Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

SOME ASPECTS OF THE COORDINATION CHEMISTRY OF IRON(III)*

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(Received October 5th, 1971)

CONTENTS

GLOSSARY OF SYMBOLS

μ_{eff}	effective magnetic moment (in Bohr magnetons, B M)	H	Hamiltonian operator
ν	vibrational stretching mode	M_s	spin quantum number
δ	vibrational bending mode	S	total spin of system
sh	shoulder	$h\nu$	microwave quantum
H	applied field	B, C	Racah parameters
D, E	zero-field splitting parameters	k	orbital reduction factor

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* No reprints available

A INTRODUCTION

Despite the industrial and biological importance of iron-containing systems, the coordination chemistry of the metal has been sadly neglected, especially in recent years Before then, a number of groups had studied a considerable number of complexes, the relevant references may be found in the book by Sidgwick [1] and in the treatises by Gmelin [2], Mellor [3] and Pascal [4] This comparative lack of interest has been especially marked in the case of iron(III), largely owing to the properties of the d^5 ion

Two of the principal physical techniques currently used for studying coordination complexes are electronic absorption spectroscopy and paramagnetic susceptibility measurements, for the high-spin Fe^{3+} ion, the free ion ground state is ^6S, becoming $^6A_1$ in a weak crystal field There are no other sextuplet states, so that all excited states of the d^5 ion have a different spin multiplicity to the ground state, and transitions to them are spin-forbidden Hence the absorption bands due to "d–d" transitions are extremely weak and are frequently obscured by charge-transfer bands trailing into the visible region of the spectrum A further consequence of the ground state being an orbital singlet is that there is no orbital contribution to the magnetic moment and thus the observed moments scarcely vary from the spin-only value It is sometimes possible to distinguish between tetrahedral and octahedral coordination on the basis of electronic spectra, but no such distinction can be made as a result of magnetic measurements It is probably mainly for these and certain chemical reasons that the study of iron(III) complexes has been neglected until quite recently.

This is unfortunate, as $S = 1/2$, $3/2$ and $5/2$ ground states are known to exist, and other physical techniques such as EPR, Mössbauer and vibrational spectra can give a good deal of information about the electronic and molecular structure of ferric complexes.

This review is mainly concerned with describing complexes that have been isolated in the solid state, and solution data are only mentioned when they have a bearing upon the species present in the solid phase. All basic complexes have been excluded, as have polynuclear systems, which merit a separate, more theoretical, treatment In addition to the sources [1-4] referred to earlier, Colton and Canterford's splendid book [5] also covers some of the ground considered here

Before proceeding to the discussion of complexes, we briefly consider the usefulness of various spectroscopic techniques for studying iron(III) systems

B PHYSICAL TECHNIQUES APPLICABLE TO IRON(III) COMPLEXES

Good treatments of EPR, Mössbauer, electronic and vibrational spectra are, for example, available in Hill and Day's text[6] whilst numerous books and review volumes have dealt with magnetism and electronic spectra At a simpler level, Greenwood's review [7] is probably still the best simple introduction to Mossbauer spectra No really good simple introduction to EPR exists although Goodman and Raynor have assembled [8] an excellent combination of theoretical and experimental data and together with a suitable text such as that by Atkins and Symons[9] this constitutes a reasonable introduction to EPR

(i) Magnetism

The ferric ion has five 3*d* electrons so that it is evident that $t_{2g}^3e_g^2$ ($S = 5/2$), $t_{2g}^4e_g^1$ ($S = 3/2$) and t_{2g}^5 ($S = 1/2$) ground states might arise. In fact, the $t_{2g}^4e_g^1$ configuration cannot be the ground term in an octahedral or tetrahedral ligand field [10] and $S = 3/2$ systems are known in relatively few cases, normally where there is a strong tetragonal field (cf refs. 11 and 12) Magnetic susceptibility measurements (preferably over a temperature range) afford excellent means of determining the ground term Ions with a $^6A_1$ ground state ($S = 5/2$) have moments close to the 5 92 B M predicted by the spin-only formula for an orbital singlet As there are no other states with the same spin multiplicity, large deviations cannot be due to the mixing-in of excited states into the ground state (as is usually invoked in the case of *A* or *E* ground states) although high-order perturbations are probably responsible for slight deviations frequently noted.

Any significant deviations are probably due either to impure materials (even a small amount of Fe_2O_3 can cause significant deviations) or to possible dimer formation, where antiferromagnetic interaction can lead to low μ_{eff} values

Little can be said about the magnetism of complexes with $S = 3/2$ ground states, owing to the paucity of experimental data. Generally moments are close to 4.0 B.M , the spin-only value being slightly less than this, thus the ground term in these systems is probably $^4A_2$, for which only a small orbital contribution to the moment is expected, in agreement with EPR results [12]

For a system with one unpaired electron, the ground state in an octahedral field is $^2T_{2g}$, thus the presence of an 'orbital' contribution to the moment, which should thus be temperature-dependent, is expected. Figgis [13] has calculated the variation of μ_{eff} with temperature as a function of the axial field, also making allowance for covalency Figgis and co-workers have, however, more recently shown [14] that this method can give ambiguous results and therefore the limitations inherent should be borne in mind when interpreting results Moments reported lie in the range 2 0–2 6 B M at ambient temperatures and decrease upon cooling The presence of high-spin impurities even in very small amount can easily inflate measured susceptibilities, as has been noted for $[Fe(S_2C_2O_2)_3]^{3-}$ (see p. 208) in particular This point is even more important in view of the instability of many low-spin iron(III) complexes

(ii) Electronic spectra

Although the basic features of the "*d–d*" spectra of high-spin ferric complexes appear to be reasonably well understