin iron mononitrosyl complexes known. Only the 5-methylsalen iron nitrosyl obeyed the Curie law and had an effective magnetic moment which did not vary with temperature. The other substituted derivatives had temperature dependent moments but obeyed the Curie-Weiss law. The unsubstituted compound, nitrosyl salen iron, exhibited a remarkable discontinuity in magnetic properties at \(180^\circ\)K where the magnetic moment decreased from that for three unpaired electrons \((S=3/2)\) to approximately that for one unpaired electron \((S=1/2)\).

vii) MISCELLANEOUS NITROSYL COMPLEXES

The confusion in the literature on the electronic configuration of the outer orbitals extends to many nitrosyls. The nitric oxide adduct of haemoglobin has been considered to contain nitric oxide co-ordinated as NO\(^+\). The unpaired electron has been assigned to a \(\pi^*_{NO}\) orbital from e.s.r. data \(^{45}\) and to the \(d_{z^2}\) orbital from Mössbauer data \(^{52}\).

Tsumaki and Ohta \(^{37}\) found that bis(salicylaldehydato)-bis(pyridine)iron(II) reacted with nitric oxide in a 1:1 molar ratio but isolated no product. Nast and Rückemann \(^{35}\) isolated the unstable, dark-brown product Fe(sal)_2pyNO (sal=salicylaldehydato) from methylene chloride at \(-78^\circ\). The N-0 stretching frequency, 1715 cm\(^{-1}\), indicated the nitric oxide to be co-ordinated as NO\(^+\). The magnetic moment of the unstable complex, over a temperature range, corresponded to three unpaired electrons (\(\mu_{\text{eff}}=4.01\) B.M.).
An oxidation state of +1 was proposed for the iron and the nitric oxide was proposed to be trans to the pyridine.

The nitric oxide adduct of iron(II)-β-phthalocyanine was low-spin ($\mu_{\text{eff}} = 2.7$ B.M.)\(^{86}\). The N-O stretching frequency, 1685 cm\(^{-1}\), was assigned to NO\(^+\).

A carbonyl complex [Fe(CO)\(_5\)NO\(^+\)]\(^{87}\), similar to the brown-ring complexes, has a N-O stretching frequency at 1610 cm\(^{-1}\) which has been assigned to the presence of NO\(^-\) and Fe(II).

Silverthorn and Feltham\(^{87}\) have prepared a series of diarsine mononitrosyls, of the general formula [FeXNO(diarsine)\(_2\)]\(^+\) (X=I, Br or Cl) which have room temperature magnetic moments corresponding to one unpaired electron. Their N-O stretching frequencies were all at ~1640 cm\(^{-1}\) and the complexes were given the formal configuration Fe(III)NO\(^-\). The nitric oxide molecule is trans to the halide.

viii) CONCLUSIONS

The controversial nature of the nitrosyl ligand has been somewhat clarified recently by X-ray diffraction studies. These have shown that in most cases nitric oxide is co-ordinated by one of two distinct modes:

a) Co-ordination as the NO\(^+\) ion, involving σ-donation from the sp-hybridised N atom to the transition metal atom, and an appreciable amount of metal-ligand π back-bonding. Co-ordination as NO\(^+\) can be represented:

$$M \leftarrow \text{N}=\text{O} : \leftrightarrow M \rightarrow \text{N}=\ddot{\text{O}}$$

classified by a linear M-N-O grouping, contracted M-N bond lengths and a N-O stretching frequency in the range 2000 to 1750 cm\(^{-1}\).

b) Co-ordination as the NO\(^-\) ion, involving predominantly σ-bonding between the sp\(^2\) hybridised nitrogen
atom and the transition metal atom, and much less π backbonding than in NO⁺. The large structural trans effect exerted by NO⁻, is consistent with strong σ- and weak π-donor properties. Co-ordination as NO⁻ can be represented:

\[ \text{M} = \text{O} \text{N} \text{M} \text{O} = \text{N} \text{O} \text{M} \]

classified by a bent M-N-O grouping, longer M-N bond lengths than in NO⁺ complexes and a N-O stretching frequency in the range 1750-1500 cm⁻¹.

X-ray diffraction studies have shown that both linear and bent M-N-O groupings may be present in the same molecule. The data for several examples are given in Table 6. The linear nitrosyls have N-O stretching frequencies ~1850 cm⁻¹ with short M-N bond lengths whilst the bent nitrosyls have lower N-O stretching frequencies, ~1650 cm⁻¹, and longer M-N bond distances.

The possibility of conformational equilibria between two forms of M-NO bonding has been recently suggested. The co-ordination geometry about the metal changes as the metal and the nitrosyl undergo a formal internal redox reaction. Compounds in the general series, CoCl₂NO(PR₃)₂ (R=C₂H₅⁻, n-C₄H₉⁻, C₆H₅⁻) have been reported and are thought to behave in this way. Two N-O stretching frequencies were observed and rapid equilibrium between a trigonal bipyramidal cobalt(I) complex with a linear nitrosyl and a square pyramidal cobalt(III) complex with a bent nitrosyl was proposed. At room temperature a N-O stretching frequency at ~1650 cm⁻¹, attributed to a bent Co-No group, was slightly more intense than a N-O stretching frequency at ~1750 cm⁻¹ attributed to a linear Co-No group. On cooling, the intensity of the band at 1750 cm⁻¹ increased, and the band at 1650 cm⁻¹ diminished in a reversible manner.
Therefore examples of nitric oxide co-ordinated with a M-N-O grouping slightly distorted from linearity. Data for several nitrosyls with 'slightly bent' M-N-O groupings are given in Table 7. Slightly bent nitrosyl-metal systems have been attributed to different degrees of π back-bonding between the nitrosyl and metal atom orbitals.

Considering a formal Fe(II)NO⁺ structure for FeNO[S₂CN(CH₃)₂]₂, Owston et al.⁵¹ have proposed that in the free molecule the Fe-N-O grouping would probably be linear. In the crystal, the molecules try and pack with the lone pair on the oxygen atom of the nitrosyl pointing towards a partially positively charged nitrogen atom on the ligand, producing the slight distortion from linearity.

Data for linear and bent nitrosyls are given in Tables 8 and 9 respectively. Tables 6 and 8 show that most linear nitrosyls contain NO⁺ as described in a) (p.36). Tables 6 and 9 show that most bent nitrosyls contain NO⁻ as described in b) (p.36). As is explained in Table 9 some doubt has been expressed on the accuracy of the data for the ruthenium nitrosyls.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(N-O) cm$^{-1}$</th>
<th>M-N-O</th>
<th>M-N</th>
<th>N-O</th>
<th>NO</th>
<th>Oxidn.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OsOH(NO)$_2$(PPh$_3$)$_2$]$^+$</td>
<td>1842</td>
<td>180°</td>
<td>1.71</td>
<td>1.25</td>
<td>NO$^+$</td>
<td>X-ray</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1632</td>
<td>128°</td>
<td>1.98</td>
<td>1.12</td>
<td>NO$^-$</td>
<td>structure</td>
<td></td>
</tr>
<tr>
<td>[RuCl(NO)$_2$(PPh$_3$)$_2$]$^+$</td>
<td>1845</td>
<td>180°</td>
<td>1.74</td>
<td>1.16</td>
<td>NO$^+$</td>
<td>X-ray</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1687</td>
<td>136°</td>
<td>1.86</td>
<td>1.17</td>
<td>NO$^-$</td>
<td>structure</td>
<td></td>
</tr>
<tr>
<td>[CoCl$_2$(NO)(PR$_3$)$_2$]$^+$</td>
<td>.1750</td>
<td>Linear</td>
<td></td>
<td></td>
<td>NO$^+$</td>
<td>Equilibrium</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>.1650</td>
<td>Bent</td>
<td></td>
<td></td>
<td>NO$^-$</td>
<td>proposed between NO$^+$ and NO$^-$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6**

**Physical Data of Compounds Possessing Linear and Bent M-N-O Groupings**
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(N-O)cm$^{-1}$</th>
<th>M-N-O Bond Angle</th>
<th>M-N Bond Dist. Å</th>
<th>N-O Bond Dist. Å</th>
<th>Oxid. State</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi$-C$_5$H$_5$CrCl(NO)$_2$</td>
<td>1818, 1711</td>
<td>166°</td>
<td>1.72</td>
<td>1.13</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[Fe(NO)$_2$I]$_2$</td>
<td>1818, 1771</td>
<td>161°</td>
<td>1.70</td>
<td>1.15</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[Fe(NO)$_2$S$_3$t$_2$]</td>
<td>1773, 1748</td>
<td>167°</td>
<td>1.67</td>
<td>1.17</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[FeNO(S$_2$CNMe$_2$)$_2$]</td>
<td>1684</td>
<td>174°</td>
<td>1.72</td>
<td>1.10</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[FeNO(S$_2$CNt$_2$)$_2$]</td>
<td>1682</td>
<td>174°</td>
<td>1.69</td>
<td>1.16</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>(NH$_4$)$_2$[FeNO(S$_2$CN$_4$)$_2$]</td>
<td>1650</td>
<td>168°</td>
<td></td>
<td></td>
<td>NO</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[Ru(NO)H(PPh$_3$)$_2$]</td>
<td>1640</td>
<td>176°</td>
<td>1.80</td>
<td></td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[Ru(NO)(diphos)$_2$]+</td>
<td>1673</td>
<td>174°</td>
<td></td>
<td></td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>[IrH(NO)(PPh$_3$)$_3$]Cl$_2$</td>
<td>1780</td>
<td>175</td>
<td>1.68</td>
<td>1.21</td>
<td>NO$^+$</td>
<td>X-ray structure</td>
</tr>
</tbody>
</table>

diphos = 1,2-bis(diphenylphosphino)ethane
<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(N-O) cm⁻¹</th>
<th>M-N-O Bond Angle</th>
<th>M-N Bond Dist. Å</th>
<th>N-O Bond Dist. Å</th>
<th>Oxidn.</th>
<th>State</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂[Fe(CN)₅NO].2H₂O</td>
<td>1939</td>
<td>180°</td>
<td>1.63</td>
<td>1.13</td>
<td>NO⁺</td>
<td>X-ray structure</td>
<td></td>
</tr>
<tr>
<td>[RuNO(S₂CNMe₂)₃]</td>
<td>1803</td>
<td>180°</td>
<td>1.72</td>
<td>1.16</td>
<td>NO⁺</td>
<td>X-ray structure</td>
<td></td>
</tr>
<tr>
<td>Na₂[Ru(NO₂)₄(NO)OH].2H₂O</td>
<td>1907</td>
<td>180°</td>
<td>1.75</td>
<td>1.13</td>
<td>NO⁺</td>
<td>X-ray structure</td>
<td></td>
</tr>
<tr>
<td>π-C₅H₅NiNO</td>
<td>1820</td>
<td>180°</td>
<td>1.75</td>
<td>1.13</td>
<td>NO⁺</td>
<td>Microwave studies</td>
<td></td>
</tr>
<tr>
<td>Cs[Fe₄(NO)₇S₃].H₂O</td>
<td>1741, 1726</td>
<td>180°</td>
<td>1.57</td>
<td>1.25</td>
<td>NO⁻</td>
<td>X-ray structure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1706, 1600</td>
<td>180°</td>
<td>1.67</td>
<td>1.19</td>
<td></td>
<td>two different NO groups</td>
<td></td>
</tr>
<tr>
<td>[MnNO(CO)₂(PPh₃)₂]</td>
<td>1661</td>
<td>178°</td>
<td>1.73</td>
<td>1.18</td>
<td>NO⁺</td>
<td>X-ray structure</td>
<td></td>
</tr>
<tr>
<td>[IrNO(PPh₃)₃]</td>
<td>1660</td>
<td>180°</td>
<td>1.67</td>
<td>1.24</td>
<td>NO⁺</td>
<td>X-ray structure</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 9
**PHYSICAL DATA OF BENT M-N-O GROUPINGS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(N-O) \text{ cm}^{-1} )</th>
<th>M-N-O Bond Angle</th>
<th>M-N Bond Dist. ( \text{A}^0 )</th>
<th>N-O Bond Dist. ( \text{A}^0 )</th>
<th>Oxidn. State</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{IrCl}(\text{NO})\text{CO}(\text{PPh}_3)_2]^{+})</td>
<td>1680</td>
<td>124°</td>
<td>1.97</td>
<td>1.16</td>
<td>NO(^-)</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>([\text{IrCl}_2(\text{NO})(\text{PPh}_3)_2]^{2+})</td>
<td>1560</td>
<td>123°</td>
<td>1.94</td>
<td>1.03</td>
<td>NO(^-)</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>([\text{IrI}(\text{NO})\text{CH}_3(\text{PPh}_3)_2]^{2+})</td>
<td>1525</td>
<td>120°</td>
<td>1.91</td>
<td>1.23</td>
<td>NO(^-)</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>([\text{CoCl}(\text{NO})(\text{en})_2]\text{ClO}_4)</td>
<td>1611</td>
<td>124°</td>
<td>1.82</td>
<td></td>
<td>NO(^-)</td>
<td>X-ray structure</td>
</tr>
<tr>
<td>([\text{RhX}_2(\text{NO})(\text{PPh}_3)_2]^-)</td>
<td>1630</td>
<td>Bent</td>
<td></td>
<td></td>
<td></td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{Cr}(\text{CN})_5\text{NO}]^3^-)</td>
<td>1645</td>
<td>Bent</td>
<td></td>
<td></td>
<td></td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{CoNO}(\text{S}_2\text{CMe}_2)_2]^-)</td>
<td>1626</td>
<td>139°</td>
<td>1.70</td>
<td>1.10</td>
<td>NO(^+)</td>
<td>Proposed to be across ( \nu ) axis</td>
</tr>
<tr>
<td>([\text{Co}(\text{CN})_5\text{NO}]^3^-)</td>
<td>1120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{Ru}(\text{NH}_3)_2(\text{NO})\text{OH}]\text{Cl}_2)</td>
<td>1845</td>
<td>150°</td>
<td>2.07</td>
<td>1.14</td>
<td>NO(^+)</td>
<td>Some doubt has been expressed on the accuracy of these results.</td>
</tr>
<tr>
<td>((\text{NH}_3)_2[\text{RuCl}_2\text{CH(NO)}])</td>
<td>1845</td>
<td>153°</td>
<td>2.04</td>
<td>1.13</td>
<td>NO(^+)</td>
<td>Proposed structure</td>
</tr>
<tr>
<td>(\text{K}_2[\text{Ru(NO)}\text{Cl}_5])</td>
<td>1916</td>
<td>150°</td>
<td>2.03</td>
<td></td>
<td>NO(^+)</td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{CrCl}(\text{NO})(\text{das})_2]\text{ClO}_4)</td>
<td>1690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{FeX}(\text{NO})(\text{das})_2]^2+)</td>
<td>1690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Proposed structure</td>
</tr>
<tr>
<td>([\text{Co}(\text{NH}_3)_2\text{NO}]\text{Cl}_2)</td>
<td>1045</td>
<td>119°</td>
<td>1.87</td>
<td>1.15</td>
<td>NO(^-)</td>
<td>X-ray structure</td>
</tr>
</tbody>
</table>

en = ethylenediamine  \ das = diarsine  \( X = \text{Cl, Br or I} \)
3) MAGNETOCHEMISTRY

i) CLASSICAL MAGNETOCHEMISTRY

Only a brief account is given here. Further details are given elsewhere (ref. 111, 112, 113).

If a substance is placed in a field of $H$ oersteds then $B$, the magnetic induction, or the number of lines of force per unit area within the substance, is given by,

$$ B = H + 4\pi I $$

...(1)

where $I$ is the intensity of magnetisation, or the magnetic moment per unit volume. Dividing equation (1) by $H$:

$$ P = 1 + 4\pi \kappa $$

...(2)

where $P$ and $\kappa$ are the permeability and susceptibility per unit volume respectively.

Susceptibility is usually more conveniently expressed per unit mass (gram susceptibility) than per unit volume,

$$ \chi = \frac{\kappa}{\text{density}} $$

...(3)

The molar susceptibility is defined as:

$$ \chi_M = \chi \times \text{molecular weight} $$

...(4)

Equation (2) leads to the fundamental magnetic classification of substances into:

i) Diamagnetic substances which have $I, \kappa$ and $\chi$ negative. Experimental values of $\chi$ are small, negative and generally independent of both field strength and temperature.

ii) Paramagnetic substances which have $I, \kappa$ and $\chi$ positive. Experimental values of $\chi$ are positive and much larger than in class i). Though independent of field strength, $\chi$ is markedly dependent on temperature.
In general, paramagnetic substances will be composed of paramagnetic centres and diamagnetic groups for which a correction must be applied. The susceptibility per gram atom, \( \chi_A \), of a paramagnetic metal ion in a particular compound can therefore be obtained by measuring the molar susceptibility of the compound and subtracting from this the diamagnetism \( \chi_L \) of the ions or molecules in the compound. Thus,

\[
\chi_A = \chi_M - \sum \chi_L 
\]

The diamagnetism of molecules can be measured directly, or estimated with reasonable accuracy from Pascal's constants

\[
\chi_L = \sum \chi_l + \sum \lambda
\]

where \( \chi_l \) is the atomic susceptibility of an atom and \( \lambda \) is a "constitutive correction" which depends on the nature of the bonds involved in the molecule.

Curie found that for a number of paramagnetic substances, \( \chi_A \) and \( T \) were inversely proportional

\[
\chi_A = \frac{C}{T}
\]

The classical explanation for the Curie law, as equation (7) is called, is based on the following assumptions:

i) Paramagnetic substances contain atoms which behave as small magnetic dipoles of magnetic moment, \( \mu \).

ii) The magnetic dipoles are independent of each other i.e. they do not interact. Such a substance is said to be magnetically dilute.

iii) In the absence of a magnetic field there is no net magnetisation, but on application of a field, the dipoles line up with the field and reinforce it.
iv) Thermal motion opposes the alignment in iii)

v) The magnetic dipoles are independent of temperature

From these assumptions it can be deduced that

\[ \chi_A = \frac{N \mu^2 \beta^2}{3kT} \quad \ldots (8) \]

where \( N \) is Avogadro's number, \( k \) is Boltzmann's constant, \( \beta \) is the Bohr magneton and \( \mu \) is the "effective magnetic moment"

If the Curie law is obeyed, the effective magnetic moment, \( \mu_{\text{eff}} \), is given by the following equation:

\[ \mu_{\text{eff}} = \left( \frac{3kT}{N\beta^2} \right)^{\frac{1}{2}} (\chi_A T)^{\frac{1}{2}} \quad \ldots (9) \]

\[ = 2.328 \sqrt{\chi_A T} \text{ B.M.} \quad \ldots (10) \]

In practice deviations occur from ideal behaviour and a more general equation is given by the Curie-Weiss law:

\[ \chi_A = \frac{C}{T+\theta} \quad \ldots (11) \]

where \( \theta \) is a measure of the departure from ideal behaviour.

The moment, \( \mu_{\text{eff}} \), is still computed from equation (10) even if the Curie-Weiss law is obeyed. Other deviations from ideal behaviour occur when:

a) interactions occur between the magnetic dipoles of different paramagnetic atoms i.e. the substances are not magnetically dilute and exhibit ferromagnetism or antiferromagnetism.

b) \( \mu_{\text{eff}} \) varies with temperature. Variation due to orbital contribution is discussed on p.47. Some substances which are expected to be diamagnetic have a very small susceptibility which is independent of temperature - so-called temperature independent paramagnetism (TIP). This arises because the magnetic field distorts the electron
distribution of an ion, on which it acts, to change
the ground state by a small amount due to interaction
between higher- and ground-states. Where the separation
of the interacting levels is greater than kT, thermal
population of the upper level does not occur and the
contribution to the susceptibility is independent
of temperature.
Since
\[ \mu_{\text{eff}} = \sqrt{\chi_{\text{TIP}} \times T} \] ....(12)
a small variation of effective magnetic moment with
\( \sqrt{T} \) results.
c) considerable even abrupt changes in \( \mu_{\text{eff}} \) occur over
a temperature range. This will be discussed in
more detail in section 3(iii).

If a single electron is considered to be rotating
around a positively charged nucleus the movement gives
rise to an orbital angular momentum. For a single
electron the orbital moment, \( \mu_1 \), is given by the following
equation
\[ \mu_1 = \beta \sqrt{l(l+1)} \] ....(13)
where \( l \) is the orbital quantum number and \( \beta \) is the
Bohr magneton. The electron is also spinning about
its own axis as well as rotating about the nucleus
which gives rise to a spin angular momentum and a spin
moment, \( \mu_s \)
\[ \mu_s = g\beta \sqrt{s(s+1)} \] ....(14)
where \( g \) is the "splitting" factor and equals two, and \( s \)
is the spin quantum number.

In poly-electron systems the spin and orbital
moments of individual electrons interact with each
other. Russell-Saunders, or LS coupling is used to
describe the interactions in poly-electron systems of the
first transition series. The magnitude of the spin
coupling is greatest and is given by the following equation:
\[ \mu_S = 2\sqrt{S(S+1)} \frac{\hbar}{2\pi} \]  
\hspace{1cm} \text{(15)}

where \( S \) is the resultant spin quantum number. The weaker coupling of the orbital angular momentum is given by:

\[ \mu_L = \sqrt{L(L+1)} \frac{\hbar}{2\pi} \]  
\hspace{1cm} \text{(16)}

where \( L \) is the resultant orbital momentum number.

The quantum number, \( J \), can take the values \( L+S \) (if \( L>S \)) or \( S-L \) (if \( S>L \)). The collection of possible values of \( J \), for a given term, is known as a "multiplet" and each \( J \) value is a "component" of that multiplet. The difference in energy between adjacent components is known as the "multiplet width".

First transition series elements are expected to have multiplet widths which are small compared to \( kT \) and have magnetic moments obeying the expression,

\[ \mu = \sqrt{L(L+1) + \frac{4S(S+1)}{B.M.}} \]  
\hspace{1cm} \text{(17)}

The moment is independent of temperature and the Curie law should be obeyed.

\[ \chi_A = \frac{N\beta^2}{3kT} [L(L+1) + 4S(S+1)] \]  
\hspace{1cm} \text{(18)}

However, the orbital momentum is often quenched since the electrostatic fields of the ligands remove the degeneracy of the 3d orbitals. Then \( L=0 \), and equation (17) reduces to the "spin-only" formula,

\[ \mu_{S0} = \sqrt{\frac{4S(S+1)}{B.M.}} \]  
\hspace{1cm} \text{(19)}

If \( n \) is the number of unpaired electrons, then \( S = \frac{n}{2} \) and equation (19) becomes

\[ \mu_{S0} = \sqrt{n(n+2)} \]  
\hspace{1cm} \text{(20)}

Experimental results follow the spin-only values quite well for octahedral complexes (see Table 10). When the orbital momentum is incompletely quenched, moments in excess of the spin-only values are obtained and are said to include an "orbital contribution" which often leads to a moderate variation of magnetic moment with
temperature. For cobalt(II) complexes, for example, the temperature variation of magnetic moment can be used to distinguish between octahedral and tetrahedral complexes.

Table 10

<table>
<thead>
<tr>
<th>n</th>
<th>Example</th>
<th>Hybrid Orbitals</th>
<th>$\mu_{\text{eff}}$</th>
<th>B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Spin-Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$d^1$, Ti$^{3+}$</td>
<td>$d^2sp^3$</td>
<td>1.73</td>
<td>1.6-1.7</td>
</tr>
<tr>
<td>2</td>
<td>$d^5$, Fe$^{3+}$</td>
<td>$d^2sp^3$</td>
<td>&quot;</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>3</td>
<td>$d^9$, Fe$^{2+}$</td>
<td>sp$^2d^2$</td>
<td>&quot;</td>
<td>1.7-2.2</td>
</tr>
<tr>
<td>4</td>
<td>$d^9$, Cr$^{3+}$</td>
<td>$d^2sp^3$</td>
<td>2.83</td>
<td>2.7-2.9</td>
</tr>
<tr>
<td>5</td>
<td>$d^7$, Co$^{2+}$</td>
<td>$d^2sp^3$</td>
<td>&quot;</td>
<td>2.9-3.3</td>
</tr>
<tr>
<td>6</td>
<td>$d^7$, Co$^{2+}$</td>
<td>$d^2sp^3$</td>
<td>3.88</td>
<td>3.7-3.9</td>
</tr>
<tr>
<td>7</td>
<td>$d^7$, Co$^{2+}$</td>
<td>$d^2sp^3$</td>
<td>&quot;</td>
<td>4.3-5.2</td>
</tr>
<tr>
<td>8</td>
<td>$d^7$, Co$^{2+}$</td>
<td>$d^2sp^3$</td>
<td>4.90</td>
<td>4.7-4.9</td>
</tr>
<tr>
<td>9</td>
<td>$d^7$, Co$^{2+}$</td>
<td>$d^2sp^3$</td>
<td>&quot;</td>
<td>5.1-5.7</td>
</tr>
<tr>
<td>10</td>
<td>$d^5$, Mn$^{2+}$</td>
<td>sp$^2d^2$</td>
<td>5.92</td>
<td>5.6-6.1</td>
</tr>
<tr>
<td>11</td>
<td>$d^5$, Fe$^{3+}$</td>
<td>sp$^2d^2$</td>
<td>&quot;</td>
<td>5.7-6.0</td>
</tr>
</tbody>
</table>

II) EXPERIMENTAL TECHNIQUES

Of the more important techniques, two have been used in this study and a brief account of each method follows. More detailed accounts are to be found elsewhere (ref. 111, 112).

a) Gouy Method

The method consists essentially of suspending a uniform rod of the specimen in a non-homogenous magnetic field, and measuring, by a conventional weighing technique,
the force exerted on it.

If a field gradient over an element of volume, \( \partial v \), of the specimen is \( \partial H/ \partial l \), then the force, \( \partial F \), exerted is

\[
\partial F = (\chi_1 - \chi_2) \partial v \frac{\partial H}{\partial l}
\]

where \( \chi_1 \) and \( \chi_2 \) are the susceptibilities per unit volume of the specimen and displaced medium respectively.

Integration over the whole length of the specimen from \( H=H_1 \) at zero length to \( H=H_0 \) at length, \( l \), gives

\[
F = \frac{(\chi_1 - \chi_2)\nu(H_1^2 - H_0^2)}{2l}
\]

If \( F \), in dynes, is replaced by \( w x g \), where \( w \) is in grams and \( (H_1^2 - H_0^2) \) by \( H^2 \), then

\[
\chi_1 = \chi_2 + \frac{2lgw}{vH^2}
\]

but

\[
\chi = \chi x \text{density} = \frac{\chi W}{v}
\]

where \( W \) is the total weight of the specimen.

Therefore

\[
\chi = \chi_2^v + \left( \frac{2gl}{H^2} \right)w
\]

If nitrogen is used as the displaced medium, then the correction, \( \chi_2^v \), is negligible. The use of nitrogen also facilitates low temperature measurements. Equation (25) then reduces to

\[
\chi = \left( \frac{2gl}{H^2} \right)w
\]

The measurement of \( \chi \) may be simply made by weighing the sample in and out of a magnetic field of known field strength, \( H \). The difference between the weighings, \( w \), can then be substituted into equation (26) and \( \chi \) calculated. To calculate the molar susceptibility, equation (26) is multiplied by the molecular weight, \( M \), of the specimen, \( So \),

\[
\chi_M = \left( \frac{2glM}{WH^2} \right)w
\]
b) **N.m.r. Method**

This method was devised by Evans for measurements in solution and is very quick and convenient.

The frequency at which proton resonance occurs depends on the magnetic environment of the proton and changes in this environment produce corresponding changes in the resonance frequency. If the environment change is caused by the presence of a paramagnetic solute, it should be possible to relate the susceptibility of this to the change ($\Delta f$) in the resonance frequency of the proton. This is the basis of the Evans method in which the resonance frequency of a standard substance in a solution is compared to that of the same substance in an otherwise pure solvent.

The solution under investigation, along with the proton-standard, is placed in a capillary tube. This is placed coaxially inside a normal n.m.r. tube containing the solvent with the same concentration of proton-standard. The tubes are spun as is usual during n.m.r. measurements. Under these circumstances it can be shown that the susceptibility of the paramagnetic solute is,

\[
\chi = \frac{3}{2\pi m} \frac{\Delta f}{f} + \chi_o + \frac{\gamma_o}{m} \left(\rho_o - \rho_s\right)
\]  \(\ldots(28)\)

where $f$ is the frequency of the proton resonance, $m$ is the mass per ml. of solute, $\chi_o$ is the bulk susceptibility of the solvent and $\rho_o$ and $\rho_s$ are the densities of the pure solvent and solution respectively. In practice, for dilute solutions, $\chi_o$ is small and therefore the third term in equation (28) is ignored. Then:

\[
\chi = \frac{3}{2\pi m} \frac{\Delta f}{f} + \chi_o
\]  \(\ldots(29)\)

It has been found best not to use concentrated solutions since the accuracy of the method is reduced by broadening of the resonance lines.
iii) **SPIN-STATE EQUILIBRIA**

a) **Introduction**

Depending upon the strength of a ligand field, octahedral transition metal complexes with $d^4$, $d^5$, $d^6$ and $d^7$ electronic configurations may exist in either high-spin or low-spin ground states. According to ligand field theory, a transition between these states should occur discontinuously provided a change in spin multiplicity is involved. The transition occurs at a certain value of ligand field strength $\Delta$, called the mean spin-pairing energy, $\pi$. This situation is illustrated in Fig. 6.

The electronic configurations $d^5$ and $d^6$ are most relevant to this study and are the only configurations discussed. Modified Tanabe-Sugano diagrams (Fig. 7a) and b) illustrate the crossing-over of ground-state terms as $\Delta$ increases. The mean spin-pairing energies for octahedral Fe(II), $d^6$ and Fe(III), $d^5$ have been calculated to be 17,600 cm$^{-1}$ and 30,000 cm$^{-1}$ respectively.

The great majority of iron(II) and iron(III) systems have a single ground state well removed from the cross-over region. If, at a ligand field strength $\Delta$, close to $\pi$, the separation of the two states of different multiplicity attains a value within the thermally accessible range i.e. $\sim kT$, equilibrium between the states is expected.

The condition under which the 'cross-over' situation is to be expected can now be expressed by the inequality

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

Many examples of spin-state equilibrium have now been observed and some will be referred to in the following discussion.

*For general references see ref. 114, 115*
The Transition Between Spin-States

Low-Spin

High-Spin
cross-over point where $\Delta = \Pi$

Ligand Field Strength, $\Delta$

Fig. 6

Term Diagrams for $d^5$ and $d^6$ Configurations

Fig. 7
b) Some Factors Affecting the Cross-over Situation

i) Mean spin-pairing energy, $\pi$

The expected cross-over situation has been expressed by the inequality

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

This is a naive treatment of the problem because it assumes that the spin-states, in their equilibrium geometries, have the same value of $\Delta$. The crossing of the energies of terms of differing spin-multiplicity represented in Fig. 7 does not correspond to states in equilibrium but to a definite transition.

ii) Chemical modification of ligands

The physical properties of a system which lies at the cross-over region should be responsive to minor chemical modifications of the co-ordinated ligands. Although several systems are known in which changes induced by substitution in the ligand produce profound effects in the cross-over region, it is almost impossible to distinguish the respective contributions of electronic and steric effects.

The first examples of spin-state equilibrium were discovered by Cambi and co-workers$^{70,71,116,117}$ with a series of iron(III)-NN-dialkyldithiocarbamates, $[\text{Fe(S}_2\text{CNR}'\text{R}''\text{)}_3]$ (for iron III, $d^5$ a $2T_g - 6A_1$ transition). Cambi and more recent workers$^{118-120}$ have shown that three types of behaviour occur depending on the alkyl substituent. Room temperature moments range from a maximum value, $\mu_{\text{eff}} = 5.83$ B.M. ($R' = R'' = \text{pyrrolidyl}$; high-spin) to a minimum value of $\mu_{\text{eff}} = 2.34$ B.M. ($R' = R'' = \text{iso-propyl}$; low-spin). Almost any intermediate value can be achieved by proper choice of alkyl group or combination thereof. For each compound $\mu_{\text{eff}}$ corresponded to a low-spin environment at 300K, which was followed by a monotonic increase with rising temperature.
Ho and Livingstone\textsuperscript{121} have reported magnetic behaviour best explained by a thermal equilibrium between $d_5^5$ and $d_5^3d_\gamma^2(2T_2^6A_1)$, spin-states for iron(III) complexes of monothio-$\beta$-diketones of the type Fe[R'CSCHCOR]\textsuperscript{3}. The magnetic behaviour is dependent on the nature of the $R$-groups and electron-withdrawing substituents appear to increase the population of the spin-paired configuration.

An extensive series of compounds having the general formula $[\text{Fe(II)}(\text{phen})_2(X)_2]$ (phen = 1,10-phenanthroline, $X$ covers a large part of the spectrochemical series) has been reported. When $X=\text{Cl}^-$, $\text{Br}^-$, $\text{N}_3^-$ and $\text{OCN}^-$ high-spin compounds are formed while $X=\text{CN}^-$, $\text{NCO}^-$ and $\text{NO}_2^-$ give low-spin compounds. Compounds of $\text{SCN}^-$ and $\text{SeCN}^-$ show room temperature moments of about 5.0 B.M., which drop sharply to about 1.5 B.M. at 110°K and 150°K respectively\textsuperscript{122}. König and Madeja\textsuperscript{123, 124} have suggested that the anomalous behaviour is better represented as a transition (for iron(II), a $^5T_2^6A_1$ transition) rather than an equilibrium when the crossover is sharp. Careful investigations of the electronic, infrared and Mössbauer spectra\textsuperscript{123} indicated a change in molecular structure between 300° and 77°K and it was assumed to occur at the point where there was a sharp reduction in magnetic moment. Magnetic and Mössbauer studies on $[\text{Fe(dipy)}_2(\text{NCS})_2]$ have revealed behaviour quite similar to that of $[\text{Fe(phen)}_2(\text{NCS})_2]$\textsuperscript{125}.

Depending on the substituents on the rings, some iron(II)-poly-(1-pyrazolyl)borates, Fig. 8a, have also been found to undergo a $^5T_2^6A_1$ spin-state equilibrium\textsuperscript{126, 127}. Where $R=\text{H}$ and $X=Y=\text{CH}_3$ (I) the complex is fully high-spin while when $R=\text{Ph}$ and $X=Y=\text{H}$ the compound is diamagnetic. When $R=Y=\text{H}$ (II) an intermediate room temperature moment (2.70 B.M.) is found. A spin-state equilibrium has been found when $R=Y=\text{H}$ and $X=\text{CH}_3$ (III). A Mössbauer study of compounds I, II and III was used to illustrate the equilibrium and to estimate the relative populations of the two states at different temperatures.
Ligands Producing Spin-State Isomerism in Iron Complexes

\[ R-B \left( \begin{array}{c} N \end{array} \right) \]

where

\[ X = \text{H or CH}_3 \]
\[ Y = \text{H or CH}_3 \]

**a**

**b**

terpy = 2,2',2''-terpyridine

**c**

**d**

**e**

**f**

Fig. 8
Some iron(II) complexes of 2-(2-pyridyl)(amino)-
4-(2-pyridyl)thiazole(papth, Fig. Sb) have been investigated. Depending on the anion and degree of hydration varying magnetic behaviour was observed e.g. a high-spin ground state was obtained for $[\text{Fe(papth)}_2]\text{H}_2\text{O}$ and a low-spin ground state for $[\text{Fe(papth)}_2]\text{Br}_2\cdot 2\text{H}_2\text{O}$. Compounds with intermediate moments were found to be strongly and reversibly dependent on temperature, particularly the anhydrous nitrate compound which required about 3 hours to attain a constant moment at low temperatures.

Spin-state equilibria have also been observed in the following systems:

i) Tris(2-aminomethylpyridine)iron(II) halides

ii) Fe(terpy)$X_2$ (Fig. Sc) ($X=\text{Cl}^-, \text{Br}^-, \text{I}^-$ or $\text{HSO}_4^-$)

iii) Tris[2-(2'-pyridyl)imidazole]iron(II) perchlorate (Fig. Sd)

iv) Tris[2-(2'-pyridyl)imidazoline]iron(II) perchlorate (Fig. Se).

v) $[\text{Fe(ppa)}_2](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (Fig. Sf) which is low-spin at room temperature whilst $[\text{Fe(Meppa)}_2](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (Fig. Sf) is high-spin. Mössbauer data confirmed the magnetic data.

The unusual magnetic behaviour of the mono-nitrosyls of Schiff base-iron complexes prepared by Larkworthy et al. has already been mentioned.

iii) Solid-state effects

The equilibrium between molecular states of differing spin should be dependent on temperature and pressure. The temperature dependence of any physical property, $P$, of a cross-over system should be given simply by the value at each temperature of the property for each of the states, weighted suitably by the appropriate population factor:
\[ P_{\text{exp}} = P_{\text{hs}} + P_{\text{ls}} \exp \left( \frac{\Delta G^0}{RT} \right) \]

where \( \Delta G^0 \) is the change in free energy when one mole of the low-spin species is transformed into one mole of the high-spin species, \( P_{\text{exp}} \) is the experimentally determined value of the property and \( P_{\text{hs}} \) and \( P_{\text{ls}} \) are the values characteristic of high-spin and low-spin states respectively. The property \( P \), must be proportional to the mole fraction of each species if equation (30) is to be valid.

The spin-state equilibrium should also respond to changes in pressure. It has been shown \(^{118}\) that the paramagnetism of iron(III)-dithiocarbamates was dependent on pressure and the equilibrium constant, \( K \), at each pressure was calculated from the following equation:

\[ K = \frac{\mu_{\text{exp}}^2 - \mu_{\text{ls}}^2}{\mu_{\text{hs}}^2 - \mu_{\text{ls}}^2} \]

where \( \mu_{\text{exp}} \), \( \mu_{\text{hs}} \) and \( \mu_{\text{ls}} \) are the experimental and characteristic high-spin and low-spin magnetic moments respectively.

Constraints placed on the system by the crystalline lattice can modify the octahedral symmetry of the complex and may even lead to compression or expansion of the metal-ligand interatomic distance. For these reasons, the occurrence of a phase change in the solid should cause discontinuities in physical properties of the cross-over system.

It has been suggested that the sharp transitions in magnetic susceptibilities for \([\text{Fe(phen)}_2(\text{NCS})_2]\), \([\text{Fe(phen)}_2(\text{NCSO})_2]\) and \([\text{Fe(dipy)}_2(\text{NCS})_2]\) have been caused by crystal lattice changes \(^{123}\) and not by phase changes. Jesson et al. \(^{127}\) have suggested that in the iron(II)poly-
(1-pyrazolyl)borate systems, molecules with low-spin ground states adopt a different crystal structure from those in the high-spin state and that a co-operative collapse of the lattice may occur at the cross-over point.

c) Qualitative Treatment of Spin-State Equilibria

A treatment is required which will fit the experimental data into an equation which will account theoretically for the temperature dependence of the properties whose magnitude is dependent on the position of the equilibrium.

It has been suggested that the variation of magnetic susceptibility with temperature for \( d^5 \) or \( d^6 \) systems involving a spin-state equilibrium can be described as follows:

\[
\chi = \frac{(2s_1+1)\chi_1 + (2s_2+1)\chi_2 \exp(-E/kT)}{(2s_1+1)+(2s_2+1)\exp(-E/kT)}
\]  

(32)

where \( \chi \) is the susceptibility of the system resulting from a population weighted average of the susceptibilities \( \chi_1 \) and \( \chi_2 \) of the two states in equilibrium, \( s_1 \) and \( s_2 \) are the spin quantum numbers of the two states and \( E \) is the energy difference between them. This equation is based on a simple Boltzmann distribution over the spin-states in equilibrium. Assuming that \( E \) is independent of \( T \), and that the temperature dependence of \( \chi_1 \) and \( \chi_2 \) can be adequately estimated, the above expression ought to produce a value for \( E \). Unfortunately this approach has been unsuccessful for iron(II) complexes.

Ewald has shown that the variation of magnetic susceptibility with temperature, for the iron(III)-dialkyl-dithiocarbamates, may be explained quite well by fitting the experimental data into a modified Van Vleck equation. The change in susceptibility with temperature was a continuous smooth curve in these examples.

Another approach has been to define an equilibrium constant in terms of relative concentrations of high-spin and low-spin forms for a spin-state equilibrium. These
relative concentrations can be obtained by assuming
values for the susceptibilities of high- and low-spin forms
and thus the equilibrium constant can be obtained as a
function of temperature, see equation (31). The standard
equation (32a) shows that a plot of \( \ln x \) from equation
(31), against \( T^{-1} \) should be straight-line from which \( \Delta H \)
may be obtained.

\[
\frac{d \ln x}{d \left( \frac{1}{T} \right)} = \frac{\Delta H}{R} \quad \ldots \ldots (32a)
\]

Most plots of this type for iron complexes exhibiting
spin-state equilibrium are unfortunately non-linear.
This would indicate that the cross-over appears to involve
intermolecular factors to an important degree and therefore
a simple equilibrium and a simple Boltzmann distribution
over the temperature range considered are not to be expected.

d) Conclusions

i) Spin-state equilibrium has been observed in many
iron(II) and iron(III) systems but at present there is no
adequate quantitative treatment of the effect.

ii) Changes in spin-state may be induced either by:

a) making small chemical changes in the ligand in a
potential cross-over system

or

b) cooling the system and observing a transition
between spin states at some low temperature.

iii) Examples are known in which the spin-state equilibrium
is time-dependent.

iv) The temperature at which cross-over occurs, the
transition temperature, and the relative values for
magnetic moments for the same system differ from one
preparation to another.

v) Mössbauer spectroscopy is a very useful technique
in determining whether the relaxation time from one spin-
state to the other is large or small. If the relaxation
time is small the iron nucleus experiences an averaged EFG (see section 4 iii) and a time average spectrum is produced. If the relaxation time is large then characteristic spectra of both spin-states should be present.

vi) Most examples of spin-state equilibrium have been observed for the iron nucleus in an octahedral or slightly-distorted octahedral environment. The compound nitrosyl salen iron, studied by Larkworthy would appear to be novel as it has a square pyramidal structure and it is the only example of a spin-state equilibrium between a triplet \( S = \frac{3}{2} \) and a singlet \( S = \frac{1}{2} \) state, exhibiting a sharp transition at \( \sim 180^\circ K \).

vii) In order to refine the qualitative treatments proposed, the crystal structures of the spin-state equilibrium systems ought to be determined either side of the transition temperature, particularly when the transition is sharp.
4) THE MöSSBAUER EFFECT

i) INTRODUCTION

The Mössbauer effect concerns the resonance fluorescence of so-called recoil-free gamma radiation from atomic nuclei.

If an atom or molecule is lifted just to the first excited state by absorbing a light quantum of sufficient energy, then the energy of the emitted light quantum will be identical to that of the absorbed light quantum on the return of the atom or molecule to the ground state. This special case of fluorescence is known as resonance fluorescence.

Gamma radiation emitted by excited atomic nuclei is electromagnetic, as is a light quantum, so resonance fluorescence should be observable for transitions between ground and excited nuclear states. The considerably higher energy of gamma quanta impart a measurable recoil to the nucleus during emission so that part of the excitation energy of the nucleus is lost as recoil energy. Hence any gamma quantum emitted has insufficient energy to excite a nucleus of the absorber. The energy of an emitted gamma-ray is given by the equation:

\[ E_γ = δE + D - E_R \]  

where \( δE \) is the difference in energy between the excited and ground states of the source nucleus, \( D \), the Doppler shift, is due to the translational motion of the nucleus and is written as:

\[ D = 2\sqrt{E_R kT} \]  

and \( E_R \) is the recoil-energy of the nucleus given by the equation:

\[ E_R = \frac{E_γ}{2Mc^2} \]  

*(For general references see refs. 135-142)*
where $M$ is the mass of the nucleus and $c$ is the velocity of light.

The fraction of the available energy which is lost to the recoiling atom is small, in the order of 5 parts in $10^7$. However, this loss becomes significant when compared to the line-width of gamma-rays. The finite width arises from the finite time which the nucleus spends in the excited state and is a direct result of Heisenberg's uncertainty principle. The uncertainty in energy, corresponding to the line width, $\Gamma$, of the gamma-ray: and the uncertainty in time, corresponding to the mean life, $\tau$, of the nuclear state, are related by the equations:

$$\Gamma \tau = \frac{\hbar}{2\pi} \quad \cdots (36)$$

and

$$\Gamma = \frac{0.693h}{\tau^4} \quad \cdots (37)$$

where $h$ is Planck's constant and $\tau^4$ is the half-life of the excited state. A half-life $\tau^4$ of $10^{-7}$ secs. results in a line-width of $4.6 \times 10^{-9}$ eV which is much smaller than the energy lost in recoil. As a result the gamma quantum has not enough energy to excite the nucleus of the absorber and nuclear resonance absorption is not observed.

In the arrangement according to Mössbauer, the loss resulting from recoil is not compensated but avoided altogether. If the radiating atom is solidly built into a crystal lattice (effectively reducing $E_R$ by increasing $M$ in equation (35)), the lattice absorbs the recoil momentum and there is virtually no loss in energy, unless vibrations are started in the lattice during emission. The condition for resonance is therefore fulfilled, but there are a number of factors which affect the magnitude of the Mössbauer effect.

Not all radiating atoms built into the crystal lattice emit quanta "without recoil", but vibrations are started in the lattice to some extent. This causes a loss of energy
from the quanta and the magnitude of the Mössbauer effect depends on the fraction of events, \( f \), which take place without lattice excitation. The fraction of events or "Mössbauer coefficient", \( f \), is given by the equation:

\[
 f = \exp \left[ -\frac{\lambda^2 \langle x^2 \rangle}{2} \right] \quad \text{.....(38)}
\]

where \( \lambda \) is the wave length of the gamma quantum and \( \langle x^2 \rangle \) is the component of the mean-square vibrational amplitude of the emitting nucleus in the direction of the gamma-ray. The Mössbauer effect is greater, the less the probability of excitation of vibrations in the lattice, i.e. the smaller the quantum energy, the lower the temperature of the crystal, and the more rigid the atomic bonding in the lattice.

The significance of the gamma-ray line-width has been noted previously. The gamma-ray width \( \Gamma \), is smaller than the total width of the excited state \( \Gamma \), and these are related by:

\[
 \Gamma_\gamma = \frac{1}{1+\alpha} \Gamma \quad \text{.....(39)}
\]

where \( \alpha \) is the internal conversion coefficient. This is the ratio of decays by internal conversion with resultant electron emission to one by gamma quanta from the excited to the ground state. The internal conversion coefficient should therefore be as small as possible.

The cross section, \( \sigma_o \), for absorption of the gamma-ray by the resonant isotope must also be considered. The Mössbauer absorption cross section is given by the equation:

\[
 \sigma_o = \frac{\lambda^2 \cdot 1+2I_e \cdot 1}{2\pi \cdot 1+2I_g \cdot 1+\alpha} \quad \text{.....(40)}
\]

where \( \lambda \) is the wavelength of the gamma quantum, \( \alpha \) is the internal conversion coefficient and \( I_e \) and \( I_g \) are the nuclear spins of the excited and ground states respectively.
The basic conditions and magnitude of the Mössbauer effect have been considered. The properties of the gamma-rays associated with the Mössbauer effect can now be summarised.

If the lattice is excited during the emission of the gamma-ray, the effective line-width will approximate to an energy of $10^{-2}$ eV. However, the line-width of gamma-rays originating in events which do not involve lattice excitation will be determined by the half-life of the excited state, equation (37).

For Fe$^{57}$, $\tau_\frac{1}{2} = 1.0 \times 10^{-7}$ secs, and hence $\Gamma = 4.6 \times 10^{-9}$ eV.

The gamma-rays which are associated with the Mössbauer effect in Fe$^{57}$ therefore possess a line-width seven orders of magnitude smaller than those which involve lattice excitation during their propagation. This extremely narrow line is smaller than the characteristic values for electric quadrupole and magnetic dipole interactions of nuclei with their surrounding electrons.

The fractional line-width is given by, $\Gamma/\varepsilon$, and for Fe$^{57}$ is approximately $10^{-13}$. An alternative statement is that the energy is defined by one part in $10^{13}$ and therefore is the most accurately defined form of electromagnetic radiation available.

The Mössbauer effect has been observed in 45 elements (Fig. 9). The properties which determine whether a nuclide is suitable for Mössbauer effect studies are given below.

a) The half-life of the excited state, $\tau_\frac{1}{2}$. This should lie in the range $10^{-6}$ to $10^{-11}$ secs. In general, the shorter the half-life the broader and less useful the resonance line becomes. With longer half-lives the absorption line becomes too narrow for detection.

b) The internal conversion coefficient, $\alpha$. This must not be larger than about 20.
Elements Showing The Mössbauer Effect

<table>
<thead>
<tr>
<th>K</th>
<th></th>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Ge</th>
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<th>Kr</th>
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<td></td>
<td></td>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>Cs</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au</td>
</tr>
<tr>
<td>Ra</td>
<td>Pr</td>
<td>Nd</td>
<td>Sm</td>
<td>Eu</td>
<td>Gd</td>
<td>Tb</td>
<td>Dy</td>
<td>Ho</td>
</tr>
<tr>
<td></td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9
c) Mössbauer absorption cross-section, $\sigma_0$. This must dominate cross-sections for rival processes. In Fe$^{57}$ this cross-section is about 200 times greater than the next most important process, photoelectric absorption. Therefore the resonant absorption process can dominate even when the resonant isotope is a minor constituent of the absorbing solid.

d) The gamma-ray energy, $E_\gamma$. The energy should lie in the region 10 to 150 eV. For low energy transitions there are problems of transmission through an absorber and the resolution of the appropriate radiation from the general low-energy gamma-ray background. For high energy transitions the $f$-factor is reduced and the recoil effects become appreciable.

e) The half-life of the radioactive source isotope. The parent isotope of the source must have a relatively long half-life so that problems of source preparation are minimised.

f) The natural abundance of the Mössbauer nuclei in the absorber must not be too low, otherwise isotopic enrichment may be necessary.

The most advantageous combination of nuclide properties is found in Fe$^{57}$. Some relevant properties of Fe$^{57}$ and the decay scheme of Co$^{57}$ to Fe$^{57}$ are given in Table 11 and Fig. 10 respectively.

The discussion so far has been assumed the chemical bonding of the source and absorber atoms to be equivalent. The diagram (Fig. 11a) represents the distribution of the energies of emitted and absorbed gamma-rays, $E_\gamma$, and the dotted line represents the energy difference, $\delta E$. The width of the curve on the left results from Doppler broadening and the average energy of the curve is the recoil energy, $E_R$, of emitted gamma-rays. The curve on the right shows the distribution of gamma-ray energies.
### Table 11

Some Relevant Properties of Fe$^{57}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Ground State</th>
<th>Excited State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (KeV)</td>
<td>0</td>
<td>14.4</td>
</tr>
<tr>
<td>Spin and Parity</td>
<td>-3/2</td>
<td>-3/2</td>
</tr>
<tr>
<td>Quadrupole Moment (barns)</td>
<td>0</td>
<td>0.29</td>
</tr>
<tr>
<td>Magnetic Moment (nm)</td>
<td>0.0903</td>
<td>-0.153</td>
</tr>
<tr>
<td>Mean Life (sec)</td>
<td>Stable</td>
<td>1.4x10^-7</td>
</tr>
<tr>
<td>Half-life ($\tau_1$)</td>
<td>Stable</td>
<td>9.77x10^-8</td>
</tr>
<tr>
<td>Line-width ($\Gamma$)</td>
<td>Stable</td>
<td>4.6x10^-9 eV</td>
</tr>
<tr>
<td>f factor in a natural iron host at room temperature</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Natural isotopic abundance</td>
<td>2.19%</td>
<td></td>
</tr>
<tr>
<td>Internal conversion factor ($\alpha$)</td>
<td>9.2±0.5</td>
<td></td>
</tr>
<tr>
<td>Mössbauer absorption cross-section ($\sigma_0$)</td>
<td>2.38x10^-18 cm$^2$</td>
<td></td>
</tr>
</tbody>
</table>
Decay Scheme for Co\(^{57}\) to Fe\(^{57}\)

- Electron Capture
- \(570\text{KeV} \quad 267\text{days} \quad \text{Co}^{57}\)

\[\begin{array}{c}
\text{I} = \frac{3}{2}^- \\
137\text{KeV} \\
\text{I} = \frac{3}{2}^- \\
14.4\text{KeV} \\
\text{I} = \frac{1}{2}^- \\
0\text{KeV}
\end{array}\]

\[\begin{array}{c}
137\text{KeV} \\
\gamma_1 \\
123\text{KeV} \\
\gamma_2 \\
14.4\text{KeV} \\
\gamma_3 \\
14.4\text{KeV}
\end{array}\]

\(t_{\gamma} = 9.77 \times 10^{-8}\text{sec}\)

Fe\(^{57}\) stable

Fig.10
necessary for absorption. The width of the curve results from Doppler broadening and $E_R$ is positive because the exciting gamma-ray must have enough energy necessary to bring about the transition and effect recoil of the absorbing nucleus. The shaded region in Fig. 11a, indicates the slight probability that the gamma-ray energy from the source will coincide with that required for absorption by the sample. The diagram (Fig. 11a) indicates that the cause for non-incidence is the recoil energy, $E_R$. By placing the source and sample in solid lattices, although not all transitions are recoilless the probability of coincidence is increased so that resonance is observed (Fig. 11b).

When the source and absorber atoms are chemically non-equivalent, the energy required by the absorber for resonance is greater or less than the energy quanta, $E_\gamma$, emitted by the source. In order to obtain resonance the source and the absorber have to be moved relative to one another and resonance absorption occurs at a finite relative velocity. The higher the velocity at which the source is moved towards the sample, the higher the average energy of the emitted gamma-ray (by the Doppler effect) and vice versa. The relative velocity of the source and the absorber are within the range of the first-order Doppler shift defined by the equation:

$$\Delta E = \frac{v}{c} E_\gamma \quad \ldots (41)$$

where $\Delta E$ is the change in gamma-ray energy produced by a velocity, $v$, in mm sec$^{-1}$ and $c$ is the velocity of light. The Doppler velocity of the relative source-absorber motion which is required to shift the gamma-ray energy by one line-width is given by the equation:

$$v = \frac{\gamma c}{E_\gamma} \quad \ldots (42)$$
Distribution of Energies of Emitting and Absorbing Gamma-Rays

Fig. 11

Geometry of a Mössbauer Spectrometer

Fig. 12

The Form of the Mössbauer Absorption Spectrum

Fig. 13
where the symbols have been defined previously. For Fe$^{57}$, \( \nu \) is 0.0945 nm sec$^{-1}$. A Doppler velocity of this magnitude is readily attained by mechanical or electromechanical devices.

The basic elements of the Mössbauer effect apparatus consist of a radioactive source emitting gamma-rays and subject to a first-order Doppler shift, an absorber and a detector (Fig. 12). If the gamma-ray count by the detector is plotted against the relative Doppler velocity, a Mössbauer spectrum is obtained, (Fig. 13). Resonant absorption is indicated by a minimum in the count-rate due to gamma-rays being absorbed and re-radiated by the absorber into \( 4\pi \) radians.

The application of the Mössbauer effect to chemistry depends on the interactions between the nuclear energy levels and the extra-nuclear electrons, which result from the nature of the chemical bonds of both the emitting and absorbing atoms. These interactions are listed in Table (12). The Mössbauer effect is therefore a useful technique for the study of bonding and structure of compounds.

TABLE 12

<table>
<thead>
<tr>
<th>Type</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0 (electric monopole)</td>
<td>Isomer Shift, ( \delta )</td>
</tr>
<tr>
<td>E2 (electric quadrupole)</td>
<td>Quadrupole Splitting, ( \Delta E )</td>
</tr>
<tr>
<td>M1 (magnetic dipole)</td>
<td>Hyperfine Zeeman splitting</td>
</tr>
</tbody>
</table>

ii) **ISOMER SHIFT, \( \delta \)**

If the source and absorber are both in identical chemical environments, no relative velocity is needed to bring about resonant absorption. When they are unequivalent there will be a difference in their transition
energies. This difference results in the isomer or chemical shift, \( \delta \), of the resonance absorption line. It arises from the fact that the nucleus is not a point charge but occupies a finite volume of space and, as a first approximation, can be considered to be spherical. As such, there is an interaction between the nucleus and the electrostatic field due to the s-electron charge cloud. Since the electronic environment of the nucleus is related to the chemical identity of the lattice in which the nucleus is embedded, the nucleus-electrostatic field interaction can be related to the chemical nature of the material. A relationship between the isomer shift and the electron density at the nucleus can be simply derived as follows.

The nucleus is assumed to be a uniformly charged sphere whose radius, \( R \), is given by the empirical radius formula, and the electronic charge density, \( \rho \), is assumed to be uniform over nuclear dimensions.

The difference between the electrostatic interaction of a hypothetical point nucleus and one of radius \( R \), both having the same charge, is calculated in order to simplify the problem.

For a point nucleus the electrostatic potential \( V_p \) is:

\[
V_p = \frac{Ze}{r} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (43)
\]

For a finite size nucleus of radius \( R \), the potential will equal \( V_p \) for \( r>R \), but equal \( V \), given by the equation:

\[
V = \frac{Ze}{R} \left[ \frac{3}{2} - \frac{r^2}{2R^2} \right] \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (44)
\]

for \( r<R \).

The energy difference, \( \delta E \), is given by the integral:

\[
\delta E = \int_{0}^{\infty} \rho(V-V_p) 4\pi r^2 dr \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (45)
\]

Since \( 4\pi r^2 \) is the area of a sphere.

Therefore, \( \delta E = \frac{4\pi}{5} \int_{0}^{R} \left( \frac{3}{2} - \frac{r^2}{2R^2} - \frac{r}{R} \right) r^2 dr \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (46) \)

\[
= \frac{2\pi}{5} Ze\rho R^2 = \frac{2\pi}{5} Ze^2 \left| \psi(0) \right|^2 R^2 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (47)
\]
where \(-e|\psi(\sigma)|^2\) is an alternative expression for the electronic charge density, \(\rho\).

Equation (47) relates the electrostatic energy of the nucleus to its radius, which will differ for the ground and excited states. Measurements are not made on the absolute location of individual nuclear levels but on the gamma-rays resulting from transitions between such levels. So the energy of the gamma-ray represents the difference in electrostatic energy of the nucleus in two different states which differ only in radius.

The expression for the change in energy of the gamma-ray due to the nuclear electrostatic interaction is the difference of two terms like equation (47), for the nucleus in the ground and excited states:

\[
\delta E_{\text{ex}} - \delta E_{\text{gd}} = \frac{2\pi}{5} Ze^2 \left|\psi(\sigma)|^2 \left(R_{\text{ex}}^2 - R_{\text{gd}}^2\right) \right.
\]

here, \(\delta E\) for the point nucleus drops out (see Fig. 14).

If a convenient substance is chosen as a standard, a measure of the small difference in energy of gamma-rays needed for resonance absorption for different environments of the nucleus can be made, i.e., for Fe\(^{57}\) differences of the order of 10\(^{-10}\) eV can be easily detected.

The shift relative to some standard absorber is obtained by taking the difference of equation (48), written both for the standard source and an absorber:

\[
\delta = \frac{2\pi}{5} Ze^2 \left( R_{\text{ex}}^2 - R_{\text{gd}}^2 \right) \left| \psi(\sigma)|^2 - \psi(\sigma)|^2 \right|
\]

\[
\delta = \frac{4\pi}{5} Ze^2 R^2 \left( \frac{\delta R}{R} \right) \left| \psi(\sigma)|^2 - \psi(\sigma)|^2 \right|
\]

\[
\delta = \text{constant} \left( \frac{\delta R}{R} \right) \left| \psi(\sigma)|^2 \right.
\]

where \(\delta\), is the isomer shift, \(\delta R = R_{\text{ex}} - R_{\text{gd}}\) and \(\delta |\psi(\sigma)|^2\) is the change in s-electron density at the nucleus in going from the source to the absorber. It can be seen that the isomer shift is the product of a constant, a nuclear term, \(\frac{\delta R}{R}\), which contains the difference between the radius
of the isomeric excited and ground states and a chemical term, \( \delta \left| \psi_n^e \right|^2 \), which is a measure of the total charge density at the nucleus (see Fig. 14).

In order to obtain information on the change in total electron density from observed isomer shift values, a value must be established for the nuclear term, \( \delta R \). For Fe\(^{57} \) it has been found to be negative and it can be concluded from equation (51) that as the electron density increases, \( \delta \) decreases i.e. moves to lower velocities (see Fig. 14).

Only the electrons in the s-orbitals have a finite probability of being found at the nucleus. The isomer shift decreases with increase in s-electron density.

In Fe\(^{57} \) the isomer shift can be said to be proportional to the sum of contributions for 1s-, 2s-, 3s- and 4s-orbitals, therefore:

\[
\delta = -K \sum_{n=1}^{4} \left| \psi_n^s \right|^2
\]

where \( K \) is the constant of proportionality. The 1s and 2s contributions are very large but virtually constant and independent of the chemical environment. The contributions from the 3s and 4s orbitals are small but variable. In chemical compounds, the isomer shift will therefore depend on the s-electron density at the nucleus, which is affected by:

a) the oxidation state of the absorbing atom.
b) the electron withdrawing power of electronegative groups near the absorbing atom.
c) the effects of p- and d-electron shielding in the nucleus of the absorbing atom.
d) covalent bonding involving s-, p- and d- electrons.
e) the de-shielding effects of d- back-bonding.

The isomer shift is also sensitive to pressure and temperature. It has been shown that for metallic iron the s-electron density increases with increase in pressure.
Origin of the Isomer Shift in Mössbauer Spectroscopy

\[ \delta E = \frac{2\pi Z e^2}{5} |\psi_s(0)|^2 R^2 \quad \text{(Relative to Point Nucleus)} \]

\[ E_s = E_0 + \frac{2\pi Z e^2}{5} |\psi_s(0)|^2 \left[ R_{ex}^2 - R_{gd}^2 \right] \]

\[ E_a = E_0 + \frac{2\pi Z e^2}{5} |\psi_a(0)|^2 \left[ R_{ex}^2 - R_{gd}^2 \right] \]

\[ \delta = E_a - E_s = \frac{2\pi Z e^2}{5} \left[ |\psi_a(0)|^2 - |\psi_s(0)|^2 \right] \left[ R_{ex}^2 - R_{gd}^2 \right] \]

Fig. 14
The temperature effect on the isomer shift is generally small. It is known that between 150°K and 350°K the temperature function is almost linear and the isomer shift increases with decrease in temperature of the absorber. This is called the 'thermal red-shift' or the second-order Doppler effect. The second-order Doppler shift does not broaden the Mössbauer line but moves it to a higher energy on cooling the absorber. If the absorber and emitter are both at the same temperature, no shift in energy is observed.

The second-order Doppler shift is the change in the energy of the emitted gamma-ray due to the fact that the vibrational energy of the host crystal increases because of the decrease in the mass of the emitting nucleus during the emission process. It has been shown that when a gamma-ray of energy \( E \), is emitted the nuclear mass \( m \), changes according to the following equation:

\[
\delta m = \frac{-E}{c^2}
\]

where \( c \) is the velocity of light. But the thermal momentum, \( p \), of the gamma-ray is unchanged, since the host crystal takes up all the recoil momentum. The reduced mass, however, causes an increase in the kinetic energy of the atom, \( E_k \).

\[
\delta E_k = \left( \frac{2E}{\delta m} \right) \delta m = \left( \frac{-p^2}{\delta m c^2} \right) \left( \frac{-E}{c^2} \right) = \frac{1}{2} \frac{E}{c^2} \left( \frac{\gamma}{c} \right)^2
\]

This energy must come from somewhere and it is in fact drained off from the energy of the gamma-rays. The centre of the peak is shifted by an amount given by equation (54).

Since the isomer shift arises from the difference in \( |\Psi_s(\phi)|^2 \) between source and absorber, absolute values of isomer shift have little significance. To overcome this, isomer shifts are reported for a particular source and a reference absorber, usually sodium nitroprusside.
The magnitude of the isomer shift in high-spin iron compounds gives direct information about the oxidation state. As d-electrons are removed in going from the $+1$ to $+6$ oxidation state, the shielding of the s-electrons diminishes and their density at the nucleus increases leading to a diminishing isomer shift as $\delta E$ is negative (see Table 13).

Table 13

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>$+1$</th>
<th>$+2$</th>
<th>$+3$</th>
<th>$+4$</th>
<th>$+6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer Shift</td>
<td>$-2.3$</td>
<td>$-1.5$</td>
<td>$-0.7$</td>
<td>$-0.2$</td>
<td>$-0.6$</td>
</tr>
</tbody>
</table>

For low-spin iron compounds the isomer shift tends to be rather independent of oxidation state from $-2$ to $+2$. This has been used as an experimental verification of Pauling's old electroneutrality rule which suggests that in low-spin complexes the central atom tends towards charge neutrality independently of its formal oxidation state.

Isomer shifts for iron in $+2$ and $+3$ oxidation states can be estimated as indicated as in Fig. 15.

In a series of low-spin complexes of the general formula $[\text{Fe(CN)}_5\text{L}]^{n-}$, information about charge delocalisation with $\pi$-bonding ligands has been obtained from the values of the isomer shift. The $\pi$-back-bonding de-shields the nucleus by removing d-electrons and hence the strongest $\pi$-bonder ($\text{NO}^+$) has the highest s-electron density at the nucleus and smallest isomer shift.

$\delta_L$: $\text{HNO}^+ > \text{CO} > \text{CN}^- > \text{SO}_2^2 > \text{Ph}_3\text{P} > \text{NO}_2^- > \text{NH}_3$

The interpretations of isomer shift data for iron compounds can be found throughout the Mössbauer literature. When applicable, various interpretations will be mentioned in the Discussion.
Isomer Shifts for Iron(II) and Iron(III) Compounds

Fig. 15

Nuclear Quadrupole Moment

Fig. 16
iii) QUADRUPOLE SPLITTING, $\Delta E$

It was assumed in the last section that the nucleus had a spherical, positive charge distribution. If both conditions are relaxed there will be a quadrupole moment associated with the nucleus. The interaction can occur if the nucleus experiences an electric field gradient (EFG) due to any non-uniformity of electronic charge. The interaction between the EFG and the nuclear quadrupole moment results in non-degeneracy of some nuclear energy levels.

**Nuclear Quadrupole Moment, $Q$.**

The nuclear quadrupole moment reflects the deviation of the nucleus from spherical symmetry with respect to the spin axis. An oblate nucleus has a negative quadrupole while a prolate one has a positive moment (see Fig. 16). Nuclei whose spin is 0 or $\frac{1}{2}$ are spherically symmetric and have a zero quadrupole moment whereas levels with spin $\geq 1$ possess nuclear quadrupole moments.

In the case of Fe$^{57}$, the ground state has $I = \frac{1}{2}$ and no quadrupole moment but the excited state has $I = 3/2$ and has been shown to have a moment.

**Electric Field Gradient, $q$.**

This depends on the electronic configuration about the nucleus and on the nature and disposition of the metal ions nearest neighbours. It has been defined by the equation:

$$ q = V_{zz} \frac{\partial^2 V}{\partial z^2} $$

where $V_{zz}$ is the second derivative $\frac{\partial^2 V}{\partial z^2}$ of the electrostatic potential, $V$. There is also an asymmetry parameter, $\eta$, which gives the deviation of the
EFG from cylindrical symmetry. This is given by the equation:

\[ \gamma = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{56} \]

where \( V_{xx} \) and \( V_{yy} \) are the second derivatives \( \frac{\partial^2 V}{\partial x^2} \) and \( \frac{\partial^2 V}{\partial y^2} \) respectively, of the electrostatic potential, \( V \).

The EFG may be expressed as the sum of the EFG's arising from the electronic configuration about the nucleus (\( q_{\text{val}} \)), and the EFG arising from the charge distribution of neighbouring ions in the lattice (\( q_{\text{lat}} \)):

\[ q = (1-R)q_{\text{val}} + (1+\gamma_{\alpha})q_{\text{lat}} \tag{57} \]

where \( R \) is the Sternheimer shielding factor (positive, \(< 1\)), which corrects for the effects of polarisation of the inner electron core by the EFG of the valence charge, and \( \gamma_{\alpha} \) is the Sternheimer anti-shielding factor (negative, \( > 1 \)), which serves to correct for the effect of polarisation at the inner core by the EFG of the lattice charge distribution. The magnitude of the Sternheimer factors depend on the spin and valence states of the atom concerned.

The lattice contribution to the EFG is defined as:

\[ q_{\text{lat}} = \sum_{i} \frac{Z_i (3 \cos^2 \theta_i - 1)}{r_i^3} \tag{58} \]

where \( Z_i \) and \( (r_i, \theta_i) \) are the charge and radial co-ordinates respectively of the \( i \)th ion in the lattice. The direct determination of \( q_{\text{lat}} \) requires an accurate knowledge of the positions and charges for all the species in the lattice.

The sign and size of the valence contribution to the EFG are dependent on the expectation values, \( EV \), for each of the 3d-orbital wave functions. The equation for the EFG produced by an electron in an atomic orbital is:
\[ q_{\text{val}} = \langle 3 \cos^2 \theta - 1 \rangle \langle r^{-3} \rangle \]  
.....(59)

where the co-ordinates of the charge are \( \theta, \phi, \) and \( r \).

For example, for an electron in the \( d^2 \) orbital, the expectation value can be written as:

\[ EV = \langle d^2 \mid 3 \cos^2 \theta - 1 \mid d^2 \rangle \]  
.....(60)

\[ = \int d^2 (3 \cos^2 \theta - 1) d^2 d\tau \]  
.....(61)

where \( d\tau = \sin \theta d\theta d\phi \)

Therefore \( EV = \int \int \int (3 \cos^2 \theta - 1)^3 \sin \theta d\theta d\phi \)  
.....(62)

Thus \( q = -\frac{\hbar^2}{\gamma} \langle r^{-3} \rangle 3d \)

The contributions made to the EFG from all the \( 3d \)-orbitals are given in Table 14.

**TABLE 14**

<table>
<thead>
<tr>
<th>Orbital</th>
<th>( d_{x^2-y^2} )</th>
<th>( d_{z^2} )</th>
<th>( d_{xy} )</th>
<th>( d_{xz} )</th>
<th>( d_{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q \langle r^{-3} \rangle )</td>
<td>+( \frac{\hbar^2}{\gamma} )</td>
<td>-( \frac{\hbar^2}{\gamma} )</td>
<td>+( \frac{\hbar^2}{\gamma} )</td>
<td>-2/( \gamma )</td>
<td>-2/( \gamma )</td>
</tr>
</tbody>
</table>

The interaction between the nuclear quadrupole moment, \( Q \), and the EFG, \( q \), is expressed by the Hamiltonian:

\[ \tilde{H} = \frac{e^2 q Q}{4I(2I-1)} [3I_{x^2} - I(I+1) + \frac{n}{2} (I_+^2 + I_-^2)] \]  
.....(63)

where \( I \) is the nuclear spin operator, \( I_x, I_y \) and \( I_z \), the resolved components of \( I \) along the \( x, y \) and \( z \)-axis respectively and \( I_+ \) and \( I_- \) the shift operators. The Hamiltonian (63), has the eigenvalues:

\[ E = \frac{e^2 q Q}{4I(2I-1)} [3m_I^2 - I(I+1)] \cdot (1+\frac{n^2}{3})^{\frac{1}{2}} \]  
.....(64)

where \( m_I = I, I-1 \ldots -I \).

For \( Fe^{57} \) the ground state has a nuclear spin \( I = \frac{3}{2} \), \( Q = 0 \), and therefore remains unsplit. The excited state has \( I = 3/2 \) and so is split into two levels which are equally spaced and separated by:
\[ \Delta E = \frac{1}{4} e^2 Q (1 + \gamma^2/3)^{3/2} \] 

\[ = \text{constant} \cdot e^2 Q \]

where \( \Delta E \) is the quadrupole splitting.

Since the nuclear quadrupole moment, \( Q \), for a particular nuclide is constant, it is evident that \( \Delta E \) is directly proportional to the EFG. The quadrupole splitting in Fe\(^{57} \) is shown in Fig. 17.

The absorber sample is studied either as a single crystal or as a powder. The intensity of the quadrupole lines may yield additional information to that obtained from the magnitude of the splitting (see below). In the case of pure quadrupole splitting the \(+\frac{3}{2}\) and \(-\frac{3}{2}\) magnetic substates remain degenerate, as do the \(+\frac{1}{2}\) and \(-\frac{1}{2}\) states. The relative transition probabilities and angular intensity dependences of the two quadrupole lines for \( I = \frac{3}{2} \) to \( I = \frac{1}{2} \) are given in Table 15, where \( \theta \) is the angle from the axis of the symmetry.

**TABLE 15**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Probability</th>
<th>Angular Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pm \frac{3}{2} \rightarrow \pm \frac{3}{2} )</td>
<td>1</td>
<td>( 3/2(1 + \cos^2 \theta) )</td>
</tr>
<tr>
<td>( \pm \frac{1}{2} \rightarrow \pm \frac{1}{2} )</td>
<td>1</td>
<td>( 1 + 3/2 \sin^2 \theta )</td>
</tr>
</tbody>
</table>

The maximum difference in intensity occurs where \( \theta = 0 \), where the ratio of intensities is 3. At \( 90^\circ \) the ratio is \( 3/5 \).

For a powdered sample the intensity averaged over a sphere is the same for both lines. It has been noted, however, for many samples that the two peaks are not always of equal intensity. Several reasons have been given to explain this effect, which is sometimes referred to as the Gol'danskii effect.

i) There may be a preferred direction of orientation in the sample.

ii) There is a magnetic effect due to a preferential orientation of the magnetically ordered domains.
Origin of the Quadrupole Splitting in Mössbauer Spectroscopy

Fig. 17
iii) The angular dependence for each transition in Table 13 will have a term \( f(\theta) \) and even after integration over a sphere the ratio of intensities will not be unity.

The magnitude of the quadrupole splitting yields the most information to the chemist and explanations of it are given below and, when necessary, in the Discussion.

**High-spin ferric compounds**

The half-filled shell of an octahedral high-spin \( 3d^5 \) (\( ^6S \)) ferric ion is spherically symmetric (see Fig. 13) and gives no valence contribution to the EFG.

Thus \( q = (1 - Y_\omega)q_{lat} \)

The small value of quadrupole splitting which may be observed is due to the EFG which arises from \( q_{lat} \).

Values of \( \Delta E \) range from zero for a cubic environment to \(-1.5 \text{ mm sec}^{-1}\) for non-cubic, the usual range lying between 0.30 to 0.70 \( \text{mm sec}^{-1} \). In some exceptional cases values of several \( \text{mm sec}^{-1} \) have been observed.

**High-spin ferrous compounds**

A high-spin \( 3d^6 \) (\( ^5D \)) ferrous ion has one electron outside the spherically symmetric half-filled shell \( d_e^3 d_g^2 \) (see Fig. 18). This single electron gives rise to a large EFG which produces large \( \Delta E \) values ranging from 1.50 to 3.6 \( \text{mm sec}^{-1} \). The extra \( d_e \)-electron has an equal probability of being found in the \( d_{xy}, d_{yz}, \) or \( d_{xz} \) orbital if the \( d_e \) levels are degenerate. If the symmetry is not cubic, this degeneracy will be removed, and at sufficiently low temperatures only the lowest \( d_e \) level will be occupied and this accounts for the temperature dependence of the quadrupole splitting. Thus the maximum value of \( \Delta E \) occurs at low temperatures. By studying the effect of temperature on \( \Delta E \) it is possible to make an estimation of the separation in energy between the \( d_e \) levels.
Low-spin ferric compounds

The low-spin $3d^5$ ($^2D$) ferric ion in an octahedral environment can be visualised as a single electron hole in an otherwise complete $d_5$ level. $\Delta E$ values similar to those of high-spin ferrous could be expected but this is not always the case. Low-spin ferric compounds can show larger variations in $\Delta E$ values than high-spin ferrous compounds, for example

$$\Delta E \text{ mm sec}^{-1} \text{ at } 300^\circ K$$

\[ K_3[\text{Fe(CN)}_6] \quad 0.30 \]
\[ \text{Na}_2[\text{Fe(CN)}_5\text{H}_2\text{O}] \quad 1.82 \]

This could be the result of d-electron delocalisation since $c_{\text{val}}$ is proportional to $<r^{-3}>$ any change in $r$ will affect $\Delta E$.

For low-spin ferric and high-spin ferrous complexes which exhibit a large variation of $\Delta E$ with temperature, the temperature coefficient is

$$\frac{-2\Delta E}{T} = 0.06 \text{ to } 0.90 \text{ mm sec}^{-1}/100^\circ K$$

The coefficient is generally large when the $d_5$ levels are close together and small when the levels are widely separated.

Low-spin ferrous compounds

Octahedral low-spin $3d^6(1S)$ ferrous complexes of the form $[\text{Fe(CN)}_6]^{4-}$ show no $\Delta E$ at any temperature. This is to be expected for a completely filled $d_5$ level (see Fig. 18) and a cubic symmetry i.e. there should be no valence contribution to the EFG. However compounds of the form $[\text{Fe(CN)}_5X]^{3-}$ can have large $\Delta E$ values, for example

$$\Delta E \text{ mm sec}^{-1} \text{ at } 80^\circ K$$

\[ \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \quad 1.73 \]
\[ \text{Na}_2[\text{Fe(CN)}_5\text{NH}_3] \quad 0.67 \]
Occupation of the d-Orbitals and the Spin-States of Iron in Various Octahedral Compounds

<table>
<thead>
<tr>
<th>Iron(III), 3d⁵</th>
<th>Iron(II), 3d⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-Spin (d_x^3 d_y^2)</td>
<td>High-Spin (d_x^4 d_y^2)</td>
</tr>
<tr>
<td>IONIC</td>
<td>IONIC</td>
</tr>
<tr>
<td>(d_y) up</td>
<td>(d_y) up</td>
</tr>
<tr>
<td>(d_x) up</td>
<td>(d_x) up</td>
</tr>
<tr>
<td>Low-Spin (d_x^5)</td>
<td>Low-Spin (d_x^6)</td>
</tr>
<tr>
<td>COVALENT</td>
<td>COVALENT</td>
</tr>
</tbody>
</table>

Fig. 18

Values for the Quadrupole Splitting in Iron(II) and Iron(III) Compounds

Low-Spin Ferrous

Low-Spin Ferric

High-Spin Ferrous

High-Spin Ferric

\[ \Delta E \text{ mm sec}^{-1} \]

Fig. 19
The appreciable quadrupole is practically independent of temperature and is due to the substitution of one of the cyanide groups by a π-bonding ligand. This distorts the octahedral symmetry and gives rise to a large EFG due to the π-delocalisation of the $d_{xz}$ and $d_{yz}$ electrons into π-antibonding orbitals on the π-bonding ligand, the stronger the π-bonding ligand the larger ΔE.

Typical values of ΔE for iron in various oxidation and spin states are given in Fig. 19.

Mössbauer spectroscopy has played a valuable role in establishing the occurrence of high-spin± low-spin equilibria. It has been shown that the temperature dependence of the magnetic moment of certain $d^5$ iron(III)-tris(diallyldithiocarbamates) was due to the $^6A_1 - ^2T_2$ crossover at lower temperatures. Room temperature results of $\delta$, ΔE and $\mu_{\text{eff}}$ for a high-spin and a low-spin complex are given in Table 16. Intermediate spin state iron(III)-tris(diallyldithiocarbamates) have intermediate values for $\delta$, ΔE and $\mu_{\text{eff}}$.

**Table 16**

<table>
<thead>
<tr>
<th>[Fe(III)-(S$_2$CNR$_2$)$_2$] at Room Temperature</th>
<th>11$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe}(S_2\text{CNR}_2)_2]_3$</td>
<td>$\delta^{\text{MM sec}^{-1}}$</td>
</tr>
<tr>
<td>R = n-butyl</td>
<td>0.72</td>
</tr>
<tr>
<td>R = iso-propyl</td>
<td>0.64</td>
</tr>
</tbody>
</table>

$^\text{x}$Relative to sodium nitroprusside

A temperature-induced $^5T_2 - ^1A_1$ transition in $d^6$, iron(II) complexes has also been established by Mössbauer spectroscopy. At room temperature $[\text{Fe(II)phen}_2(\text{NCS})_2]$ (phen = 1,10-phenanthroline) has $\delta$ and ΔE typical of high-spin iron(II) compounds. At lower temperatures $\delta$ and ΔE
diminish to values characteristic of low-spin iron(II) in a distorted octahedral environment (see Table 17)

Table 17
High-spin ($^5T_2$) - Low-spin ($^1A_1$) Transition in [Fe(II)phen$_2$(NCS)$_2$]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T^0$K</th>
<th>$\delta$ mm sec$^{-1}$</th>
<th>$\Delta E$ mm sec$^{-1}$</th>
<th>$\mu_{eff}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Fe(II)($^5T_2$)</td>
<td>-</td>
<td>1.30</td>
<td>2.50</td>
<td>5.2</td>
</tr>
<tr>
<td>[Fe(II)phen$_2$(NCS)$_2$]</td>
<td>293</td>
<td>1.33</td>
<td>2.67</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>0.72</td>
<td>0.34</td>
<td>0.6</td>
</tr>
<tr>
<td>Typical Fe(II)($^1A_1$)</td>
<td>-</td>
<td>0.80</td>
<td>0.30</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Relative to sodium nitroprusside

iv) MAGNETIC HYPERFINE SPLITTING

A brief discussion will be given on magnetic hyperfine splitting which arises because of the interaction of the nuclear magnetic dipole moment with a magnetic field, although no such measurements were made in this work.

Magnetic hyperfine splitting is effectively the hyperfine Zeeman splitting of the nuclear energy levels in the presence of a magnetic field which can arise from several sources:

i) ferromagnetic exchange interaction as in iron metal.

ii) antiferromagnetic exchange as in Fe$_2$O$_3$.

iii) paramagnetic species provided that the spin-lattice relaxation time is long with respect to the life time of the Mössbauer excited state.

iv) application of a substantial external magnetic field.

Each level of spin quantum number I will be split into $(2I+1)$ sub-levels except when I=0, in which case there is no hyperfine splitting.
The Hamiltonian of the magnetic interaction is given as:

\[ \mathcal{H} = -\mu \cdot H \]  \hspace{1cm} \ldots (67)

where \( \mu \) is the nuclear magnetic dipole moment and \( H \) the magnetic field at the nucleus.

The energies of the sub-levels are given by:

\[ E_m = \frac{-\mu H m_I}{I} \]  \hspace{1cm} \ldots (68)

where \( m_I \), the magnetic quantum number, takes the values \( I, I-1 \ldots -I \). The splitting between adjacent levels is \( \frac{\mu H}{I} \).

The magnetic field will cause the nuclear levels \( I=\frac{3}{2} \) and \( I=3/2 \) to split further into two and four energy levels respectively (see Fig. 20). As a result of the selection rule \( (\Delta m_I=0,\pm 1) \), only six of the possible lines are observed as shown in Fig. 20.

The probabilities of transition as well as the relative intensities of the lines are given in Table 18.

<table>
<thead>
<tr>
<th>Transition</th>
<th>( \Delta m_I )</th>
<th>Relative Probability</th>
<th>Angular Dependence ( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( +3/2 \rightarrow +\frac{1}{2} )</td>
<td>-1</td>
<td>3</td>
<td>( 9/\lambda (1+\cos^2\theta) )</td>
</tr>
<tr>
<td>( -3/2 \rightarrow -\frac{1}{2} )</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( +\frac{1}{2} \rightarrow +\frac{1}{2} )</td>
<td>0</td>
<td>2</td>
<td>( 3 \sin^2 \theta )</td>
</tr>
<tr>
<td>( -\frac{1}{2} \rightarrow -\frac{1}{2} )</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( +\frac{1}{2} \rightarrow +\frac{1}{2} )</td>
<td>+1</td>
<td></td>
<td>( 3/\lambda (1+\cos^2\theta) )</td>
</tr>
<tr>
<td>( +\frac{1}{2} \rightarrow -\frac{1}{2} )</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\( \theta \) is the angle between the direction of the magnetic field and the direction of the emission of the gamma-ray.
Origin of the Magnetic Hyperfine Splitting in Mössbauer Spectroscopy

$I$

$\frac{1}{2}$

$\frac{1}{2}$

ISOMER SHIFT

MAGNETIC DIPOLE SPLITTINGS

$\frac{1}{2}$

$\frac{1}{2}$

$-\frac{1}{2}$

$+\frac{1}{2}$

$+\frac{3}{2}$

source velocity mm sec$^{-1}$

relative count rate

$\text{Fig. 20}$
Good agreement has been found for the ground state splitting \((+\frac{1}{2}, -\frac{1}{2})\) in metallic iron from Mössbauer and n.m.r. data. The splittings of the excited state are separated by equal intervals and this has been widely used as a calibration standard and to test the linearity of the velocity scale.

The magnetic hyperfine interaction of the Mössbauer effect has been used in the study of magnetically ordered structures and in the determination of the Curie and Neel temperatures. The Curie temperature is the temperature at which the saturation magnetisation goes to zero. The temperature at which the thermal motion destroys the antiparallel orientation of neighbouring dipoles characteristic of antiferromagnetic materials is known as the Neel temperature.
5. **OBJECT OF THE WORK**

The objects of the work were:

(1) To prepare certain of the salen-iron(II) complexes which had been reported during a previous study, with a view to improve the method of preparation and to investigate the Mössbauer properties of the complexes.

(2) To prepare and investigate the Mössbauer properties of the nitrosyl salen and 5-nitrosalen iron which had previously been shown to exhibit spin-state isomerism; then to attempt the preparation of new nitrosyls of Schiff base iron(II) complexes and investigate their magnetic and Mössbauer properties.

(3) To prepare and investigate the adducts of bis(salicylaldehydehydato)iron(II).

(4) To investigate the magnetic and Mössbauer properties of other iron complexes in which spin-state isomerism might occur.
EXPERIMENTAL
1. PREPARATION OF LIGANDS

The aldehydes were obtained commercially unless otherwise stated, the preparative methods of Diehl being generally successful.

i) NN'-Ethylenebis(salicylideneimine) [Salen]

An ethanolic solution of ethylenediamine (30.5g = 0.5mole) was added to a boiling ethanolic solution of salicylaldehyde (121.7g = 1.0mole). The yellow solid which immediately precipitated was filtered off and recrystallised from 96% ethanol. The yellow crystals were dried in air at 100-110°, m.p. = 125-6°; Lit.m.p. = 123°:

Found: C, 71.72; H, 6.09; N, 10.61%.

C16H16N2O2 requires C, 71.63; H, 6.01; N, 10.44%.

ii) NN'-Phenylenebis(salicylideneimine) [Salphen]

Salicylaldehyde was condensed with σ-phenylenediamine as in (i), the product being recrystallised from dimethylformamide. The orange crystals were dried in air at 120°, m.p. = 162-4°; Lit.m.p. = 163°:

Found: C, 75.98; H, 5.18; N, 8.86%.

C20H16N2O2 requires C, 75.91; H, 5.10; N, 8.86%.

iii) NN'-Ethylenebis(3-methoxysalicylideneimine) [3-methoxysalen]

The preparation was performed as in (i) from commercial σ-vanillin. The yellow-orange crystals were dried in air at 120-140°, m.p. = 161-2°; Lit.m.p. = 161°:

Found: C, 65.82; H, 6.23; N, 8.56%.

C18H20N2O4 requires C, 66.25; H, 5.57; N, 8.59%.

iv) NN'-Ethylenebis(5-methylsalicylideneimine) [5-methylsalen]

5-Methylsalicylaldehyde was prepared from p-cresol by Liggett and Diehl's modification of the Duff reaction. The aldehyde was condensed with ethylenediamine as in (i), the product being recrystallised from 96% ethanol. The yellow crystals were dried in air at 110-120°, m.p. = 165°;
Lit.m.p. = 164°:
Found C, 72.52; H, 6.67; N, 9.37%.
C_{18}H_{20}N_{2}O_{2} requires C, 72.75; H, 6.82; N, 9.45%.

v) 5-Nitrosalicylaldehyde

Salicylaldehyde was nitrated by Diehl's method^{143}.
The mononitration yielded both 3- and 5-nitrosalicylaldehydes. The isomers were separated as described^{143} and the 5-nitrosalicylaldehyde was recrystallised from 96% ethanol. The yellow-tan needles were dried in a vacuum desiccator, m.p. = 105-116° (dec.); Lit.m.p. = 126°:
Found: C, 50.98; H, 3.03; N, 7.94%.
C_{7}H_{5}NO_{4} requires C, 50.30; H, 3.02; N, 8.38%.
To ensure that the 5-nitro isomer was free from the 3-nitro isomer, thin-layer chromatography was used. Solutions of approximately equal concentrations of each isomer in acetone, and a mixture of equal volumes of each acetone solution were used. With silica-gel plates and chloroform as solvent the following Rf values were obtained.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Solution</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-nitro</td>
<td>Pure</td>
<td>0.47</td>
</tr>
<tr>
<td>&quot;</td>
<td>Mixture</td>
<td>0.46</td>
</tr>
<tr>
<td>5-nitro</td>
<td>Pure</td>
<td>0.74</td>
</tr>
<tr>
<td>&quot;</td>
<td>Mixture</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Both isomers gave only one spot on the plate, and consequently were considered pure.

2. PREPARATION OF BIS(ACETATO)IRON(II)

Owing to the extreme air-sensitivity of bis(acetato)iron(II), as noted by King^{145}, all operations were carried out under nitrogen and all solvents were deoxygenated.
An excess of iron powder was heated in aqueous 1:1 glacial acetic acid until the evolution of hydrogen ceased. The solution was cooled, the excess of iron filtered off and the filtrate evaporated to approximately one-half its original volume. A white precipitate was formed when acetone was added to the pale-green solution. The acetone was decanted and the precipitate washed by further decantation with acetone. The product was then dried by continuous pumping to give a white or pale-green powder. Initially the product, suspended in acetone, was filtered off and then was sealed in pyrex tubes under vacuum. However, hydrolysis occurred immediately when the bis(acetato)iron(II), prepared in this manner, was dissolved in water.

To avoid this difficulty the following method was used to prepare bis(acetato)iron(II) for the preparations described in section 3. The above procedure was performed using 1g of iron powder in 25ml of 1:1 glacial acetic acid. This gave approximately 2.0g of bis(acetato)iron(II) which was kept in the preparation vessel until required. The vessel had been weighed previously so that the weight of the acetate could be approximately obtained. The off-white solid dissolved in water to give a clear, pale-green solution with no apparent hydrolysis provided the solution was used within half an hour. The solid was assumed to be a dihydrate for preparative purposes although the following analyses of samples isolated in sealed tubes show that the degree of hydration can be variable.

Found: (White solid): Fe, 26.48, 26.63%.
C₄H₆O₄Fe.2H₂O requires Fe, 26.60%.

Found: (White solid): Fe, 30.33%.
C₆H₆O₄Fe.½H₂O requires Fe, 30.52%.

Found: (Pale-green solid): Fe, 30.80%.
C₄H₆O₄Fe.½H₂O requires Fe, 30.52%.
3. **PREPARATION OF SCHIFF BASE COMPLEXES OF IRON(II)**

The choice of a suitable iron(II) starting material for the preparation of Schiff base complexes was a problem. If iron(II) sulphate or chloride were used, the strong acid liberated in the reaction had to be removed with sodium hydroxide so as to reduce the chance of ligand hydrolysis. The amount of base had to be accurately known otherwise any excess caused hydrolysis of the iron(II) solution, presumably to hydrated iron oxides which were ferromagnetic. Consequently, bis-(acetato)iron(II) was used as the iron(II) starting material. Then, on reaction, weak acetic acid was liberated which lessened, and in some cases removed, the need for base, and therefore minimised the formation of hydrolysis products. The disadvantage of bis(acetato)-iron(II) was its extreme air-sensitivity. The main problem with the preparation of Schiff base complexes of iron(II) was their ease of oxidation, and the preparative techniques for air-sensitive compounds described elsewhere have been used. Two methods of preparation were used:

**Type (1).** Reaction of an aqueous solution of bis(acetato)iron(II) with a solution of the preformed Schiff base.

**Type (2).** Reaction of a primary amine with bis(salicylaldehydato)diaquoiron(II).

(The preparation of this complex is described in section 5)

Bis(acetato)iron(II) was the iron(II) starting material for all the following preparations except NN'-bis-(salicylideneiminato)iron(II) for which aqueous iron(II) sulphate was used. All operations were carried out under nitrogen and all solvents were deoxygenated. All compounds were dried by continuous pumping and sealed in pyrex tubes unless otherwise mentioned. The colour code for each compound is given in brackets after its colour.
(a) Preparations of Type 1

(i) Salen iron(II)

An ethanolic solution of salen (2.04 g = 7.66 x 10^{-3} moles) was added slowly to an aqueous solution of bis(acetato)iron(II) (1.43 g = 6.81 x 10^{-3} moles). A red-brown crystalline solid appeared and the reaction mixture was boiled for ten minutes. After the suspension had cooled the solid was filtered off and washed with 96% ethanol. The dry product was a finely crystalline, brown (7E6) solid, moderately stable in air.

Found: Fe, 16.73; C, 59.53; H, 5.04; N, 8.73%.

(Fe residue analysis 17.3%) 

C_{16}H_{14}N_{2}O_{2}Fe requires Fe, 17.34; C, 59.65; H, 4.39; N, 8.70%

(ii) 5-Methylsalen iron(II)

The product was obtained as in (i) from bis(acetato)iron(II) (2.10 g = 1.00 x 10^{-2} moles), 5-methylsalen (2.96 g = 1.01 x 10^{-2} moles) and sodium hydroxide (0.64 g = 1.60 x 10^{-2} moles) but using a 9:1 96% ethanol:water mixture for the Schiff base and sodium hydroxide. The dry product was a reddish-brown (8D6) powder which oxidised very rapidly in air. The rapid oxidation is reflected in the analysis figure for iron.

Found: Fe, 15.27; C, 61.42; H, 5.14; N, 7.92%.

C_{18}H_{18}N_{2}O_{2}Fe requires Fe, 15.95; C, 61.73; H, 5.19; N, 8.00%.

(iii) Salphen iron(II) monohydrate

The product was obtained as in (i) from bis(acetato)iron(II) (1.62 g = 7.71 x 10^{-3} moles) dissolved in 1:1 dimethylformamide: water and salphen (2.44 g = 7.76 x 10^{-3} moles) in dimethylformamide. The product was washed with acetone and when dry was a "fluffy", olive (1E6) solid, moderately stable in air.

Found: Fe, 14.04; C, 61.90; H, 4.51; N, 7.33%.

(Fe residue analysis 14.26%)

C_{20}H_{14}N_{2}O_{2}Fe.H_{2}O requires Fe, 14.39; C, 61.88; H, 4.16; N, 7.22%.
A sample of this compound was heated under reduced pressure for 12 hours at 80-90° with no apparent weight loss. Thermogravimetric analysis in nitrogen indicated that the compound lost weight at 170°.

Found: 4.5% weight loss. A monohydrate requires 4.6%.

iv) 3-Methoxysalen iron(II) monohydrate

The product was obtained as in (i) from bis-(acetato)iron(II) (2.77g=1.32x10^{-2} moles), 3-methoxysalen (4.33g=1.33x10^{-2} moles) and sodium hydroxide (0.80g=2.0x10^{-2} moles) but using a 9:1 96% ethanol:water as solvent for the Schiff base and sodium hydroxide. The product was washed with acetone and when dry was a reddish-brown (8D6) powder moderately stable in air.

Found: Fe, 13.84; C, 54.02; H, 5.02; N, 6.89%.

C_{18}H_{18}N_{2}O_{4}Fe.H_{2}O requires Fe, 13.95; Cm 54.01; H, 5.05; N, 7.00%.

Thermogravimetric analysis in nitrogen indicated that the compound lost weight at 170°.

Found: 3.8% weight loss. A monohydrate requires 4.5%.

(b) Preparations of Type 2

(i) Salen iron(II)

A methanolic solution of freshly distilled salicylaldehyde (2.98g=2.44x10^{-2} moles) and potassium hydroxide (1.02g=1.82x10^{-2} moles) was added slowly to an aqueous solution of bis(acetato)-iron(II) (2.56g=1.22x10^{-2} moles). The purple solid (later shown to be bis(salicylaldehydato)diaquo-iron(II)) which precipitated was filtered off on a weighed sinter protected by taps, washed with acetone, dried under reduced pressure, and the apparatus containing the compound re-weighed.

The dry purple solid (3.64g=1.09x10^{-2} moles) was suspended in 96% ethanol, and an ethanolic solution of ethylenediamine (0.69g=1.15x10^{-2} moles) was slowly added. The reaction mixture was boiled for thirty minutes and allowed to cool. The brown solid obtained was filtered off and washed with acetone. The dry product was brown (7E6) and moderately stable in air.
Found: Fe, 16.93; C, 59.48; H, 4.56; N, 8.66%.

\[ C_{16}H_{14}N_2O_2Fe \] requires Fe, 17.34; C, 59.65; H, 4.39; N, 8.70%.

(ii) Salphen iron(II) monohydrate

The salicylaldehydato-iron(II) complex was obtained as in (i) from bis(acetato)iron(II) 
(2.56g \equiv 1.22 \times 10^{-2} \text{ moles}), salicylaldehyde (2.98g \equiv 2.44 \times 10^{-2} \text{ moles}) and potassium hydroxide (1.02g \equiv 1.82 \times 10^{-2} \text{ moles}).

The salphen complex was then obtained in suspension as in (i) from the dry salicylaldehydato-complex 
(2.57g \equiv 7.47 \times 10^{-3} \text{ moles}) and \( \sigma \)-phenylenediamine 
(0.83g \equiv 7.68 \times 10^{-3} \text{ moles}). A magnetic stirrer was added to the reaction flask at this stage. On heating, a thick, green "sludge" was obtained which prevented any further heating and so the precipitate was stirred for two days to ensure complete reaction. The green solid was filtered off and washed with acetone. The dry product was olive (1D6) and moderately stable in air.

Unfortunately, as reflected in the analyses, products obtained by this method were not as pure as that obtained in (a)(iii) for salphen iron(II) monohydrate.

Found: Fe, 14.75; C, 60.65; H, 4.32; N, 6.42%.

\[ C_{20}H_{14}N_2O_2Fe\cdot H_2O \] requires Fe, 14.39; C, 61.88; H, 4.16; N, 7.22%.

(iii) 5-Nitrosalen iron(II)

A 1:1 96% ethanol:water solution of 5-nitrosalicylaldehyde (3.26g \equiv 9.15 \times 10^{-3} \text{ moles}) and potassium hydroxide (0.82g \equiv 1.46 \times 10^{-2} \text{ moles}) was added slowly to an aqueous solution of bis(acetato)-iron(II) (1.99g \equiv 9.48 \times 10^{-3} \text{ moles}). The brilliant purple solid which precipitated was filtered off on a weighed sinter as in (i) and washed with acetone.
The dry purple-brown solid (2.40g=5.82×10⁻³ moles, assumed to be bis(5-nitrosalicylideneaceta)-iron(II)) was suspended in 96% ethanol, and an ethanolic solution of ethylenediamine (0.37g=6.17×10⁻³ moles) slowly added. The dry brown (6F5) product was obtained as in (i), and was moderately stable in air. Analysis for iron by ignition and by oxine gave similar low results, but the microanalyses were reasonable.

Found: Fe, 12.08; C, 46.85; H, 4.08; N, 13.75%.

C₁₆H₁₂N₄O₆Fe requires Fe, 13.55; C, 46.62; H, 2.94; N, 13.60%.

A different preparation, carried out under similar conditions, yielded what appeared to be a monohydrate.

Found: Fe, 13.01; C, 44.43; H, 3.24; N, 16.01%.

C₁₆H₁₂N₄O₆Fe.H₂O requires Fe, 12.98; C, 44.67; H, 3.29; N, 13.03%.

No explanation for the unsatisfactory nitrogen analyses of this compound can be offered.

Thermal analysis of the monohydrate in nitrogen gave a weight loss of 2.5% at 170°. It was noted that initially the compound appeared to gain weight. A monohydrate requires 4.4% weight loss. However, if oxidation was taking place simultaneously with loss of water the net weight loss would be 2.4%.

(c) Other Preparations

(i) NN'-bis(salicylideneiminato)iron(II)

An ethanolic solution of freshly distilled salicylaldehyde (2.0g=1.64×10⁻² moles) and 0.88 ammonia solution (5.0ml) were added slowly to an aqueous solution of iron(II) sulphate heptahydrate (2.5g=8.99×10⁻³ moles). The brown solid which precipitated was filtered off, washed with
water, dried under reduced pressure for nine hours and then at 110° for three hours, and sealed in pyrex tubes. The dry product was a brownish-red (10D6) powder, rapidly oxidised by air. Found: Fe, 18.99; C, 55.17; H, 4.12; N, 7.49%.

\[ \text{Fe}_{14} \text{H}_{12} \text{N}_{2} \text{O}_{2} \text{Fe} \text{ requires Fe, 18.86; C, 56.78; H, 4.09; N, 9.46%.} \]

The poor microanalytical data reflect the ease of oxidation and the consequent difficulty in analysis.

(ii) Attempted preparation of anhydrous salphen iron(II)

A dimethylformamide solution of salphen (3.37g = 1.05x10^{-2} moles) was added slowly to a suspension of bis(acetato)iron(II) (2.17g = 1.03x10^{-2} moles) in methanol. The reaction mixture was boiled for twenty minutes and left to cool overnight. Shiny black crystals precipitated from the solution. These were filtered off, washed with methanol, dried under reduced pressure for eight hours at 120° and sealed in pyrex tubes. The dry product was black and crystalline, and moderately stable in air. There was no broad band at 3150 cm^{-1} which could be ascribed to water. Two different methods of analysis for iron gave identical but somewhat low results for which no explanation can be suggested.

Found: Fe, 14.37; C, 64.61; H, 4.25; N, 7.39%.

\[ \text{Fe}_{20} \text{H}_{14} \text{N}_{2} \text{O}_{2} \text{Fe requires Fe, 15.09; C, 64.88; H, 3.82; N, 7.57%.} \]

4. PREPARATION OF NITRIC OXIDE DERIVATIVES

Apparatus and methods used in the present work for the preparation of the nitrosyls were as described by King. The nitrosyls were prepared by reacting nitric oxide with the preformed Schiff base complex suspended in 96% ethanol. In order to provide evidence for the nitric oxide: complex stoichiometry, and to see when the reaction was complete, the volume of nitric oxide absorbed was measured.
with a gas burette. The measured molar uptake was always low because:-

a) no correction was made for the vapour pressure of the solvent.

b) nitric oxide was let into the reaction vessel without previous equilibration. However, the suspension was left unstirred until the gas burette and apparatus were filled with nitric oxide, and little reaction appeared to occur so the gas uptake was measured with reasonable accuracy.

c) there was mechanical loss of the iron(II)-Schiff base complex before reaction with nitric oxide.

However, within experimental accuracy one mole of nitric oxide was absorbed by one mole of each Schiff base complex.

i) **Nitrosyl salen iron**

Salen iron(II) was obtained as in section 3a(i) from bis(acetato)iron(II) \((2.26 \text{ g} \equiv 1.08 \times 10^{-2} \text{ moles})\) and salen \((2.88 \text{ g} \equiv 1.07 \times 10^{-2} \text{ moles})\). The brown precipitate was filtered off and resuspended in 96% ethanol in a flat-bottomed flask containing a magnetic stirrer. The nitrogen atmosphere was replaced by nitric oxide and the nitric oxide uptake measured at room temperature, the solution being continuously stirred.

The salen iron(II) gradually darkened and when the nitric oxide uptake was complete the black precipitate was filtered off, washed with acetone and dried under reduced pressure. The product was air-stable, microcrystalline and black.

Nitric oxide uptake 0.8 moles.

Found: Fe, 15.68; C, 54.40; H, 4.11; N, 11.78%.

\(\text{C}_{16}\text{H}_{14}\text{N}_{3}\text{O}_3\text{Fe}\) requires Fe, 15.86; C, 54.46; H, 4.01; N, 11.93%.
ii) **Nitrosyl salphen iron**

Salphen iron(II) monohydrate was prepared as in section 3a(iii) from bis(acetato)iron(II) (1.00g × 4.76x10^{-3} moles) and salphen (1.55g × 4.77x10^{-3} moles). The nitrosyl was obtained as in (i). The product was filtered off, washed with acetone, dried under reduced pressure and sealed in pyrex tubes. It was an air-stable, greyish-brown (SF3) powder.

Nitric oxide uptake 0.8 moles.

Found: Fe, 13.76; C, 60.02; H, 3.64; N, 10.41%.

C_{20}H_{14}N_3O_3Fe requires Fe, 13.95; C, 60.02; H, 3.53; N, 10.50%.

iii) **Nitrosyl 5-nitrosalen iron**

5-nitrosalen iron(II) was prepared in section 3b(iii) from bis(acetato)iron(II) (1.99g × 9.48x10^{-3} moles), 5-nitrosalicylaldehyde (3.26 × 9.15x10^{-3} moles) and potassium hydroxide (0.82g × 1.46x10^{-2} moles). An ethanolic solution of ethylenediamine (0.23g × 3.83x10^{-3} moles) was added to the purple complex (1.51g × 3.66x10^{-3} moles) suspended in 96% ethanol. The nitrosyl was obtained as in (ii). The dry product was an olive (3F5) powder, moderately stable in air.

Nitric oxide uptake 1.0 mole.

Found: Fe, 12.16; C, 44.15; H, 3.12; N, 15.41%.

C_{16}H_{12}N_5O_7Fe requires Fe, 12.63; C, 43.36; H, 2.74; N, 15.84%.

5. **PREPARATION OF ADDUCTS OF BIS(SALICYLALDEHYDATO)-IRON(II)**

These complexes were synthesised from iron(II) sulphate heptahydrate (A.R. grade). The exception was the use of bis(acetato)iron(II) for the preparation of bis(salicylaldehydato)diaquoiron(II). The air-sensitive compounds were prepared under nitrogen using deoxygenated solvents.
a) **Air-sensitive Complexes**

i) **Bis(salicylaldehydato)diaquoiron(II)**

An ethanolic solution of freshly distilled salicylaldehyde (4.21g = 3.45x10^{-2} moles) was slowly added to an aqueous solution of bis(acetato)-iron(II) (2.92 = 1.42x10^{-2} moles). Immediately a heavy, purple solid precipitated from the solution, which was filtered off, washed with 96% ethanol, dried under reduced pressure and sealed in pyrex tubes. The dry product was a brownish-grey (7F2) solid, moderately stable in air.

Found: Fe, 16.33; C, 50.05; H, 4.49%.

C_{14}H_{14}O_6Fe requires Fe, 16.71; C, 50.32; H, 4.23%.

A sample dried under reduced pressure at 100° still showed water absorption at ~ 3300 cm^{-1}.

ii) **Bis(salicylaldehydato)bis(piperidine)iron(II)**

A solution of freshly distilled salicylaldehyde (3.0ml = 2.12x10^{-2} moles) in piperidine (20ml) was added slowly to an aqueous solution of iron(II) sulphate heptahydrate (3.0g = 1.08x10^{-2} moles). A dark-green solid precipitated which was filtered off, washed with acetone, dried under reduced pressure and sealed in pyrex tubes. The dry dark-green (27F4) product decomposed slowly in air and had an unpleasant odour. On washing with water the green precipitate decomposed to the purple diaquo complex.

Found: Fe, 12.35; C, 59.73; H, 6.83; N, 5.87%.

C_{24}H_{32}N_{2}O_4Fe requires Fe, 11.92; C, 61.53; H, 6.90; N, 5.98%.

The analytical data reflect the decomposition of the complex in air.

b) **Air-stable Complexes**

i) **Bis(salicylaldehydato)bis(pyridine)iron(II)**

A solution of freshly distilled salicylaldehyde (3.0g = 2.45x10^{-2} moles) in pyridine (15ml) was
added rapidly to an aqueous solution of iron(II) sulphate heptahydrate (3.0g = 1.08x10^-2 moles).
The reaction mixture was shaken vigorously and a black-purple crystalline solid precipitated. This was filtered off, washed with 1:1 pyridine: water, and water, and dried in a vacuum desiccator to give a dark purple-black crystalline solid which decomposed on standing.
Yield 3.0g, 61%.
Found: Fe, 12.09%. \( \text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4\text{Fe} \) requires Fe, 12.24%.

ii) Bis(salicylaldehydato)bis(\( \beta \)-picoline)iron(II)

The product was obtained as b(i) from iron(II) sulphate heptahydrate (2.5g = 8.99x10^-3 moles), salicylaldehyde (2.0ml = 1.41x10^-2 moles) and \( \beta \)-picoline (25ml). It was washed with acetone and petroleum ether (40-60°), and was a dark green (26F4) crystalline solid which decomposed on standing.
Yield 2.1g, 48%.
Found: Fe, 11.87; C, 62.58; H, 4.99; N, 5.61%.
\( \text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{Fe} \) requires Fe, 11.53; C, 64.47; H, 5.00; N, 5.78%.
The analytical data reflect the rapid decomposition of the complex.

iii) Bis(salicylaldehydato)bis(\( \gamma \)-picoline)iron(II)

The product was obtained as in b(ii) from iron(II) sulphate heptahydrate (2.5g = 8.99x10^-3 moles), salicylaldehyde (2.0ml = 1.41x10^-2 moles) and \( \gamma \)-picoline (25ml), and was a finely crystalline, deep purple-black solid.
Yield 2.8g, 64%.
Found: Fe, 11.30; C, 64.39; H, 5.08; N, 5.97%.
\( \text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{Fe} \) requires Fe, 11.53; C, 64.47; H, 5.00; N, 5.78%.
iv) **Bis(salicylaldehydato)bis(3,5-lutidine)iron(II)**

The product was obtained as in b(ii) from iron(II) sulphate heptahydrate (2.5g = 8.99x10^-3 moles), salicylaldehyde (2.0ml = 1.41x10^-2 moles) and 3,5-lutidine (10ml). The dry product was a black powder.

Yield 3.7g, 80%.

Found: Fe, 10.97; C, 65.10; H, 5.49; N, 5.53%.

C_{28}H_{28}N_2O_4Fe requires Fe, 10.90; C, 65.62; H, 5.52; N, 5.47%.

Attempts to prepare the α-picoline derivative were unsuccessful, bis(salicylaldehydato)diaquoiron(II) being the only product isolated from the reaction mixture probably because of the steric hindrance of the α-methyl group.
RESULTS AND DISCUSSION
The results will be discussed under the headings:

1) Schiff base complexes of iron(II)
2) Nitric oxide derivatives
3) Adducts of bis(salicylaldehydato)iron(II).

1) SCHIFF BASE COMPLEXES OF IRON(II)

Magnetic and Mössbauer Results

Iron(II) has an outer electronic configuration 3d^6 and in complexes can have four, two or no unpaired electrons. As shown in Table 19 and Fig. 21, the Schiff base complexes obeyed the Curie-Weiss law with small θ values and room temperature magnetic moments in the range 4.8-5.5 B.M. All were therefore high-spin with four unpaired electrons. Minor differences, ~0.2 B.M., in absolute values of magnetic moments were observed between preparations in this work and with those reported by Larkworthy, probably due to differences in preparative technique with these highly air-sensitive compounds. Schiff base complexes which were analytically and magnetically pure, i.e. the compounds showed no field dependence, had 'clean' Mössbauer spectra (typical spectra are shown in Fig. 22a). The Mössbauer data are reported in Table 20. Some complexes, although analytically and magnetically pure, had poor spectra (see Fig. 22b for typical spectra of partially oxidised samples) due to sample oxidation during the measurements. De Vries has reported similar data for salen iron(II) and salphen iron(II) to that given in Table 20, however the green colour quoted for the salphen iron(II) complex would indicate from our observations that the complex is the mono-hydrate (see Tables 1 and 21). No analyses were reported by de Vries.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp (°K)</th>
<th>Molecular Weight (g/mol)</th>
<th>$\gamma_A \times 10^6$</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Diamagnetic Correction (10^{-6}) c.g.s.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen iron(II) [Preparation 3a(i)]</td>
<td>294.4</td>
<td>322.2</td>
<td>1.0652</td>
<td>5.01</td>
<td>182.0</td>
</tr>
<tr>
<td>Salen iron(II) [Preparation 3b(i)]</td>
<td>294.2</td>
<td>322.2</td>
<td>1.1082</td>
<td>5.10</td>
<td>182.0</td>
</tr>
<tr>
<td>Salphen iron(II).H$_2$O [Preparation 3a(iii)]</td>
<td>294.7 274.8 234.2 152.3 86.6</td>
<td>10762 11482 13562 20842 36312</td>
<td>0.929 0.871 0.738 0.480 0.275</td>
<td>5.03 5.04 5.04 5.01</td>
<td>182.03 3x10^{-6} c.g.s.u.</td>
</tr>
<tr>
<td>Salphen iron(II).H$_2$O [Preparation 3b(ii)]</td>
<td>291.2</td>
<td>388.2</td>
<td>1.1502</td>
<td>5.17</td>
<td>182.3</td>
</tr>
<tr>
<td>5-Methylsalen iron(II)</td>
<td>292.4</td>
<td>350.2</td>
<td>1.1220</td>
<td>5.11</td>
<td>179.6</td>
</tr>
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</table>
### Table 19 cont.

#### vi) 3-Methoxysalen iron(II), H₂O

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>292.5</th>
<th>274.7</th>
<th>234.2</th>
<th>152.8</th>
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<tr>
<td>γₐ x 10⁶</td>
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<td>11903</td>
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<td>36718</td>
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<td>γₐ x 10⁻²</td>
<td>0.887</td>
<td>0.840</td>
<td>0.712</td>
<td>0.466</td>
<td>0.272</td>
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<tr>
<td>μₑffect (B.M.)</td>
<td>5.14</td>
<td>5.11</td>
<td>5.13</td>
<td>5.12</td>
<td>5.07</td>
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</tbody>
</table>

Molecular Weight 400.3 Diamagnetic Correction 217 x 10⁻⁶ c.g.s.u.

θ = 0°

#### vii) 5-Nitrosalen iron(II)

<table>
<thead>
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<th>Temp (°K)</th>
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</thead>
<tbody>
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<td>γₐ x 10⁶</td>
<td>9928</td>
</tr>
</tbody>
</table>

Diamagnetic Correction 157.8 x 10⁻⁶ c.g.s.u.

μₑffect (B.M.) 4.81

#### viii) 5-Nitrosalen iron(II), H₂O

<table>
<thead>
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<th>Temp (°K)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>γₐ x 10⁶</td>
<td>11011</td>
</tr>
</tbody>
</table>

Diamagnetic Correction 170.8 x 10⁻⁶ c.g.s.u.

μₑffect (B.M.) 5.06

#### ix) Salphen iron(II)

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>289.5</th>
<th>274.8</th>
<th>234.4</th>
<th>152.8</th>
<th>95.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>γₐ x 10⁶</td>
<td>10379</td>
<td>10819</td>
<td>12819</td>
<td>19809</td>
<td>31609</td>
</tr>
<tr>
<td>γₐ x 10⁻²</td>
<td>0.964</td>
<td>0.924</td>
<td>0.780</td>
<td>0.505</td>
<td>0.316</td>
</tr>
<tr>
<td>μₑffect (B.M.)</td>
<td>4.90</td>
<td>4.88</td>
<td>4.90</td>
<td>4.92</td>
<td>4.91</td>
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</table>

Molecular Weight 370.2 Diamagnetic Correction 169.3 x 10⁻⁶ c.g.s.u.

θ = 0°

#### x) Bis(salicylideneiminato)iron(II)

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>294.8</th>
<th>274.7</th>
<th>234.2</th>
<th>153.0</th>
<th>87.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>γₐ x 10⁶</td>
<td>12716</td>
<td>13556</td>
<td>15746</td>
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<td>39836</td>
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<tr>
<td>γₐ x 10⁻²</td>
<td>0.786</td>
<td>0.737</td>
<td>0.635</td>
<td>0.427</td>
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<tr>
<td>μₑffect (B.M.)</td>
<td>5.48</td>
<td>5.46</td>
<td>5.43</td>
<td>5.35</td>
<td>5.23</td>
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Molecular Weight 296.1 Diamagnetic Correction 126.0 x 10⁻⁶ c.g.s.u.

θ = 12°
Table 20

Mössbauer Results of Iron(II) Schiff Base Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. °K</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen iron(II)[Prep. 3a(i)]</td>
<td>300</td>
<td>1.23</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.32</td>
<td>2.35</td>
</tr>
<tr>
<td>Salen iron(II)[Prep. 3b(i)]</td>
<td>300</td>
<td>1.23</td>
<td>2.22</td>
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<tr>
<td></td>
<td>80</td>
<td>1.27</td>
<td>2.28</td>
</tr>
<tr>
<td>Salphen iron(II).H$_2$O [Prep. 3b(ii)]</td>
<td>80</td>
<td>1.27</td>
<td>2.28</td>
</tr>
<tr>
<td>Salphen iron(II).H$_2$O [Prep. 3n(iii)]</td>
<td>80</td>
<td>1.20</td>
<td>2.19</td>
</tr>
<tr>
<td>5-Methylsalen iron(II)$^*$</td>
<td>300</td>
<td>1.22</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.28</td>
<td>2.15</td>
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<tr>
<td>3-Methoxysalen iron(II).H$_2$O</td>
<td>300</td>
<td>1.20</td>
<td>2.36</td>
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<td></td>
<td>80</td>
<td>1.29</td>
<td>2.54</td>
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<tr>
<td>5-Nitrosalen iron(II)</td>
<td>300</td>
<td>1.28</td>
<td>1.99</td>
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<td></td>
<td>80</td>
<td>1.43</td>
<td>2.22</td>
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<tr>
<td>5-Nitrosalen iron(II).H$_2$O$^*$</td>
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<td>1.28</td>
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<td>Salphen iron(II)$^*$</td>
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<td>80</td>
<td>1.31</td>
<td>2.30</td>
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<tr>
<td>Bis(salicylideneiminato)-iron(II)</td>
<td>300</td>
<td>1.20</td>
<td>2.30</td>
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<tr>
<td></td>
<td>80</td>
<td>1.31</td>
<td>2.30</td>
</tr>
</tbody>
</table>

$^*$These products oxidised during the measurement.
Typical Mössbauer Spectra of Schiff-Base Iron(II) Complexes

Fig. 22a
Typical Mössbauer Spectra of Oxidised Schiff-Base Iron(II) Complexes

![Graph showing typical Mössbauer spectra at 300°K and 80°K with relevant axes labeled](image_url)

**Fig. 22b**
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp $^\circ$K</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
<th>Ref 15</th>
<th>Ref 31</th>
<th>Ref 32</th>
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<td>Salen iron(II)</td>
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<td>0.97</td>
<td>0.49</td>
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<tr>
<td></td>
<td>80</td>
<td>0.60</td>
<td>0.81</td>
<td>0.51</td>
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<tr>
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<td>0.66</td>
<td>0.76</td>
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<tr>
<td>3-Methoxy-salen iron(II)</td>
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<td>80</td>
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<tr>
<td>Bis(salicylaldehydeato)iron(II)</td>
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<tr>
<td></td>
<td>80</td>
<td>0.65</td>
<td>0.75</td>
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<td></td>
<td>1.43</td>
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<td>2</td>
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<td></td>
</tr>
<tr>
<td>Bis(salicylideneiminato)iron(II)</td>
<td>300</td>
<td>0.66</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.71</td>
<td>0.70</td>
<td></td>
<td></td>
<td>1.47</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The most common stereochemistry of high-spin iron(II) complexes in octahedral, and as such a room temperature magnetic moment of ~5.5 B.M. is expected. However, increasing electron delocalisation and distortion from cubic symmetry cause the magnetic moments to approach the spin-only value, 4.9 B.M., and to vary little with temperature. Larkworthy suggested from the magnetic behaviour of the iron-salen complexes that they had highly distorted or even planar structures with considerable delocalisation. The same conclusions have been reached by Calderazzo and Berrett. The Mössbauer data reported by Stukan and Kulgaiczuk were interpreted in terms of planar iron(II) structures but this work and that of de Vries show that in fact Stukan and Kulgaiczuk had studied oxidised products (see data in Table 2). The assumption that the complexes were planar needs consideration as pentaco-ordination in Schiff base complexes with bivalent metals is well established (see the following discussion).

Although most high-spin iron(II) complexes are octahedral, several tetrahedral compounds are known. These have room temperature magnetic moments in the range 5.0-5.4 B.M. and isomer shifts between 1.13-1.25 mm sec$^{-1}$. Examples of planar iron(II) compounds are rare, only two have been well authenticated: phthalocyanine iron(II), which is believed to be in an intermediate ($S=1$) spin-paired state; and the mineral gillespite, BaFeSi$_4$O$_{10}$, which contains high-spin iron(II) (5.12 B.M.) in planar co-ordination to oxygen. Gillespite has an isomer shift typical for high-spin iron(II) but an unexpectedly small quadrupole splitting with little temperature dependence. The valency contribution to the electric field gradient, $q_{\text{val}}$, (see equation (57)) and hence the quadrupole splitting, was expected to be large in a planar and therefore distorted structure, but in gillespite the lattice contribution, $q_{\text{lat}}$, to the electric field gradient, which is
normally small, is said to be almost equal and opposite. It was calculated for gillespite that $q_{\text{lat}} \approx q_{\text{val}}$, which is very unusual for high-spin iron(II) compounds. The small temperature dependence of the quadrupole splitting was attributed to $q_{\text{val}}$ remaining independent of temperature whilst $q_{\text{lat}}$ decreased with the thermal expansion of the solid.

Pentacoordination in high-spin iron(II) complexes is also rare. The few examples\textsuperscript{155-159} have room temperature magnetic moments in the range 4.9-5.4 B.M. The stereochemistry of these complexes is not well established. It has been suggested that Fe(terpy)Br\textsubscript{2}\textsuperscript{155} (terpy = terpyridine) has a pentacoordinate structure nearer square-pyramidal than trigonal-bipyramidal, and it is the only complex, so far, on which Mössbauer data have been obtained.

In principle, the s-electron density at the nucleus of an iron complex, in a given oxidation state, should differ depending on the occupancy of the $3d$ orbitals in different stereochemistries. Therefore moderate differences should be observable in isomer shift values for different co-ordination geometries. However, with so many variables possible between different chemical systems it is only reasonable to compare systems with equivalent or nearly equivalent ligands. Then for some high-spin iron(II) compounds definite decreases in isomer shift are observed in changing co-ordination number from 6 to 4 and 3 to 4 (see Tables 22 and 23).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C.N.</th>
<th>Stereochemistry</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_2$</td>
<td>6</td>
<td>Octahedral</td>
<td>1.34</td>
</tr>
<tr>
<td>[FeCl$_4$]$_2$</td>
<td>6</td>
<td>Octahedral</td>
<td>1.34</td>
</tr>
<tr>
<td>[Fe(NCS)$_6$]$_4^-$</td>
<td>6</td>
<td>Octahedral</td>
<td>1.37</td>
</tr>
<tr>
<td>[Fe(NCS)$_6$]$_2^-$</td>
<td>4</td>
<td>Tetrahedral</td>
<td>0.97</td>
</tr>
<tr>
<td>[Fe(NCS)$_4$]$_2^-$</td>
<td>4</td>
<td>Tetrahedral</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Table 23

Correlation of Isomer Shift and Co-ordination Number for Silicate Minerals Containing High-Spin Iron(II)

<table>
<thead>
<tr>
<th>C.N.</th>
<th>Stereochemistry</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Distorted Cube</td>
<td>1.57</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>1.29-1.49</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>1.08-1.25</td>
</tr>
<tr>
<td>4</td>
<td>Planar</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Information concerning the stereochemistry of iron complexes may also be obtained from the quadrupole splitting, $\Delta E$. $\Delta E$ depends on the electric field gradient experienced by the iron atom which is dependent on the 3d-electron distribution and the stereochemistry of the molecule. The more distorted the molecule the greater will be the quadrupole splitting.

The Mössbauer data of the iron-salen complexes (Table 20) show that the isomer shifts of all the complexes increase on cooling, due to the second-order Doppler effect. The values of $\Delta E$ are large and temperature dependent which is typical for high-spin iron(II). The very small values of $-\partial\Delta E/\partial T$ (Table 24) and large values of $\Delta E$ indicate that the stereochemistry of iron-salen complexes is highly distorted from octahedral symmetry.

Table 24

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\partial\Delta E/\partial T/100^oK$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen iron(II) [Prep 3a(i)]</td>
<td>0.06</td>
</tr>
<tr>
<td>Salen iron(II) [Prep 3b(i)]</td>
<td>0.02</td>
</tr>
<tr>
<td>Salphen iron(II),H$_2$O[Prep 3a(ii)]</td>
<td>0.03</td>
</tr>
<tr>
<td>Salphen iron(II),H$_2$O[Prep 3b(ii)]</td>
<td>0.02</td>
</tr>
<tr>
<td>5-Methylsalen iron(II)</td>
<td>0.02</td>
</tr>
<tr>
<td>3-Methoxysalen iron(II)</td>
<td>0.03</td>
</tr>
<tr>
<td>5-Nitrosalen iron(II),H$_2$O</td>
<td>0.11</td>
</tr>
<tr>
<td>Salphen iron(II)</td>
<td>0.00</td>
</tr>
</tbody>
</table>
It is suggested from the magnetic and Mössbauer data that no unambiguous co-ordination geometry may be inferred about the iron-salen complexes. Table 25 lists the available data of various co-ordination numbers for high-spin iron(II) complexes.

The quadridentate ligands, salen, x-salen and salphen (Fig. 1) take up planar configurations about a central bivalent transition metal ion, but the complexes need not be planar. The structures of the anhydrous complexes, salen copper(II) and salen cobalt(II) (oxygen-inactive), have been shown to be dimeric, the metal atom completing a pentaco-ordinate configuration with oxygen atoms of adjacent molecules (Fig. 2). The structures of metal-salen complexes involving co-ordinated water, salen zinc(II) monohydrate and salpn copper(II) monohydrate, have been shown to have a distorted square-pyramidal structure. The fifth co-ordination position is filled by water and the metal atom is slightly raised above the plane of the ligand (Fig. 3). Thus a pentaco-ordinate structure is not unusual for anhydrous or hydrated Schiff base metal complexes. A dimeric structure, similar to that of salen copper(II), has been observed for salen iron(III) chloride (Fig. 2) with the sixth co-ordination position filled with a chlorine atom. Some data of the pentaco-ordinate structures are given in Table 26.

Table 26

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-O bond distance</th>
<th>Bond Angle</th>
<th>Stereocchemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen Cu(II)</td>
<td>2.41</td>
<td>90°</td>
<td>Square-pyramidal</td>
</tr>
<tr>
<td>Salen Co(II)</td>
<td>2.26</td>
<td>90°</td>
<td>&quot;</td>
</tr>
<tr>
<td>Salen Zn(II),H₂O</td>
<td>2.13</td>
<td>90°</td>
<td>Distorted square-pyramidal</td>
</tr>
<tr>
<td>Salpn Cu(II),H₂O</td>
<td>2.52</td>
<td>90°</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

*Metal-oxygen bond distance of fifth co-ordination position

†Bond angle between the M-O* bond and the plane of the salen ligand.
<table>
<thead>
<tr>
<th>Co-ordination Number</th>
<th>4</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Present Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereochemistry</td>
<td>tetrahedral</td>
<td>planar</td>
<td>square-pyramidal</td>
<td>octahedral</td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ B.M.</td>
<td>5.0-5.4</td>
<td>5.12</td>
<td>5.3-5.4</td>
<td>-5.5</td>
<td>4.8-5.5</td>
</tr>
<tr>
<td>$\delta$, mm sec$^{-1}$</td>
<td>1.13-1.25</td>
<td>1.01</td>
<td>1.15</td>
<td>1.00-1.50</td>
<td>1.15-1.28</td>
</tr>
<tr>
<td>$\Delta E$, mm sec$^{-1}$</td>
<td>0.80-2.80</td>
<td>0.51</td>
<td>2.76</td>
<td>1.50-3.00</td>
<td>1.99-2.40</td>
</tr>
<tr>
<td>Reference</td>
<td>152,153</td>
<td>157</td>
<td>158</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The isomer shifts and quadrupole splittings for the iron-salen complexes reported here are closer to the results of Fe(terpy)Br₂, which has a distorted square-pyramidal structure, than to the results for the planar gillespite structure. The Fe-O bonds in gillespite are reduced from the average bond length, ~2.1 Å, to 1.97 Å, indicating the highly distorted environment of the iron atom. Metal-oxygen bond distances are also short in the known salen-metal structures e.g. the Fe-O bond distance in (Fe Salen Cl)₂ is ~1.94 Å. A planar structure for salen iron(II) is therefore quite possible. The structure of salen cobalt(II) (oxygen-active) has been proposed to be planar. Although this work is now in doubt and the structure is being reinvestigated, salen iron(II) may also be considered to be "active" and have a planar structure. The unexpectedly low quadrupole splitting in gillespite has already been mentioned (p.117) and it is possible that a similarly low value would be expected for a planar, salen -O₂N₂ structure as was obtained for the -O₄ configuration. As indicated before, the magnetic and Mössbauer results do not unambiguously distinguish between a planar or a square-pyramidal structure. However, a dimeric, pentaco-ordinate structure is proposed for the anhydrous iron-salen complexes (Fig. 4). This structure is based on:

i) The known structures of anhydrous salen complexes.
ii) The similarity of the Mössbauer results to those of Fe(terpy)Br₂.
iii) A structure distorted from octahedral symmetry, indicated by the magnetic and Mössbauer data.

If the structure is dimeric then some magnetic interaction between the metal atoms may be expected as in the proposed dimeric structures for salen cobalt(II) (oxygen-inactive)₂⁴, salen manganese(II)⁹ and salen iron(III) chloride. Any interaction would have reduced the magnetic moment and caused considerable deviations from the Curie-Weiss law. However, no such anomalous magnetic behaviour was observed,
but this does not preclude a dimeric structure as the salen copper(II) dimer is magnetically normal. In this structure the Cu-O bond distance between the monomer units is large enough to prevent any appreciable Cu-Cu interaction. Similarly a large Fe-O bond distance may be present in a dimer proposed for salen iron(II).

The anhydrous complexes seem to have higher isomer shifts and lower quadrupole splittings than the hydrated complexes (Table 20). (Unfortunately the results for 5-nitrosalen iron(II) and bis(salicylideneiminato)iron(II) were not available by September 1971.) The hydrated complexes were assumed to contain co-ordinated and not lattice water because of:

i) The difficulty of removing the water under reduced pressure.

ii) Thermogravimetric analysis indicated a high temperature, ~170°C, for water removal.

iii) Hydration affected magnetic and Mössbauer data for the complexes of salphen (Tables 19 and 20).

iv) Co-ordinated water is found in salen zinc(II) monohydrate, salpn copper(II) monohydrate, 3-methoxy- and 3-ethoxy-salen cobalt(II) monohydrate.

The Mössbauer data for salphen iron(II) and salphen iron(II) monohydrate (Table 27) show

| Table 27 |
|---|---|
| Room Temperature Mössbauer Data | of Anhydrous and Hydrated Salphen Iron(II) |
| Compound | δ (mm sec⁻¹) | ΔE (mm sec⁻¹) |
| Salphen iron(II) | 1.20 | 2.30 |
| Salphen iron(II) monohydrate | 1.15 | 2.40 |

an increase in quadrupole splitting and a slight decrease in isomer shift on hydration. The increase in quadrupole splitting indicates a more distorted structure for the
hydrate. If the anhydrous complex is a dimeric, pentacoordinate structure, as proposed, then the hydrate has to be a more distorted structure, such as that of salen zinc(II) monohydrate, a monomeric, distorted square-pyramidal structure. If a distorted octahedral complex were formed by filling the sixth co-ordination position in the dimer with a water molecule, as Cl\(^-\) does in salen iron(III) chloride, then a decrease in the quadrupole splitting would be expected because the hydrate molecule would be more symmetric than the anhydrous structure. The decrease in isomer shift may therefore be due to the change in structure from a square-pyramidal dimer to a distorted square-pyramidal monomer. Therefore based on the known structures of hydrated salen complexes and on the Mössbauer results a monomeric, pentaco-ordinate structure is proposed for hydrated iron-salen complexes.

Molecular weight studies would help in distinguishing whether the proposed complexes were monomeric or dimeric. Unfortunately the lack of a suitable solvent for these complexes and their air-sensitivity prevented any such studies. Ideally structural analyses are required but the difficulty in growing crystals and the air-sensitivity of the complexes made any measurements impossible.

Infrared and Thermogravimetric Analysis Data

Infrared spectra of the iron-salen complexes were recorded for comparison with the nitrosyls. The spectra were also used to demonstrate the presence of water. The 3-methoxysalen iron(II) and salphen iron(II) monohydrate had reasonably sharp -OH stretching absorptions at 3400 cm\(^{-1}\) and 3150 cm\(^{-1}\) respectively whereas the 5-nitrosalen iron(II) monohydrate had rather a broad absorption at 3300-3600 cm\(^{-1}\), but the -OH bend was usually obscured by strong ligand absorptions. As mentioned (p.123), thermogravimetric analysis showed the presence of approximately one molecule of water in the monohydrates, but as the compounds were air-sensitive and the water percentage low the results were not very accurate.
Bis(salicylideneiminato)iron(II)

The bidentate ligand, salicylidimine, does not force a planar configuration on the metal (p.17). The magnetic moment at room temperature shows the complex to be high-spin (Table 19) but does not distinguish between the possible structures. Unfortunately no Mössbauer data for our sample are yet available but de Vries has obtained Mössbauer data (Table 21) consistent with high-spin iron(II). The infrared spectrum has two absorptions at 3170 and 3200 cm\(^{-1}\) characteristic of N-H stretching frequencies. This is presumably due to hydrogen-bonding since only one band would have been predicted for an imine group, -N-H.

Bis(acetato)iron(II)

The Mössbauer spectrum (Table 28) was recorded to ensure that no bis(acetato)iron(II) contaminated the iron-salen complexes.

<table>
<thead>
<tr>
<th>T(^{0})K</th>
<th>(\delta) (mm sec(^{-1}))</th>
<th>(\Delta\delta) (mm sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.39</td>
<td>2.30</td>
</tr>
<tr>
<td>80</td>
<td>1.68</td>
<td>2.87</td>
</tr>
</tbody>
</table>

The isomer shifts and quadrupole splittings are much larger than those of the iron-salen complexes (Table 20), therefore any contamination would have been apparent.

The Mössbauer data indicated that bis(acetato)iron(II) is a high-spin iron(II) complex, as expected. Calderazzo has reported the room temperature magnetic moment of anhydrous bis(acetato)iron(II) (5.19 B.M.). As the degree of hydration was uncertain (see p.96) no detailed magnetic or Mössbauer studies were undertaken.
2. NITRIC OXIDE DERIVATIVES

Reaction with Nitric Oxide

The complexes of the quadridentate ligands, salen, salphen and 5-nitrosalen absorbed one mole of nitric oxide per mole of complex, within experimental accuracy (see p. 103).

Quadridentate Schiff base ligands such as salen are known to take up an effectively planar configuration about bivalent metals but metal-salen complexes usually have pentaco-ordinate structures (see Part 1 of this discussion). Larkworthy assumed that the cobalt- and iron-salen mononitrosyls obtained from various Schiff base complexes had similar square-pyramidal structures to the related systems discussed in the Introduction 2vi). Monomeric, square-pyramidal structures have been assumed in this discussion also for the iron-salen mononitrosyls.

Infrared Measurements at Room Temperature

The spectra of the nitrosyls and parent complexes in the appropriate region are shown in Fig. 23a) and b). Each nitrosyl shows a strong additional absorption compared with the parent complex which has been assigned to the nitric oxide stretching frequency (Table 29).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>νN=O (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen</td>
<td>1712</td>
</tr>
<tr>
<td>§Salen</td>
<td>1712</td>
</tr>
<tr>
<td>5-nitrosalen</td>
<td>1792 (1720sh)</td>
</tr>
<tr>
<td>§5-nitrosalen</td>
<td>1792 (1720sh)</td>
</tr>
<tr>
<td>salphen</td>
<td>1720 (1662sh)</td>
</tr>
</tbody>
</table>

The infrared data agree very well with those reported by Larkworthy 84. The nitric oxide stretching frequencies of the nitrosyls are in the range more indicative of co-ordinated NO⁻ than NO⁺ i.e. 1750-1500 cm⁻¹. [Also the known crystallographic structures of the square-pyramidal...
iron mononitrosyls of systems related to salen indicate slightly bent Fe-N-0 groupings\(^5\)\(^{50-52,80}\) (\(\sim 170^\circ\)), characteristic of co-ordinated NO\(^-\). Although other related iron mononitrosyl systems have formally been assigned Fe(I)NO\(^+\) structures (Introduction 2vi), assuming similar stereochemistry, it has been suggested by Larkworthy\(^8\) and supported here that the salen-iron nitrosyls may formally be regarded as Fe(III)NO\(^-\).

Co-ordination as NO\(^-\) is more compatible with the chemical properties of nitric oxide which behaves as an oxidising rather than a reducing agent towards the iron(II) in this type of complex. For example, in some conditions no salen-iron nitrosyls, but oxidation products, were obtained\(^8\). The formulation of co-ordinated nitric oxide as NO\(^-\) or NO\(^+\) is purely for convenience since the true situation is probably between the two extremes, the exact state of the nitric oxide and metal differing from compound to compound.

No apparent relationship between the electronic effects of the substituents and the N-O stretching frequencies were observed by Larkworthy\(^8\). Presumably \(\pi\)-bonding is relatively unimportant with the high-spin salen-iron nitrosyls; the N-O stretching frequency in a particular compound being the net result of \(\sigma\)-and \(\pi\)-effects acting in opposition so that no simple relationship with substituent emerges.

**Magnetic Properties**

The magnetic moments of the compounds at room temperature were \(\sim 3.67\) B.M., close to the value expected for three unpaired electrons. These and the related nitrosyls\(^8\) are the only reasonably stable high-spin iron nitrosyls known. The nitric oxide adduct of bis(salicylaldehydato)iron(II) and the brown ring compounds decompose too readily for extensive study. Many stable low-spin iron nitrosyl complexes are known (see Introduction 2i-viii)).
Fig. 23a
Salphen Iron

Nitrosyl Salphen Iron

Fig. 23b
The salen-iron nitrosyls were of two classes; those that obeyed the Curie-Weiss law and those that did not. The magnetic results, summarised in Table 30, agree reasonably well with those reported for nitrosyl salen iron but not very well for nitrosyl 5-nitrosalen iron.

Table 30

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( \mu_{\text{eff}} )</th>
<th>B.M.</th>
<th>( \theta ) (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen</td>
<td>3.66</td>
<td>1.86</td>
<td>-</td>
</tr>
<tr>
<td>Salen(^x)</td>
<td>3.61</td>
<td>2.10</td>
<td>-</td>
</tr>
<tr>
<td>5-nitrosalen</td>
<td>3.69</td>
<td>3.41</td>
<td>20</td>
</tr>
<tr>
<td>5-nitrosalen(^x)</td>
<td>3.08</td>
<td>2.60</td>
<td>65</td>
</tr>
<tr>
<td>Salphen</td>
<td>3.65</td>
<td>1.80</td>
<td>-</td>
</tr>
<tr>
<td>5-methylsalen(^x)</td>
<td>3.98</td>
<td>4.00</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^x\)Ref. 84

Although the same trends are observed, marked differences in the values of \( \mu_{\text{eff}} \) occur. The earlier preparations lost nitric oxide readily, as judged from infrared spectra, whereas the present product appeared indefinitely stable. Only compounds having unusual magnetic behaviour were studied.

The 5-nitrosalen nitrosyl had temperature-dependent moments, but obeyed the Curie-Weiss law (\( \theta=20^\circ \), Table 31, Fig. 24). The salen and salphen nitrosyls did not obey the Curie-Weiss law (Table 31, Figs. 25-27) and had discontinuities in magnetic properties at \( \approx 175^\circ \text{K} \) and between \( 160-180^\circ \text{K} \) respectively where the magnetic moment decreased from that for three unpaired electrons (\( S=3/2 \)) to that for one unpaired electron (\( S=1/2 \)). Similar data for nitrosyl salen iron have been reported. The temperature ranges which were investigated above and below the discontinuity were not large, but the results suggest Curie law behaviour at temperatures below the discontinuity and Curie-Weiss behaviour with a large value above. The magnetic measurements were made from high to
Table 31
Magnetic Susceptibility Measurements on
Iron Schiff Base Nitrosyls

I. Compound obeying the Curie-Weiss Law

i) Nitrosyl 5-nitrosalen iron

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>290.4</th>
<th>274.8</th>
<th>234.2</th>
<th>194.4</th>
<th>153.0</th>
<th>125.5</th>
<th>105.4</th>
<th>87.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>5825</td>
<td>6189</td>
<td>7164</td>
<td>8481</td>
<td>10630</td>
<td>12833</td>
<td>14443</td>
<td>16593</td>
</tr>
<tr>
<td>$\chi_A^{-1} \times 10^{-2}$</td>
<td>1.708</td>
<td>1.615</td>
<td>1.396</td>
<td>1.179</td>
<td>0.943</td>
<td>0.798</td>
<td>0.692</td>
<td>0.603</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ (B.M.)</td>
<td>3.69</td>
<td>3.69</td>
<td>3.66</td>
<td>3.63</td>
<td>3.60</td>
<td>3.54</td>
<td>3.49</td>
<td>3.41</td>
</tr>
</tbody>
</table>

Molecular Weight 442.2 Diamagnetic Correction 163.0x10^-6 c.g.s.u.

II. Compounds not obeying the Curie-Weiss Law

i) Nitrosyl salen iron

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>288.6</th>
<th>274.9</th>
<th>234.7</th>
<th>194.3</th>
<th>184.2</th>
<th>179.4</th>
<th>174.0</th>
<th>169.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>5822</td>
<td>6014</td>
<td>6690</td>
<td>7544</td>
<td>7592</td>
<td>7477</td>
<td>2998</td>
<td>2801</td>
</tr>
<tr>
<td>$\chi_A^{-1} \times 10^{-2}$</td>
<td>1.718</td>
<td>1.663</td>
<td>1.495</td>
<td>1.325</td>
<td>1.329</td>
<td>1.338</td>
<td>3.335</td>
<td>3.570</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ (B.M.)</td>
<td>3.66</td>
<td>3.64</td>
<td>3.54</td>
<td>3.42</td>
<td>3.33</td>
<td>3.28</td>
<td>2.04</td>
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</tbody>
</table>

Molecular Weight 352.2 Diamagnetic Correction 192.0x10^-6 c.g.s.u.

ii) Nitrosyl salphen iron

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>294.8</th>
<th>274.9</th>
<th>234.5</th>
<th>194.2</th>
<th>184.1</th>
<th>180.0</th>
<th>175.8</th>
<th>172.0</th>
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</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>5647</td>
<td>6005</td>
<td>6857</td>
<td>7622</td>
<td>6842</td>
<td>5664</td>
<td>4899</td>
<td>4376</td>
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<tr>
<td>$\chi_A^{-1} \times 10^{-2}$</td>
<td>1.771</td>
<td>1.665</td>
<td>1.459</td>
<td>1.312</td>
<td>1.462</td>
<td>1.766</td>
<td>2.041</td>
<td>2.285</td>
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<tr>
<td>$\mu_{\text{eff}}$ (B.M.)</td>
<td>3.65</td>
<td>3.63</td>
<td>3.58</td>
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<td>3.17</td>
<td>2.86</td>
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<td>2.45</td>
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</tbody>
</table>

Molecular Weight 400.2 Diamagnetic Correction 179.5x10^-6 c.g.s.u.
Nitrosyl 5-Nitrosalen Iron

\[ \theta = 20^\circ \]

Fig. 24
Nitrosyl Salen Iron

![Graph showing the relationship between temperature and a parameter, labeled Fig. 25.](image-url)
Nitrosyl Salphen Iron

Fig. 26
Fig. 27
low temperatures on the complexes studied here but Larkworthy has shown for nitrosyl salen iron that the discontinuity occurred at a slightly higher temperature when measurements were made in the opposite direction.

The shape of the reciprocal susceptibility v. temperature graphs (Figs. 25 and 26) for the salen and salphen nitrosyls are similar to those in which spin equilibria occur (see Introduction iii)) and sharp transitions as experienced here are still uncommon. Some factor in addition to the effect of thermal energy raises the ligand field above the crossover value and causes spin-pairing.

The magnetic behaviour of the nitrosyl 5-nitrosalen iron showed a lowering of magnetic moment with temperature (θ=20°, Fig. 24). If magnetic measurements on nitrosyl salen iron had been restricted to temperatures above the discontinuity, results similar to those with the 5-nitrosalen compound would have been obtained. To observe the complete curve measurements on the latter, down to 4.2°K say, are necessary. It is therefore suggested that nitrosyl 5-nitrosalen iron is undergoing spin-state isomerism but the proportions of isomers change slowly with temperature.

Larkworthy has reported the magnetic moment of nitrosyl salen iron in pyridine and dimethylformamide solution. The solutions were dilute and measurements were carried out in sealed tubes because of air-sensitivity, so that results were not highly accurate, but they showed the nitrosyl to be in the $S=3/2$ state in solution. It would appear that co-ordination of nitric oxide brings the ligand field so close to its value at the crossover point that otherwise minor changes e.g. lattice effects consequent upon replacing H by CH$_3$ or NO$_2$, greatly modify the magnetic behaviour. Dissolution removes the lattice and could lead to the formation of one spin isomer only.
The nitrosyls studied here all have room temperature magnetic moments slightly reduced from the spin-only value for three unpaired electrons. The decrease of one in the number of unpaired electrons compared with the parent complexes is best explained by considering one unpaired electron of the Schiff base chelate to be paired with the odd electron of the nitric oxide. The position of the electron pair just formed determines whether the compounds contain NO\(^+\) or NO\(^-\). This information cannot be determined from bulk susceptibility measurements, but the magnetic data are compatible with the formation of iron as iron(III) or iron(I) and hence the nitric oxide as NO\(^-\) or NO\(^+\).

### Infrared Measurements Over a Temperature Range

In view of the anomalous magnetic and Mössbauer data (see later discussion), infrared measurements were made over the temperature range 300\(^\circ\)K-80\(^\circ\)K. The infrared spectra of nitrosyl salen- and 5-nitrosalen-iron were previously studied at room temperature and 90\(^\circ\)K only. The magnetically normal nitrosyls showed only a general sharpening and increased intensity of bands at the lower temperature.

The peak of nitrosyl salen iron attributed to the N-O stretching frequency (Fig. 28 and Table 32) moved to a slightly higher frequency and eventually almost disappeared on cooling to liquid nitrogen temperature, but returned when the sample was reheated to room temperature. Other infrared studies showed the spectrum to be unchanged in the 1500 cm\(^{-1}\) region suggesting that the nitric oxide did not become bridging. Apart from the disappearance of the peak found at 1703 cm\(^{-1}\) with the P.E. 457 and 1712 cm\(^{-1}\) with the SP. 200, both instruments being calibrated with polystyrene, no other change was observed in the range 650-4000 cm\(^{-1}\). However a slight shift in the N-O stretching frequency to higher frequency, \(\Delta 16\) cm\(^{-1}\), and a relative
Infrared Spectra of Nitrosyl Salen Iron Over a Temperature Range

Fig. 28
Table 32

Infrared Data Over a Temperature Range

<table>
<thead>
<tr>
<th>Nitrosyl salen iron</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
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<td>Rel.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>str.freq.</td>
<td>Area</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1703</td>
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<td>1719</td>
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<td>5</td>
<td>4</td>
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<table>
<thead>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>Rel.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>str.freq.</td>
<td>Area</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1724</td>
<td>127</td>
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<tr>
<td>1727</td>
<td>118</td>
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<td>1728</td>
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<tr>
<td>1727</td>
<td>4</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrosyl 5-nitrosalen iron</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>νN=0</td>
<td>Rel.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>str.freq.</td>
<td>Area</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1792</td>
<td>367</td>
<td>86</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>1800</td>
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<td>1805</td>
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<td>79</td>
</tr>
<tr>
<td>1805</td>
<td>264</td>
<td>71</td>
<td>63</td>
<td>72</td>
</tr>
</tbody>
</table>

**Note:** Temperatures recorded with variable temperature infrared apparatus could be in error by ±10° outside room and liquid nitrogen temperatures.
increase in intensity of the ligand absorption at \( \nu = 1624 \text{ cm}^{-1} \) compared to the absorption at \( \nu = 1598 \text{ cm}^{-1} \) was observed on cooling. It is possible that the band at 1703 cm\(^{-1}\) moved to approximately 1620 cm\(^{-1}\) on cooling, where a strong ligand absorption would mask any new peaks. This shift could be due to a change in orientation or to a change in crystal lattice causing spin-pairing. Metal-nitrogen \( \pi \)-bonding would be expected to be greater in low-spin compounds giving a lower N-O stretching frequency.

In order to detect the change in metal-nitrogen stretching and metal-nitric oxide deformation frequencies, which should accompany the change in N-O stretching frequency, spectra were recorded down to \( 400 \text{ cm}^{-1} \) (using KBr plates). No conclusive evidence was obtained although a very weak band appeared at 500 cm\(^{-1}\). A decrease in the N-O stretching frequency would mean an increase in the metal-nitrogen stretching frequency, and it is possible that at room temperature this occurs below 400 cm\(^{-1}\).

Nitrosyl salphen iron showed very similar behaviour to that of the salen complex. On cooling the peak at 1724 cm\(^{-1}\) disappeared completely whilst the room temperature shoulder, at 1663 cm\(^{-1}\), grew into a peak, at 1643 cm\(^{-1}\), at 83 K. The new peak disappeared when the sample was reheated to room temperature. The change in the spectrum with temperature is shown in Fig. 29 and changes in data in Table 32. No other changes were observed in the spectrum in the 400-4000 cm\(^{-1}\) region. The intensities of the ligand peaks at \( \nu = 1600-1620 \text{ cm}^{-1} \) remained unchanged over the temperature range. Two new peaks were observed in the nitrosyl spectrum, 605 and 490 cm\(^{-1}\), which were not present in the parent complex. On cooling these peaks shifted to 611 and 508 cm\(^{-1}\) respectively. No assignments have been made for these adsorptions.

The 5-nitrosalen nitrosyl, as shown in Fig. 30 and Table 32, gave a peak at 1718 cm\(^{-1}\); which occurred as a shoulder at room temperature. The new peak disappeared when
Infrared Spectra of Nitrosyl Salphen Iron Over a Temperature Range

Fig. 29
Infrared Spectra of Nitrosyl 5-Nitrosalen Iron Over a Temperature Range

298°K

213°K

123°K

83°K

Fig. 30

$\nu_{lsNO}$

$\nu_{hsNO}$

$\nu_{lsNO}$

$\nu_{hsNO}$

$\nu_{lsNO}$

$\nu_{hsNO}$

$\nu_{lsNO}$

$\nu_{hsNO}$

$\nu_{lsNO}$

$\nu_{hsNO}$

1700 1800 1900 cm$^{-1}$

1900 1800 1700 cm$^{-1}$

Fig. 30
the sample was reheated to room temperature. The absorption at 1792 cm\(^{-1}\) showed no loss of intensity on cooling; however, the decrease expected could be small enough to be more than offset by the increased intensities obtained at liquid air temperatures. The peak at 1792 cm\(^{-1}\) moved by about 13 cm\(^{-1}\) to a higher frequency on cooling. No other changes were observed in the spectrum in the 400-4000 cm\(^{-1}\) region. A new peak was observed in the nitrosyl spectrum, 432 cm\(^{-1}\), which was not present in the parent complex. No assignment has been made for this absorption.

It would seem that the N-O stretching frequency of the high-spin isomer is at a higher frequency than that of the low-spin isomer and that as the relative proportions of \(S=3/2\) and \(S=1/2\) change the infrared spectra change in accord with the magnetic data. The infrared behaviour of the 5-nitrosalen nitrosyl is similar to that of the other two, but the relative proportions of \(S=3/2\) and \(S=1/2\) isomers change much more slowly with temperature. This is consistent with the magnetic data.

The differences between the N-O stretching frequencies for high- and low-spin isomers for the nitrosyls of salen, salphen and 5-nitrosalen iron are ~95, 82 and 86 cm\(^{-1}\) respectively. (It is assumed that the low-spin isomer of salen absorbs in the same region as the ligand peak and is obscured.) Compounds containing nitric oxide co-ordinated as NO\(^+\) and NO\(^-\) have N-O stretching frequencies separated by 100-200 cm\(^{-1}\) (Table 6). This indicates that as the M-N-O grouping goes from ~180\(^\circ\) to ~120\(^\circ\) there will be a lowering of the N-O stretching frequency. Also the greater the \(\pi\)-bonding between the metal-nitrogen bond the lower the expected N-O stretching frequency. As it has been suggested that the nitrosyls contain nitric oxide co-ordinated as NO\(^-\), it is believed that the change in N-O stretching frequency is primarily caused by an increase in the \(\pi\)-bonding between
the metal-nitrogen bond on spin-pairing. It is possible that the stretching frequency may also be lowered if further bending of the already bent Fe-N-0 grouping took place on cooling. A recent X-ray crystallographic examination of FeNO[S₂CN(CH₃)₂]₂⁵¹ has shown for the low-spin complex that the Fe-N-0 bond angle reduces on cooling. However as the complex was considered to contain nitric oxide co-ordinated as NO⁺ and as no low temperature data are available, no correlation between Fe-N-0 bond angle and N-0 stretching frequency may be made.

**Correlation of Magnetic and Infrared Data over the Temperature Range 300-80°K**

Some interesting correlations between the percentages of spin-states in the nitrosyls, at different temperatures, have been made using the magnetic data and the areas of the peaks assigned to N-0 stretching frequencies.

The equation (69) used by Sylva et al.¹²⁸ for the calculation of mole fractions of high- and low-spin states in compounds exhibiting spin-state isomerism was used.

\[ M_H \mu_H^2 + M_L \mu_L^2 = \mu_{exp}^2 \]  

\( M_H \) and \( M_L \) are the mole fractions of high- and low-spin states respectively, \( \mu_H \) and \( \mu_L \) the spin-only values of high-spin (\( S=3/2 \)) and low-spin (\( S=1/2 \)) magnetic moments, \( 3.88 \) B.M. and \( 1.73 \) B.M. respectively and \( \mu_{exp} \) is the experimentally observed magnetic moment. The percentages of high- and low-spin states were calculated for the complete temperature range and are shown in Table 33.

In any quantitative analysis of a compound exhibiting an absorption spectrum it is necessary to choose an absorption peak such that there is a minimum interference by other peaks. Then for such an absorption peak, Beer's law may be applied

\[ A = \varepsilon c l \]
Table 33
Percentages of Spin-States Calculated Over a Temperature Range, from Magnetic Data

<table>
<thead>
<tr>
<th>Nitrosyl salen iron</th>
<th>T°K</th>
<th>% High-Spin</th>
<th>% Low-Spin</th>
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<tbody>
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<td></td>
<td>290.4</td>
<td>88</td>
<td>12</td>
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<tr>
<td></td>
<td>274.8</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>234.2</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>194.4</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>153.0</td>
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<td>17</td>
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<tr>
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<td>125.5</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>105.4</td>
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<td>25</td>
</tr>
<tr>
<td></td>
<td>87.5</td>
<td>72</td>
<td>28</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrosyl salphen iron</th>
<th>T°K</th>
<th>% High-Spin</th>
<th>% Low-Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>294.8</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>274.9</td>
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<td>18</td>
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<tr>
<td></td>
<td>194.2</td>
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</tr>
<tr>
<td></td>
<td>184.1</td>
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<td></td>
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</table>

<table>
<thead>
<tr>
<th>Nitrosyl 5-nitrosalen iron</th>
<th>T°K</th>
<th>% High-Spin</th>
<th>% Low-Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>290.4</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>274.8</td>
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</tr>
<tr>
<td></td>
<td>87.5</td>
<td>72</td>
<td>28</td>
</tr>
</tbody>
</table>
where \( A \) is the absorbance of the peak being analysed, \( \varepsilon \) is the molar extinction coefficient, \( l \) is the cell thickness and \( c \) is the concentration of the compound in moles litre\(^{-1}\). Beer's law assumes that the number of molecules in the path of the incident radiation depends directly on the concentration of the substance.

The integrated absorption coefficient \( \kappa \), is the area under the optical density curve after back-ground absorption has been removed and is given by equation (71).

\[
\kappa = \int_{-\infty}^{+\infty} \varepsilon \, d\nu = \frac{1}{cl} \int_{-\infty}^{+\infty} A \, d\nu \quad \cdots \quad (71)
\]

Therefore the area under a peak, for practical purposes using \( \varepsilon_{\text{max}} = \varepsilon_{\nu} \), is proportional to the concentration of the absorbing species.

The percentages of high- and low-spin states in the nitrosyls, at different temperatures, were calculated using the peak areas of the N-O stretching frequencies. As the infrared spectra of absorbance \( v \), cm\(^{-1}\) for each nitrosyl, over the temperature range, was recorded using the same nujol mull, the quantity \( l \) in equation (70) was considered to be constant. It was further assumed that the molar extinction coefficient of the complex in the different spin-states were equal, and that the coefficient for each spin-state was temperature independent.

The results for the nitrosyls are given in Table 32, for nitrosyls salphen- and 5-nitrosalen-iron column 1 represents the percentage of each spin-isomer, calculated for the same temperature, from the ratio of the peak areas of the two spin-states. For nitrosyl salen iron column 1 represents the percentage of high-spin isomer calculated from the ratio of peak areas over the temperature range; using the room temperature peak area as 100%. Column 2, for all compounds, represents the percentage of each spin isomer calculated from
the ratio of peak areas over the temperature range, assuming the peak areas at room temperature represent the percentage of high- and low-spin states calculated from the room temperature magnetic data. The data obtained from the magnetic measurements for percentages of spin-states are given in column 3.

There is reasonable agreement between the results calculated from the magnetic and infrared data. The nitrosyl 5-nitrosalen iron showed the best agreement. However this was to be expected as the relative proportions of high- and low-spin states change much more slowly with temperature compared with the other nitrosyls. The results for nitrosyl salphen iron show a reasonable correlation between the percentages of spin-states calculated from peak areas of the same spectrum and percentages calculated from the magnetic data. Comparing the percentages calculated from peak areas between spectra gave a fair correlation with those calculated from the magnetic data for the high-spin state but poor agreement for the low-spin state. However, for the nitrosyls of salen and salphen iron, reasonable agreement between the percentages calculated from the infrared and magnetic data from the room and liquid nitrogen temperatures was observed. The explanations for the lack of correlation at intermediate temperatures are

i) The infrared measurements are not so sensitive to temperature changes as were the magnetic measurements

ii) Temperature control of the infrared measurements was much less precise than in the magnetic measurements.

Mössbauer Properties

The Mössbauer spectra (Table 34, Figs 31-33) show a dramatic change from room to liquid nitrogen temperatures for the salen and salphen nitrosyls. The spectrum of the nitrosyl 5-nitrosalen iron remained unaltered with temperature.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosyl salen iron</td>
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<td>0.29</td>
</tr>
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<td></td>
<td>80</td>
<td>0.51</td>
<td>1.92</td>
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<tr>
<td>Nitrosyl salphen iron</td>
<td>300</td>
<td>0.62</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.53</td>
<td>1.72</td>
</tr>
<tr>
<td>Nitrosyl 5-nitrosalen iron</td>
<td>300</td>
<td>0.76</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.76</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Nitrosyl Salen Iron

300°K

80°K

VELOCITY (mm sec⁻¹)

Fig. 31
Nitrosyl Salphen Iron

300°C

80°C

RELATIVE COUNT RATE

VELOCITY (mm sec⁻¹)

Fig. 32
Nitrosyl 5–Nitrosalen Iron

Fig. 33

300°K

80°K

RELATIVE COUNT RATE

VELOCITY (mm sec⁻¹)

Fig. 33
From the infrared and magnetic data it has been suggested that the nitrosyls are formally Fe(III)NO$^-$ although the results can be explained in terms of Fe(I)NO$^+$. However, the Mössbauer parameters given here (Table 34) at room temperature are typical of high-spin iron(III) compounds i.e. isomer shifts of $\sim 0.6-0.7$ mm sec$^{-1}$ and small quadrupole splittings (see Introduction 4ii-iii)). The isomer shift values suggest that at room temperature, the nitrosyls contain Fe(III) and NO$^-$. The nitrosyls have been assumed to have square-pyramidal structures and considered to be high-spin iron(III) complexes. They are not 'normal' high-spin iron(III) complexes in that they contain only three and not five unpaired electrons. The zero or low quadrupole splitting values indicate a spherical or nearly spherical symmetry for the d-electrons at the nucleus typical of high-spin iron(III) complexes. It is unlikely, however, that the nitrosyls have no valence contribution to the electric field gradient (as expected for high-spin iron(III)) but that the valence and lattice contributions may be equal and opposite as suggested for Gillespith.$^{154}$

The nitrosyls salen and salphen iron have (Table 34) a slight reduction in the isomer shift on cooling. This suggests that on cooling there is a decrease of d-electron density and an increase in s-electron density at the nucleus. The quadrupole splittings for these nitrosyls increase dramatically from zero or nearly so to $\sim 1.8$ mm sec$^{-1}$. The large quadrupole splittings observed for low-spin iron(II) and iron(III) complexes containing $\pi$-bonding ligands have been attributed to d-electron delocalisation into the $\pi$-antibonding orbitals on the $\pi$-acceptor ligand, disturbing the symmetry of the molecule and giving rise, therefore, to a large electric field gradient.

Thus a similarly large quadrupole splitting would be expected for the nitrosyls, if on spin-pairing, the d-electron
delocalisation increased. An increase of d-electron delocalisation would increase the s-electron density at the nucleus and produce a smaller isomer shift. Both an increase of quadrupole splitting and a decrease in isomer shift are observed for these nitrosyls on spin-pairing.

Oxidation State of Iron and Nitric Oxide and Factors Causing Spin-Pairing

The nitrosyls have been interpreted as examples of Fe(IXX)NO\textsuperscript{-} in the high- and low-spin states using the infrared, magnetic, Mössbauer and chemical data.

There are three possible ways in which spin-pairing may take place

i) simple pairing to maintain an iron(III) environment

ii) formation of an iron(II) species with NO\textsubscript{2}, the unpaired electron being on the nitric oxide.

iii) transfer of two electrons to formally produce Fe(I)NO\textsuperscript{+}.

Spin-pairing via any of these mechanisms would lead to an increased ability of the iron nucleus to back bond to the π-antibonding orbitals of the nitric oxide. It is suggested from the chemical evidence that it is unlikely that nitric oxide co-ordinated as NO\textsuperscript{-} becomes NO\textsuperscript{+} on cooling, and the infrared data also suggest NO\textsuperscript{-} at lower temperatures. If NO\textsuperscript{+} were formed, the bond order of the co-ordinated nitric oxide would be expected to increase and therefore the N-O stretching frequency would be expected to move to a higher, not lower, frequency.

The magnetic data gave an exact temperature at which spin-pairing takes place, in the salen and salphen nitrosyls, but no unambiguous assignment of the oxidation state of the iron.

High-spin iron(III) complexes with three unpaired electrons have been reported with isomer shifts similar to the nitrosyls, but usually with large quadrupole
splittings$^{163,81}$. The complex Fe(dtc)$_2$Cl$^{164}$ (dtc = diethyldithiocarbamate) has a square-pyramidal structure and a large quadrupole splitting$^{165}$ which has been attributed to a large valence contribution to the electric field gradient opposed by a small lattice contribution. Various iron(III) complexes [Fe(py)$\left\{S_2C_2R_2\right\}_2$]$^-$ (R=CN or CF$_3$) have three unpaired electrons and have been assumed to be square-pyramidal$^{166}$. These complexes have similar isomer shifts to those of the nitrosyls but with larger quadrupole splittings$^{81}$.

The low-spin iron mononitrosyls of related systems to salen ligands have similar isomer shifts to those reported here but the complexes have been interpreted as Fe(I)NO$^+$ compounds. The unstable brown-ring complexes with three unpaired electrons have been variously described as complexes of Fe(I)$^{60}$ and Fe(III)$^{69}$. With the uncertainty of the oxidation state of the iron and the differing stereochemistries involved no correlation between these results and the results here has been made. However low-spin iron(III) systems having one strongly $\pi$-bonding ligand would be expected to have a large quadrupole splitting as had been mentioned (p.152). It is suggested therefore that the Mössbauer data may be interpreted favourably for Fe(III) for both the high- and low-spin states.

The assignment of the electronic configuration of the nitrosyls may help to determine the quadrupole splittings in high- and low-spin states. Using the system of molecular orbitals considered present in complexes like these$^{46}$ in which one strongly $\pi$-bonding ligand dominates the overall ligand field, Larkworthy$^{6^4}$ suggested the following electronic configurations,

$$(e^b)^{4} (d_{xy})^{1} (e^* )^{2} \text{ for the high-spin state}$$

and

$$(e^b)^{4} (d_{xy})^{2} (e^* )^{1} \text{ for the low-spin state}.$$
The levels occupied are \( e^b(d_{xz,yz}) \), \( d_{xy} \), \( e^x(\pi^{NO}) \) in which the \( e^b \) and \( e^x \) orbitals are the bonding and antibonding orbitals derived from the \( d_{xz} \) and \( d_{yz} \) and the nitric oxide orbitals. The \( \pi \)-bonding properties of the salen ligands are likely to be small because of the lack of suitable orbitals on the phenolic oxygen atoms, and an alternative molecular orbital scheme requiring considerable delocalization to the non-nitrosyl ligands may be less appropriate. The first configuration corresponds immediately to Fe(III)NO\(^-\), whereas the second is apparently neutral NO\(^-\) and Fe(II). Nevertheless the relative proportions of \( d \)-orbital and \( \pi \) character in the \( e^b \) and \( e^x \) levels vary greatly and the configuration can still correspond to Fe(III)NO\(^-\).

Assuming the \( e^b \) orbitals to be entirely \( d \) orbital in character, then using the expectation values (Introduction 4iii) a large quadrupole splitting is expected for the high-spin state compared to zero splitting for the low-spin form. Slightly better results are calculated placing the \( d_{xy} \) level lowest, as determined for Fe(dtc)\(_2\)Cl. However as \( e^b \) is a mixture of \( d_{xz,yz} \) and \( \pi \)-bonding orbitals of nitric oxide no definite quadrupole splittings may be accurately predicted. An increase in the \( d \)-electron delocalisation for the low-spin state may be predicted if the following electronic configurations were assumed

\[
\begin{align*}
(d_{xy})^2 & \quad (e^b)^3 \quad (e^x)^2 \quad \text{high-spin} \\
(d_{xy})^1 & \quad (e^b)^4 \quad (e^x)^1 \quad \text{low-spin}
\end{align*}
\]

whereas no increase is directly apparent from the configurations proposed by Larkworthy\(^{84}\).

Although visible and ultra-violet spectra of the nitrosyls have been recorded by King\(^{145}\) no band assignments could be made, except for \( e^b \rightarrow e^x \), because of intense ligand absorptions.
Until more data is available no definite electronic configurations are proposed here for the high- and low-spin states of the nitrosyls.

It has been suggested that contraction of the lattice, a change in Fe-N-O bond angle from linear to end-on bonding, or the formation of bridging nitric oxide groups could cause spin-pairing. The last has been excluded by the failure to observe, on spin-pairing, new bands around 1500 cm\(^{-1}\), where bridging nitric oxide groups usually absorb. It is now known that as the lattice contracts the Fe-N-O grouping in the low-spin complex, FeNC\([S_2CN(CH_3)_2]_2\)\(^{51}\), becomes slightly more bent. The nitric oxide remains bonded via the nitrogen atom to the iron nucleus.

Coordination of nitric oxide may bring the ligand field close to the crossover point, and comparatively minor solid-state effects could determine whether a particular substituted salen nitrosyl will exist as the \(S = \frac{3}{2}\) or \(S = \frac{1}{2}\) isomers, or a mixture of the two. It is uncertain whether any change in the bond angle of the Fe-N-O grouping on cooling would be the cause or a result of spin-pairing.

It is uncertain at this time whether spin-pairing is caused individually or by a combination of chemical, solid-state or temperature effects. It is probable however that spin-pairing is a combination of many effects. X-ray crystallographic measurements over a temperature range, on these nitrosyls, would be of great interest.
3. ADDUCTS OF BIS(SALICYLALDEHYDATO)IRON(II)
Magnetic and Mössbauer Measurements

As described in Part I of this discussion, octahedral, high-spin iron(II) complexes are expected to have four unpaired electrons and effective magnetic moments of ~5.5 B.M. at room temperature. Any distortion from cubic symmetry will cause the magnetic moments to approach the spin-only values (4.9 B.M.) and vary little with temperature.

As shown in Table 35 and Fig. 34, the complexes obeyed the Curie-Weiss law with small or zero values and magnetic moments in the range 4.9-5.2 B.M., which were almost independent of temperature. The room temperature magnetic moment of the pyridine adduct is 5.19 B.M. The Mössbauer data, Table 36, show that the room temperature isomer shift values all lie in the range 1.28-1.40 mm sec⁻¹, typical for high-spin iron(II) complexes. The quadrupole splittings are in the range 2.15-2.48 mm sec⁻¹ indicating a large distortion from cubic symmetry. The quadrupole splittings also show some temperature dependence, Table 36, and small values of $-\Delta E/\Delta T$ (Table 37) indicating a large distortion from cubic symmetry. The isomer shifts of all complexes increase on cooling due to the second-order Doppler effect. Typical Mössbauer spectra are shown in Fig. 35.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta E/\Delta T/100^\circ\text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(sal)$_2$(H$_2$O)$_2$</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe(sal)$_2$py$_2$</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe(sal)$_2$pip$_2$</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe(sal)$_2$β-pic$_2$</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe(sal)$_2$γ-pic$_2$</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe(sal)$_2$lut$_2$</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 35
Magnetic Susceptibility Measurements on
Adducts of Bis(salicylaldehydato)iron(II)

i) Bis(salicylaldehydato)diaquoiron(II)

<table>
<thead>
<tr>
<th>Temp(°K)</th>
<th>294.6</th>
<th>275.0</th>
<th>234.2</th>
<th>193.8</th>
<th>152.3</th>
<th>125.0</th>
<th>105.0</th>
<th>87.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>10618</td>
<td>11358</td>
<td>13454</td>
<td>16288</td>
<td>20898</td>
<td>25528</td>
<td>30218</td>
<td>36388</td>
</tr>
<tr>
<td>$\gamma_A \times 10^{-2}$</td>
<td>0.942</td>
<td>0.880</td>
<td>0.738</td>
<td>0.614</td>
<td>0.479</td>
<td>0.392</td>
<td>0.331</td>
<td>0.275</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}(B.M.)$</td>
<td>5.00</td>
<td>5.01</td>
<td>5.04</td>
<td>5.02</td>
<td>5.04</td>
<td>5.05</td>
<td>5.04</td>
<td>5.04</td>
</tr>
</tbody>
</table>

Molecular Weight 334.1 Diamagnetic Correction 147.9 x 10$^{-6}$ c.g.s.u.

$\theta = 0^\circ$

ii) Bis(salicylaldehydato)bis(\(\beta\)-picoline)iron(II)

<table>
<thead>
<tr>
<th>Temp(°K)</th>
<th>291.4</th>
<th>274.7</th>
<th>234.2</th>
<th>153.0</th>
<th>87.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>11347</td>
<td>12027</td>
<td>14017</td>
<td>21427</td>
<td>37097</td>
</tr>
<tr>
<td>$\gamma_A \times 10^{-2}$</td>
<td>0.281</td>
<td>0.313</td>
<td>0.713</td>
<td>0.467</td>
<td>0.270</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}(B.M.)$</td>
<td>5.14</td>
<td>5.14</td>
<td>5.12</td>
<td>5.12</td>
<td>5.09</td>
</tr>
</tbody>
</table>

Molecular Weight 434.4 Diamagnetic Correction 246.5 x 10$^{-6}$ c.g.s.u.

$\theta = 2^\circ$

iii) Bis(salicylaldehydato)bis(\(\gamma\)-picoline)iron(II)

<table>
<thead>
<tr>
<th>Temp(°K)</th>
<th>294.9</th>
<th>274.9</th>
<th>234.5</th>
<th>152.9</th>
<th>87.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>10477</td>
<td>11337</td>
<td>13107</td>
<td>20157</td>
<td>35117</td>
</tr>
<tr>
<td>$\gamma_A \times 10^{-2}$</td>
<td>0.954</td>
<td>0.882</td>
<td>0.763</td>
<td>0.496</td>
<td>0.285</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}(B.M.)$</td>
<td>4.97</td>
<td>4.99</td>
<td>4.96</td>
<td>4.96</td>
<td>4.96</td>
</tr>
</tbody>
</table>

Molecular Weight 434.4 Diamagnetic Correction 246.5 x 10$^{-6}$ c.g.s.u.

$\theta = 0^\circ$

iv) Bis(salicylaldehydato)bis(3,5-lutidine)iron(II)

<table>
<thead>
<tr>
<th>Temp(°K)</th>
<th>295.9</th>
<th>274.8</th>
<th>234.4</th>
<th>153.0</th>
<th>93.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>10900</td>
<td>11560</td>
<td>13550</td>
<td>20810</td>
<td>34210</td>
</tr>
<tr>
<td>$\gamma_A \times 10^{-2}$</td>
<td>0.918</td>
<td>0.865</td>
<td>0.738</td>
<td>0.478</td>
<td>0.292</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}(B.M.)$</td>
<td>5.07</td>
<td>5.04</td>
<td>5.04</td>
<td>5.05</td>
<td>5.04</td>
</tr>
</tbody>
</table>

Molecular Weight 512.4 Diamagnetic Correction 270.2 x 10$^{-6}$ c.g.s.u.

$\theta = 1^\circ$

v) Bis(salicylaldehydato)bis(piperidine)iron(II) was found to be slightly ferromagnetic.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. °K</th>
<th>$\delta$ (mm sec$^{-1}$)</th>
<th>$\Delta E$ (mm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(sal)$_2$(H$_2$O)$_2$</td>
<td>300</td>
<td>1.40</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.52</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe(sal)$_2$py$_2$</td>
<td>300</td>
<td>1.31</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.40</td>
<td>2.55</td>
</tr>
<tr>
<td>Fe(sal)$_2$py$_2$ [Ref. 36]</td>
<td>300</td>
<td>1.31</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.44</td>
<td>2.26</td>
</tr>
<tr>
<td>Fe(sal)$_2$pip$_2^X$</td>
<td>300</td>
<td>1.32</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.42</td>
<td>2.30</td>
</tr>
<tr>
<td>Fe(sal)$_2$β-pic$_2$</td>
<td>300</td>
<td>1.33</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.41</td>
<td>2.34</td>
</tr>
<tr>
<td>Fe(sal)$_2$γ-pic$_2$</td>
<td>300</td>
<td>1.34</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.40</td>
<td>2.24</td>
</tr>
<tr>
<td>Fe(sal)$_2$lut$_2$</td>
<td>300</td>
<td>1.28</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.43</td>
<td>2.15</td>
</tr>
</tbody>
</table>

py = pyridine  pip = piperidine  β-pic = β-picoline  
γ-pic = γ-picoline  lut = 3,5-lutidine.

$^X$This product showed signs of oxidation during the measurement.
Typical Mössbauer Spectra of Adducts of Bis(salicylaldehydato)iron(II)

Fig. 35
Thus, the magnetic and Mössbauer data indicate that the adducts are distorted octahedral and high-spin iron(II) complexes.

Unfortunately the piperidine adduct was found to be slightly ferromagnetic probably due to a trace of oxidation. However, the complex was expected to be high-spin iron(II), and as the Mössbauer data indicated that it was predominantly in this state the data are used in the following discussion.

The known base adducts of bis(salicylaldehydato)-iron(II) and related systems have been described (p.19). It has been suggested that these have trans tetragonal distorted octahedral structures (Fig. 5) analogous to that of bis(salicylaldehydato)diaquonickel(II) which has been crystallographically determined\(^{167}\). All the Ni-O bonds were approximately 2.0\(\AA\). Mössbauer data for bis(salicylaldehydato)iron(II) have been reported by Stukan\(^{15}\) and de Vries\(^{32}\), the former's sample probably being oxidised. The colour of the complex and the Mössbauer data reported by de Vries\(^{32}\) (Table 21) are very similar to the data presented here, although it does not appear that he realised that the complex contains co-ordinated water. The water molecules in bis(salicylaldehydato)diaquiron(II) are considered co-ordinated because of the great difficulty in removing the water and the known structure of Ni(sal)_2(H_2O)_2.

The order of the isomer shifts and quadrupole splittings, at room temperature are as follows (from Table 36):

**Isomer shift**

\[
\text{H}_2\text{O} > \gamma\text{-pic} \approx \beta\text{-pic} \approx \text{pip} \approx \text{py} > \text{lut}
\]

**Quadrupole splitting**

\[
\text{H}_2\text{O} > \text{py} > \beta\text{-pic} > \text{pip} > \gamma\text{-pic} > \text{lut}.
\]

The differences between the isomer shifts of the unsaturated heterocyclic nitrogen adducts are very small and probably insignificant.
It has been suggested and verified that for high-spin iron(II) complexes, there is a correlation between the isomer shift and the nephelauxetic effect. Correlations between quadrupole splitting values and chemical bonding parameters are usually less apparent than with isomer shift values.

Mössbauer parameters depend on the covalency of the bond between the metal and donor atom. Since the isomer shift is proportional to the total s-electron density, the correlation between isomer shift and the nephelauxetic series indicates an increase of the s-electron density at the iron atom with an increasing tendency of the ligand to undergo covalent formation. This has been attributed to

i) the increasing tendency of the electrons of the ligands to occupy the outer s-orbitals of the iron with increasing covalent bonding.

ii) the decrease in shielding of s-electrons due to the delocalisation of d-electrons in molecular orbitals.

The decreasing order of the isomer shift for high-spin iron(II) complexes will be approximately the same as the increase in the order of covalency i.e., the nephelauxetic series of the ligands.

F < 0 < N < Cl < Br < I < S < Se

nephelauxetic series → decreasing isomer shift

In the iron(II) complexes of more or less strongly π-acceptor ligands, increasing covalent character of the bond between metal and donor atom transfers d-electrons from π-bonding orbitals of the ligand. In high-spin iron(II) complexes this electron transfer results in an increase of the symmetry of the d shell. The d^6 electronic configuration of iron(II) gradually approaches the symmetric, high-spin, d^5 configuration of iron(III). Thus a transfer of d-electrons
will increase the symmetry of charge distribution about the nucleus, reduce the electric field gradient and reduce the quadrupole splitting. The decreasing order will run approximately parallel with the increasing order of covalency i.e., the nephelauxetic series

\[ F < O < N < Cl < Br < I \]

decreasing quadrupole splitting

The Mössbauer data in Table 36 indicate the general trend of decreasing isomer shift and quadrupole splitting with the nephelauxetic series i.e., both parameters for the oxygen donor ligand, H\(_2\)O, are greater than for the nitrogen donor ligands. However, for the closely related series of nitrogen donor ligands, the relative order of ligand field strength or covalency depends upon the ligand basicity, \( pK_a \). The greater the \( pK_a \) value the greater the donor power will be. The \( pK_a \) values of some unsaturated heterocyclic nitrogen adducts are given in Table 38.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyridine</td>
<td>5.23</td>
</tr>
<tr>
<td>( \beta )-picoline</td>
<td>5.68</td>
</tr>
<tr>
<td>( \alpha )-picoline</td>
<td>5.97</td>
</tr>
<tr>
<td>( \gamma )-picoline</td>
<td>6.02</td>
</tr>
<tr>
<td>3,5-lutidine</td>
<td>6.15</td>
</tr>
</tbody>
</table>

It has been shown that steric effects of the ligands must also be considered, as the relative order of ligand field strengths in complexes containing these ligands does not always follow the \( pK_a \) values\(^\text{171,172}\). It may be expected therefore that the isomer shifts and quadrupole splittings for a series of nitrogen donor atom adducts, with no strong steric effects to consider, should follow the \( pK_a \) values of the adducts. The Mössbauer data for a series of complexes \([\text{Fe(dimethylglyoxime)}_2].2L (L = \text{py, } \beta\text{-pic}\)
and α-pic) showed that the isomer shift value, at 80°C, decreased in the order

\[ \beta\text{-pic} > \text{py} > \alpha\text{-pic} \]

which did not follow the \( pK_a \) values. The quadrupole splittings, however, at 80°C decreased in the order

\[ \text{py} > \beta\text{-pic} > \alpha\text{-pic} \]

which did follow the \( pK_a \) values and contradicts the series above, as both series should have the same order.

The Mössbauer data shown in Table 36 indicate that the isomer shifts, for the pyridine and substituted pyridine adducts, are so close that no correlation with the nephelauxetic series or basicity of the ligand with the isomer shift values may reasonably be made. The general series, showing a decrease in isomer shift, may be written as follows

\[ \gamma\text{-pic} \approx \beta\text{-pic} \approx \text{py} > \text{lut} \]

As 3,5-lutidine was the most basic adduct (Table 38) the isomer shift was expected to be the smallest in the series as observed. The quadrupole splitting values, however, gave a good correlation with basicity of the adducts. The quadrupole splitting values decreased as the \( pK_a \) value increased i.e. as the covalency of the adduct increased \( \Delta E \) became smaller. The order is as follows

\[ \text{py} > \beta\text{-pic} > \gamma\text{-pic} \approx \text{lut} \]

The piperidine adduct was not considered as part of the related series of pyridine heterocycles as it is a saturated molecule. The results show (Table 36) that the complex is high-spin iron(II) and no further investigations were carried out as the complex was found to be partially oxidised (p.162).

It was concluded that the adducts were high-spin iron(II) complexes with a tetragonally distorted octahedral symmetry, the monodentate ligands being in a \textit{trans} position (Fig. 5).

It was also found that there was a partial correlation between
the isomer shift and quadrupole splittings, the nephelauxetic series of the ligands, and pKₐ values for the unsaturated heterocyclic nitrogen ligands.

**Infrared Data**

The infrared spectrum of each complex was recorded over the region 650-2000 cm⁻¹ but no band assignments were attempted. The spectrum of Fe(sal)₂(H₂O)₂ shows two -OH stretching frequencies at 3250 and 3480 cm⁻¹. The -OH bending frequency was not observed as there was a strong carbonyl absorption at 1620 cm⁻¹. The spectrum of Fe(sal)₂(pip)₂ shows a single -NH stretching frequency at 3250 cm⁻¹, typical of a secondary amine.
TRIS(MONOTHIOL-β-DIKETONATO)IRON(III) COMPLEXES
TRIS(MONOTHIO-β-DIKETONATO)IRON(III) COMPLEXES

Introduction

In the general Introduction (3iii)) spin-state isomerism and factors governing spin-pairing have been discussed. Ho and Livingstone\textsuperscript{121} reported magnetic behaviour best explained by a thermal equilibrium between high-spin ($^6A_g$) and low-spin ($^2T_2$) isomers for certain iron(III) complexes of monothio-β-diketones of the general formula Fe[R$^1$CSCHCOR$^2$]$_3$. The magnetic behaviour depended on the nature of the R$^-$ groups and electron-withdrawing substituents appeared to increase the population of the spin-paired configuration.

An investigation has been carried out on a series of tris(monothio-β-diketonato)iron(III) complexes shown in Fig. A.

\[
\begin{array}{c}
\text{Fe} \\
\begin{array}{c}
\text{S} \\
\text{R}^1 \\
\hline
\text{O} \\
\text{R}^2
\end{array}
\end{array}
\]

I = $R^1$=R$^2$=Ph
II = $R^1$=R$^2$=Me
III = $R^1$=Me; $R^2$=Ph
IV = $R^1$=Ph; $R^2$=Me

Fig. A.

Spin isomerism has been observed for compound (I)$^{121}$. Compounds (II)-(IV) are new and were supplied by Dr. M. Cox and J. Darken of the Polytechnic, Hatfield. The complexes were prepared by the reaction of anhydrous iron(III) chloride with the ligand in a tertiary amine solvent.

The magnetic and Mössbauer data of the related iron(III) complexes, Fe[CH$_3$COCHCOCH$_3$]$^{173}$ and Fe[CH$_3$CSCHCSCH$_3$]$^{174}$, are shown in Table 39. The complex with the ligand with two oxygen donor atoms is high-spin whilst two sulphur donor atoms produce a low-spin complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T^0K$</th>
<th>$5\text{mm sec}^{-1}$</th>
<th>$\Delta E \text{ mm sec}^{-1}$</th>
<th>$\mu_{\text{eff}} \text{B.M.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe[CH$_3$COCHCOCH$_3$]</td>
<td>300</td>
<td>0.61</td>
<td>unresolved</td>
<td>5.94</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.61</td>
<td>unresolved</td>
<td>5.94</td>
</tr>
<tr>
<td>Fe[CH$_3$CSCHCSCH$_3$]</td>
<td>300</td>
<td>0.46</td>
<td>1.84</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.55</td>
<td>1.90</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Magnetic Properties

The magnetic moments of the complexes (I) to (IV), i.e., with one sulphur and one oxygen donor atom were observed to be intermediate between those expected for high- and low-spin states at room temperature (Table 40). The plots of reciprocal susceptibility and $\mu_{\text{eff}}$ versus temperature are shown in Figs. 36 and 37, 38 and 39 respectively. The complexes were observed to be of two types; those obeying and those not obeying the Curie-Weiss law.

The most important feature of the magnetic data is the temperature dependence of the magnetic moments. This temperature dependence is attributed to a $^6\Delta_1 \rightarrow 2T_2$, thermal equilibrium.

Compound (I) possesses similar magnetic behaviour to that reported by Ho$^{121}$ for this complex. No sharp transition from one spin-state to the other was observed, but there was a gradual change similar to that of the tris(dialkyldithiocarbamato)iron(III) complexes$^{118}$. The room temperature magnetic moment was reduced from the normal high-spin value (5.92 B.M.) and it was calculated from equation (69) that the compound was 84% high-spin. (In equation (69) $\mu_H = 5.92$ B.M. and $\mu_L = 2.30$ B.M. This value of $\mu_L$ was used as the moment for low-spin iron(III) always includes some orbital contribution. As no single value could be assigned for low-spin iron(III), 2.30 B.M. was used as a typical value.) At 90°K the magnetic moment was not reduced completely to that of a low-spin isomer, but retained 8% high-spin character (as calculated from equation (69)).

If at room temperature there was a 1:1 mixture of spin-states, assuming equation (69) to be valid, the magnetic moment should be 4.49 B.M. Using the more general equation (32), provided the energy terms between the spin-states do not differ by more than about kT, the total
Table 40

Magnetic Susceptibility Measurements on Tris(monothio-β-diketonato)-iron(III) Compounds

I) Compounds not obeying the Curie-Weiss Law

i) Tris(pent-3-ene-4-thiono-2-onato)iron(III) \( \text{Fe(CH}_3\text{CSCHCOCH}_3 \text{)}_3 \)

Temperature reduction in half-hour intervals

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( \chi \times 10^6 )</th>
<th>( \chi^{-1} \times 10^{-2} )</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>301.0</td>
<td>265.5</td>
<td>230.1</td>
<td>193.7</td>
</tr>
<tr>
<td>265.5</td>
<td>15213</td>
<td>17363</td>
<td>20523</td>
</tr>
<tr>
<td>230.1</td>
<td>0.755</td>
<td>0.658</td>
<td>0.576</td>
</tr>
<tr>
<td>193.7</td>
<td>5.68</td>
<td>5.65</td>
<td>5.64</td>
</tr>
<tr>
<td>173.9</td>
<td>153.5</td>
<td>150.4</td>
<td>148.5</td>
</tr>
<tr>
<td>162.0</td>
<td>24593</td>
<td>24933</td>
<td>23803</td>
</tr>
<tr>
<td>160.5</td>
<td>0.405</td>
<td>0.401</td>
<td>0.420</td>
</tr>
<tr>
<td>157.7</td>
<td>5.53</td>
<td>5.35</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Temperature reduction in hour intervals

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( \chi \times 10^6 )</th>
<th>( \chi^{-1} \times 10^{-2} )</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150.5</td>
<td>148.7</td>
<td>146.0</td>
<td>143.5</td>
</tr>
<tr>
<td>148.7</td>
<td>11413</td>
<td>8905</td>
<td>8332</td>
</tr>
<tr>
<td>146.0</td>
<td>0.520</td>
<td>0.876</td>
<td>1.123</td>
</tr>
<tr>
<td>143.5</td>
<td>3.68</td>
<td>3.23</td>
<td>3.09</td>
</tr>
</tbody>
</table>

Temperature increase in half-hour intervals

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( \chi \times 10^6 )</th>
<th>( \chi^{-1} \times 10^{-2} )</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.0</td>
<td>98.7</td>
<td>110.3</td>
<td>140.4</td>
</tr>
<tr>
<td>98.7</td>
<td>7929</td>
<td>7330</td>
<td>7951</td>
</tr>
<tr>
<td>110.3</td>
<td>1.213</td>
<td>1.261</td>
<td>1.364</td>
</tr>
<tr>
<td>140.4</td>
<td>2.50</td>
<td>2.54</td>
<td>2.99</td>
</tr>
<tr>
<td>142.5</td>
<td>155.4</td>
<td>157.5</td>
<td>160.0</td>
</tr>
<tr>
<td>147.5</td>
<td>8472</td>
<td>8687</td>
<td>11013</td>
</tr>
<tr>
<td>149.9</td>
<td>1.180</td>
<td>1.151</td>
<td>0.908</td>
</tr>
<tr>
<td>152.4</td>
<td>3.24</td>
<td>3.30</td>
<td>3.75</td>
</tr>
</tbody>
</table>
Temperature increase in hour intervals

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>141.0</th>
<th>142.0</th>
<th>143.4</th>
<th>145.4</th>
<th>150.0</th>
<th>152.7</th>
<th>155.7</th>
<th>157.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_A \times 10^6$</td>
<td>7831</td>
<td>7790</td>
<td>7845</td>
<td>7551</td>
<td>7818</td>
<td>7943</td>
<td>6994</td>
<td>7860</td>
</tr>
<tr>
<td>$\chi_A \times 10^{-2}$</td>
<td>1.276</td>
<td>1.283</td>
<td>1.275</td>
<td>1.324</td>
<td>1.279</td>
<td>1.259</td>
<td>1.430</td>
<td>1.273</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$(B.M.)</td>
<td>2.97</td>
<td>2.97</td>
<td>3.00</td>
<td>2.99</td>
<td>3.06</td>
<td>3.11</td>
<td>2.95</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Molecular Weight 401.4 Diamagnetic Correction 192.6x10^{-6} c.g.s.u.

ii) Tris(1,3-diphenylprop-2-ene-3-thiono-1-onato)iron(III)

Fe(C₆H₅COCHSC₆H₅)₂₃

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>300.1</th>
<th>265.3</th>
<th>229.5</th>
<th>193.4</th>
<th>157.4</th>
<th>119.5</th>
<th>98.0</th>
<th>89.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_A \times 10^6$</td>
<td>12616</td>
<td>13146</td>
<td>12996</td>
<td>12226</td>
<td>10526</td>
<td>9624</td>
<td>10324</td>
<td>10916</td>
</tr>
<tr>
<td>$\chi_A \times 10^{-2}$</td>
<td>0.792</td>
<td>0.761</td>
<td>0.769</td>
<td>0.818</td>
<td>0.950</td>
<td>1.039</td>
<td>0.969</td>
<td>0.916</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$(B.M.)</td>
<td>5.50</td>
<td>5.23</td>
<td>4.88</td>
<td>4.35</td>
<td>3.64</td>
<td>3.04</td>
<td>2.84</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Molecular Weight 773.8 Diamagnetic Correction 416.1x10^{-6} c.g.s.u.

iii) Tris(1-phenylbut-2-ene-3-thiono-1-onato)iron(III)

Fe(C₆H₅COCHSC₆H₅)₃

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>300.4</th>
<th>265.4</th>
<th>229.7</th>
<th>193.8</th>
<th>157.2</th>
<th>119.6</th>
<th>98.2</th>
<th>89.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_A \times 10^6$</td>
<td>7886</td>
<td>7660</td>
<td>7417</td>
<td>6449</td>
<td>5353</td>
<td>5735</td>
<td>6486</td>
<td>7010</td>
</tr>
<tr>
<td>$\chi_A \times 10^{-2}$</td>
<td>1.286</td>
<td>1.305</td>
<td>1.348</td>
<td>1.551</td>
<td>1.868</td>
<td>1.744</td>
<td>1.542</td>
<td>1.427</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$(B.M.)</td>
<td>4.35</td>
<td>4.03</td>
<td>3.69</td>
<td>3.16</td>
<td>2.59</td>
<td>2.34</td>
<td>2.26</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Molecular Weight 587.7 Diamagnetic Correction 304.5x10^{-6} c.g.s.u.

II) Compound obeying the Curie-Weiss Law

i) Tris(4-phenylbut-3-ene-4-thiono-2-onato)iron(III)

Fe(C₆H₅CSCHCOCH₅)₃

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>300.5</th>
<th>265.4</th>
<th>229.4</th>
<th>193.0</th>
<th>157.0</th>
<th>118.8</th>
<th>97.5</th>
<th>87.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_A \times 10^6$</td>
<td>13555</td>
<td>15215</td>
<td>17275</td>
<td>19855</td>
<td>23045</td>
<td>28115</td>
<td>32295</td>
<td>35185</td>
</tr>
<tr>
<td>$\chi_A \times 10^{-2}$</td>
<td>0.738</td>
<td>0.657</td>
<td>0.579</td>
<td>0.504</td>
<td>0.434</td>
<td>0.356</td>
<td>0.310</td>
<td>0.284</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$(B.M.)</td>
<td>5.75</td>
<td>5.68</td>
<td>5.63</td>
<td>5.60</td>
<td>5.38</td>
<td>5.17</td>
<td>5.02</td>
<td>4.95</td>
</tr>
</tbody>
</table>

Molecular Weight 587.7 Diamagnetic Correction 304.5x10^{-6} c.g.s.u. 

$\theta = 51^\circ$
Fig. 36

- 

$\text{Compound} \{1\}$

$\times = \text{Decrease, half-hour intervals}$

$++ = \text{Increase, half-hour intervals}$

$\Delta = \text{Hour}$

$\text{Temp.}^\circ \text{K}$
Fig. 37

- Compound (III)
- Compound (I)
- Compound (IV)

\[ X_{A}^{50} \times 10^{-2} \]

Temp.°K

\[ \theta = 5^\circ \]
Fig. 38

Compound (II)

- Decrease, half-hour intervals
- Increase, half-hour
- Hour

μeff vs Temp. °K
susceptibility, $\gamma_A$, should be the population-weighted average of the susceptibilities of the two spin-states. In the limit, when there is a 1:1 distribution of spin-states, the room temperature magnetic moment is 4.49 B.M. As usually found compound (I) does not obey a simple Boltzmann distribution between the spin-states.

Compound (II) shows a sharp transition in the reciprocal susceptibility and $\mu_{\text{eff}}$ versus temperature plots at $\sim 150^\circ\text{K}$ as the complex changes from high-spin ($^6A_1$) to low-spin ($^2T_2$). The nature of the transition is very similar to that of nitrosyl salen iron (see Figs. 25 and 27). The room temperature magnetic moment was reduced (as compound (I)) from the normal high-spin value and at $30^\circ\text{K}$ the magnetic moment was almost equivalent to one unpaired electron, with some orbital contribution. It was calculated that at $300^\circ\text{K}$ the complex was 90% high-spin and at $80^\circ\text{K}$ 3% high-spin. The results (see Figs. 36 and 38) show that on cooling the sample, from 300-80$^\circ\text{K}$, the sharp transition occurred at $\sim 150^\circ\text{K}$ but on warming the sample, from 80-300$^\circ\text{K}$, the transition took place at $\sim 130^\circ\text{K}$ higher. Otherwise the curves obtained on heating or cooling coincided. The magnitude of the discontinuity also varied with different preparations. The results indicated that time was not an important factor in the temperature equilibrium. Measurements were taken at hourly and half-hourly intervals, both on cooling and warming the sample, and all the results lay, within experimental error, on the same curve for $\gamma_A^{-1} v. T$ and $\mu_{\text{eff}} v. T$ (see Figs. 36, 38). A sharp transition between spin-state isomers has been suggested to be due to a phase change in the solid. However, the explanation may not be as simple as this.

Compound (III) showed like compound (I) a gradual transition from high-spin to low-spin. At room temperature the magnetic moment is 4.35 B.M., which corresponds
to 46% high-spin character. The complex is completely low-spin at 80°C.

Compound (IV) was the only compound to obey the Curie-Weiss law. All the other complexes show a transition from high- to low-spin states. It may be that measurements on this complex have not been made to a sufficiently low temperature to observe a complete transition, as has been suggested for nitrosyl 5-nitrosalen iron. The room temperature magnetic moment indicates that the complex is 94% high-spin and the 80°C moment indicates 65% high-spin character.

In order to estimate the energy separation between the $^6A_1$ and $^2T_2$ levels, a form of Arrhenius plot was used by Smith

$$\log \frac{1K}{T} = \log A - \frac{E}{2.303RT} \quad \ldots \ldots (72)$$

where $K$ is defined by equation (31), using $\mu_{hs} = 5.92$ B.M. and $\mu_{ls} = 2.30$ B.M.. A plot of $\log \frac{1K}{T}$ v. $T^{-1}$ is shown for the four complexes, in Fig. 40. Compound (III) was the only compound observed to yield a straight line plot. Compounds (I) and (IV) did not have straight line plots but curved off due to the breakdown of the simple model used. The abrupt transition of spin-states in compound (II) showed clearly in the plot. The value of the energy separation between the $^6A_1$ and $^2T_2$ levels, for compound (III), was calculated to be 216 cm$^{-1}$. A rough estimate of the relative size of $E$ for the compound was: Compound (III) > Compound (I) > Compound (IV) > Compound (II).

The magnetic data have shown that the complexes all exist in spin-state equilibrium between the $^6A_1$ and $^2T_2$ states. The series of complexes provides examples of all types of experimentally-observed magnetic behaviour arising from spin-state isomerism. These are

i) An abrupt transition between spin-states (Compound (II)).
Fig. 40
ii) A smooth, gradual transition from one spin-state to the other (Compounds (I) and (III)).

iii) A slow transition from high- to low-spin states, with the magnetic data obeying the Curie-Weiss law, (Compound (IV)), whereas compounds (I-III) do not.

These complexes may exist as facial (fac) or meridional (mer) isomers (see Fig. 41) and it was hoped that p.m.r. and e.s.r. data would distinguish the two. E.s.r. data have indicated that the complexes may be mer rather than fac isomers.

P.m.r. data have not yielded any conclusive evidence.

The p.m.r. studies were carried out on chloroform solutions. In order to determine whether spin-state isomerism was taking place in solution, the magnetic moments of the complexes were determined using the n.m.r.

Tris(pentan-2,4-dionato)iron(III) was prepared as a calibrant, and excellent agreement between the literature value for its magnetic moment, measured by the Gouy technique, and the moment from the n.m.r. data was observed (Table 41). Typical n.m.r. spectra are shown in Fig. 42.

The solution studies of compounds (I), (III) and (IV), at 33.5°, indicated that the complexes were essentially high-spin (Table 41), the moment of compound (III) was, however, still reduced from the spin-only value. It would seem that on dissolution of the complexes in chloroform some lattice effect is reduced and the complexes become more high-spin. Compound (II) decomposed in the air and in solution so its low moment in solution is not reliable.
N.M.R. Paramagnetic Susceptibility Measurements at 306°K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>mass/ml gm x10^5</th>
<th>Δf Hz</th>
<th>X</th>
<th>X_u10^5</th>
<th>X_r10^5</th>
<th>H_eff B.M. solution</th>
<th>H_eff B.M. solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CH₃COCHCOCH₃)₃</td>
<td>353.2</td>
<td>1080</td>
<td>5.5</td>
<td>40.03</td>
<td>14140</td>
<td>14296</td>
<td>5.92</td>
<td>5.95</td>
</tr>
<tr>
<td>(PERKIN-ELMER R1G)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(CH₃CSCHCOCH₃)₃</td>
<td>401.4</td>
<td>1015</td>
<td>2.6</td>
<td>19.94</td>
<td>8004</td>
<td>8196</td>
<td>4.48</td>
<td>5.66</td>
</tr>
<tr>
<td>Fe(PhCSCHCOPh)₃</td>
<td>773.8</td>
<td>2805</td>
<td>6.7</td>
<td>18.55</td>
<td>14350</td>
<td>14766</td>
<td>6.02</td>
<td>5.50</td>
</tr>
<tr>
<td>Fe(PhCSCHCOCH₃)₃</td>
<td>587.7</td>
<td>1715</td>
<td>5.14</td>
<td>23.39</td>
<td>13750</td>
<td>14054</td>
<td>5.87</td>
<td>5.75</td>
</tr>
<tr>
<td>Fe(PhCOCHCSCCH₃)₃</td>
<td>587.7</td>
<td>1720</td>
<td>4.0</td>
<td>18.03</td>
<td>10590</td>
<td>10894</td>
<td>5.17</td>
<td>4.35</td>
</tr>
</tbody>
</table>

Table 41
N.M.R. Paramagnetic Susceptibility Spectra

Fe(CH₃COCHCOCH₃)₃

Fe(PhCSCHCOCH₃)₃

Fe(PhCSCHCOPh)₃

Fig. 42

1 unit = 1 Hz
Mössbauer Measurements

The spectra (Table 42 and Figs. 43-46) were recorded by Dr. A. W. Smith of the Chemistry Department, Birbeck College, London.

If at any given temperature, both spin isomers are present in appreciable amounts, the superposition of the characteristic Mössbauer spectrum for each spin-state might be expected. However, one of two situations may arise:

i) The relaxation time to change from one spin-state to the other is much greater than the effective quadrupole period. In this case a resolved superposition of the low-spin (large $\Delta E$) and the high-spin (small or no $\Delta E$) spectrum should be observed.

ii) The relaxation time is much less than the effective quadrupole period. Here, the iron nucleus will experience an averaged electric field gradient, the magnitude of which is determined by the relative population of the $^6A_1$ and $^2T_2$ states. This will lead to a two-line spectrum, the splitting of which should be temperature dependent.

The Mössbauer data of the tris(dialkyldithiocarbamato)iron(III) complexes exhibiting spin-state isomerism have time-average spectra of only two lines (category 2) but the tris-(monothio-β-diketonato)iron(III) complexes have Mössbauer data belonging to category 1.

Compounds (I) and (II) present similar spectra at 300° and 80°K. At 300°K, only the high-spin isomer is clearly discernible (85% and 90% for (I) and (II) respectively from the magnetic data). The Mössbauer parameters are characteristic of high-spin iron(III) compounds. Slight asymmetry in the spectra may be due to the presence of a small amount of the low-spin isomer. On cooling to 80°K
<table>
<thead>
<tr>
<th>Compound</th>
<th>$300^\circ$K</th>
<th>$80^\circ$K</th>
<th>Spin State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(PhCSCHCOPh)$_3$</td>
<td>0.66 0.62</td>
<td>0.66 0.94</td>
<td>$6_{A_1}$</td>
</tr>
<tr>
<td>Compound I</td>
<td></td>
<td>0.62 1.94</td>
<td>$2_{T_2}$</td>
</tr>
<tr>
<td>Fe(CH$_3$CSCHCOCH$_3$)$_3$</td>
<td>0.78 0.21</td>
<td></td>
<td>$6_{A_1}$</td>
</tr>
<tr>
<td>Compound II</td>
<td></td>
<td>0.65 1.86</td>
<td>$2_{T_2}$</td>
</tr>
<tr>
<td>Fe(CH$_3$CSCHCOPh)$_3$</td>
<td>0.60 0.56</td>
<td>0.62 1.93</td>
<td>$6_{A_1}$</td>
</tr>
<tr>
<td>Compound III</td>
<td></td>
<td>0.59 1.46</td>
<td>$2_{T_2}$</td>
</tr>
<tr>
<td>Fe(CH$_3$COCHCSPh)$_3$</td>
<td>0.83 0.00</td>
<td>0.85 0.14</td>
<td>$6_{A_1}$</td>
</tr>
<tr>
<td>Compound IV</td>
<td></td>
<td>0.62 1.83</td>
<td>$2_{T_2}$</td>
</tr>
</tbody>
</table>
Compound (I)

Fig. 43

RELATIVE COUNT RATE

300°K

80°K

VELOCITY (mm sec⁻¹)
Compound (II)

Fig. 44

RELATIVE COUNT RATE

VELOCITY (mm sec⁻¹)

300°K

80°K

Fig. 44
RELATIVE COUNT RATE

VELOCITY (mm sec$^{-1}$)

Compounded (III)

300ºK

80ºK

Fig. 45
Relative Count Rate

Compound (IV)

300°K

80°K

Velocity (mm sec⁻¹)

Fig. 46
two strong peaks of the predominating low-spin isomer are observed (92% and 97% for (I) and (II) respectively from the magnetic data) together with weak peaks attributed to the high-spin isomer. Peaks 1 and 4 in Fig. 43 and 44 are attributed to the low-spin isomer and peaks 2 and 3 to the high-spin. The quadrupole splittings for the low-spin isomers fall within the range expected for iron(III) and indicate a distortion from octahedral symmetry.

The Mössbauer spectrum of compound (III) at 300°C shows poor resolution (see Fig. 45). However, four discernible peaks have been attributed to the high- and low-spin isomers, both being present in appreciable amounts (46% high-spin, 54% low-spin from the magnetic data). On cooling to 80°C, strong absorption peaks for the low-spin isomer are seen but no trace of the high-spin component can be observed. This is consistent with the magnetic data for 80°C. Mössbauer parameters for the spin-states are similar to those in compounds (I) and (II), and a temperature dependence of ΔE in the 2T2 spin-state was observed.

For compound (IV) at 300°C, only a single absorption peak is observed due to the predominance of the high-spin isomer (94% from magnetic data). The asymmetry of the spectrum (see Fig. 46) may be due to the presence of a small amount of the low-spin isomer. On cooling to 80°C, peaks due to the presence of the low-spin isomer are resolved, together with those of the high-spin isomer (65% from magnetic data).

If the high-spin isomers are placed in order of increasing isomer shifts, the order is as follows:

\[
\text{Fe[CH}_3\text{CSCHOC}_6\text{H}_5\text{]}_3 < \text{Fe[C}_6\text{H}_5\text{CSCHOC}_6\text{H}_5\text{]}_3 < \text{Fe[CH}_3\text{CSCHOCOH}_3\text{]}_3 < \text{Fe[C}_6\text{H}_5\text{CSCHOCOH}_3\text{]}_3
\]

The order also follows the percentage of high-spin character of each compound and is the reverse order to the estimated energy separation between spin-states given previously (p. 177). No correlations for these results have been attempted.
As a sulphur atom is more polarisable than an oxygen atom, smaller isomer shifts than obtained for Fe[CH₂COCHCOCH₃]₃ would be expected for high-spin complexes. However, the isomer shifts for the high-spin isomers are large and imply a low s-electron density at the nucleus. There is no immediate correlation with these anomalous results and the structures of the complexes.

The isomer shifts of the low-spin isomers are all approximately the same and are closer to the high-spin isomer values (~0.6 mm sec⁻¹) than to those normally found in low-spin ferric compounds (~0.3 mm sec⁻¹). However, isomer shifts of ~0.5 mm sec⁻¹ have been reported for the low-spin complex Fe[CH₂CSCHCSCH₃]₃¹⁷½ (see Table 39).
EXPERIMENTAL TECHNIQUES
1. **PREPARATIVE METHODS**

a) **Air-Sensitive Compounds**

Similar apparatus and preparative techniques as described by King\textsuperscript{145} were employed in this study. The only modification to the apparatus was the use of B.T.S. catalyst (supplied by B.A.S.F.) to remove any last traces of oxygen from 'oxygen-free' nitrogen, in place of a chromous bubbler and a heated copper column.

b) **Nitric Oxide Derivatives**

Similar apparatus and preparative techniques as described by King\textsuperscript{145} were employed in the generation of nitric oxide and the preparation of the nitric oxide derivatives.

2. **ANALYTICAL METHODS**

**Iron**

Most iron analyses were carried out by ignition of the complex to the oxide, Fe\textsubscript{2}O\textsubscript{3}. This method was usually accurate to within 1-2%. However, the compounds studied were usually of high molecular weight compared to the oxide; therefore approximately 0.2-0.4g of the complex had to be used for each determination to give this accuracy. This quantity of material was not always available for analysis; also some compounds decomposed explosively when ignited and ignition problems were encountered with 'North Sea Gas' burners at Guildford. Therefore, in certain cases, the iron was estimated gravimetrically as the oxinate.

The chelate (-0.1g) was destroyed by evaporation to dryness with concentrated sulphuric acid (5.0 ml), concentrated nitric acid (3.0 ml) and concentrated perchloric acid (0.5 ml). The residue was re-dissolved in water, usually warming was necessary for complete dissolution. The iron was then estimated as the oxinate using the method given by Vogel\textsuperscript{177}. The method was accurate to within ±1%.
Carbon, Hydrogen and Nitrogen

Microanalyses for these elements were carried out by Dr. A. Bernhardt at the Microanalytical Laboratories of the Max Planck Institute, West Germany and by Mr. E. Hopwood of the Microanalytical Service, University of Surrey.

3. MAGNETIC MEASUREMENTS

a) Solid State Measurements

The magnetic susceptibilities of the solids were measured by the 'Gouy' method over the temperature range 300-90°C.

The apparatus used, at Battersea, has been described by Earnshaw. That used at Guildford was a Variable Temperature Gouy Balance System, as supplied by Newport Instruments, with a Type A 4" Electromagnet. The temperature control of this system was ±0.25°C.

b) Solution Measurements

These measurements were made using the n.m.r. method which has been described (Introduction 3ii)). A Perkin-Elmer P.E. R10 N.M.R. Spectrometer and 5 mm n.m.r. tubes with coxial spacing capillaries, supplied by Wilmad Glass Corp., New Jersey, U.S.A., were used for the measurements.

4. INFRARED MEASUREMENTS

a) Room Temperature Measurements

Infrared spectra of nujol mulls of the compounds were recorded, for qualitative spectra, using a Unicam S.P.200 Infrared Spectrophotometer.

b) Measurements Over a Temperature Range

Spectra over a temperature range were recorded using a variable temperature cell VLT-1, with KBr plates, and a temperature controller TEM-1, supplied by Research and Industrial Instruments Co.. The temperature control
of this system was stated to be \( \pm \frac{1}{2} \). The infrared spectro-
photometer used was a Perkin-Elmer P.E. 457, grating
instrument.

5. \textbf{MÖSSBAUER MEASUREMENTS}

All Mössbauer spectra were recorded at Birkbeck College,
University of London. Either sodium nitroprusside or
iron foil were used to calibrate spectra. Sodium
nitroprusside was used for spectra shown in Figs. 22 and 35
and iron foil was used for spectra shown in Figs. 23, 31-33
and 43-46. All Mössbauer data in the Tables have been
reported with respect to sodium nitroprusside.

The counting equipment has been described by Fitzsimmons\textsuperscript{14}. A Centronic Mössbauer Effect Analyser (20th Century Electronics)
drive unit and Intertechnic SA41 400 channel analyser were
used to complete the Mössbauer effect apparatus.
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Well-resolved Mössbauer Spectra for Spin-isomeric Tris(monothio-β-diketonato)-iron(III) Compounds

By M. Cox and J. Darken
(The Polytechnic, Hatfield, Herts.)

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and L. F. Larkworthy and K. A. Rogers
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Summary The coexistence of individual spin isomers has been observed in the Mössbauer spectra of tris(monothio-β-diketonato)-iron(III) complexes.

Although the concept of thermal equilibrium between 4A1 and 2T2 spin isomers accounts for the magnetic susceptibility data observed1,2 for tris(NN-diakylidithiocarbamato)-iron(III) complexes, unfavourable relaxation times prevent the detection of the individual isomers using Mössbauer spectroscopy. We have investigated a different system which is more favourable in this respect, specifically tris(monothio-β-diketonato)-iron(III) complexes, (I), for which spin isomerism was discovered by Ho and Livingstone3 using paramagnetic measurements. We have measured paramagnetic susceptibilities and Mössbauer spectra in the temperature range 80—300°K of four compounds of general formula (I).

\[
\begin{array}{c}
\text{Fe} \\
\begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\end{array}
\]

\begin{array}{l}
(Ia) R_1 = R_2 = \text{Ph} \\
(Ib) R_1 = R_2 = \text{Me} \\
(Id) R_1 = \text{Ph}, R_2 = \text{Me} \\
(Id) R_1 = \text{Me}, R_2 = \text{Ph}
\end{array}

Compound (Ia) has been prepared before.3 The other compounds are new and were prepared by the reaction of freshly synthesised ligand4 with anhydrous iron(III) chloride in the presence of triethylamine in suitable solvents. The ligands were prepared by a multistage synthesis4 which enabled us to prepare geometrical isomers (Ic) and (Id). Preparation of the ligand from the parent β-diketone allows the synthesis of isomer (Ic) only.5

The important feature of the Mössbauer study is that both spin-isomers can be seen in the Mössbauer spectrum if present in appreciable amounts. A typical example is provided by compound (Ia) (see Table and Figure 1 and 2).

\[
\begin{array}{c|c|c}
\text{Mössbauer parameters* for tris(monothio-β-diketonato)-iron(III) compounds} & \text{High-spin} & \text{Low-spin} \\
& 300°K & 80°K \\
\hline
\Delta E & \delta & \Delta E & \delta & \Delta E & \delta & \Delta E & \delta \\
(Ia) & 0.61 & 0.65 & — & — & 0.63 & 0.65 & 1.90 & 0.60 \\
(Ib) & 0.26 & 0.75 & — & — & — & — & 0.24 & 0.61 \\
(Id) & 0.56 & 0.60 & 1.47 & 0.57 & — & — & 1.91 & 0.61 \\
(Id) & 0.00 & 0.85 & 1.68 & 0.58 & — & — & — & — \\
\end{array}
\]

* \(\Delta E\) is the quadrupole splitting and \(\delta\) the chemical isomeric shift relative to disodium pentacyanonitrosylferrate(II); † Room temperature spectrum too weak to measure.

Peaks 1 and 2 (Figure 1) are assigned to the low-spin (2T2) isomer whilst peaks 3 and 4, corresponding to a much lower quadrupole splitting, are due to the high-spin (4A1) isomer. The observed quadrupole splittings have values similar to those previously obtained for 2T2 and 4A1 iron(III) compounds.6 Because the ligand field is close to the critical cross-over value, the chemical isomeric shifts are not expected to be much different as is here observed. As can be seen from
Figure 1, the low-spin form predominates at this temperature in agreement with the observed magnetic moment of 2.80 BM, which is somewhat higher than the previously reported value.\(^3\) The magnetic moments at the higher temperatures agree well (Figure 2).

Compound (Ib) shows a sharp transition between the \(^6\)A\(_1\) and \(^2\)T\(_2\) states at ca. 150°k but the Mössbauer spectra of the two forms are very similar. Neither spin isomer appears to have appreciable quadrupole splitting and we conclude that this is a case where the ferric ion lies at a site of near-cubic symmetry despite the presence of asymmetric chelating ligands. Compound (Ic) behaves similarly to (Ia); no trace of the \(^6\)A\(_1\) state can be seen in the Mössbauer spectrum at 80°k whilst both are clearly discernible at 300°k in agreement with the magnetic data (Figure 2). Compound (Id) does not give a satisfactory Mössbauer spectrum at 300°k but both spin-isomers can be seen at 80°k and the correlation with the magnetic data is good (\(\mu_{\text{eff}} = 5.75\) BM at 300°k and 4.95 BM at 87°k).

This is the first observation of spin isomers by Mössbauer spectroscopy in a \(^6\)A\(_1\) \(\leftrightarrow\) \(^2\)T\(_2\) cross-over situation. It is reasonable to conclude that the relaxation time to change from one spin-state to another is long compared with the effective quadrupole period in contrast to the behaviour so far reported for the Fe\(^{III}\) trisdithiocarbamato-complexes which exhibit time-averaged spectra of only two lines whose separation varies slightly with temperature.

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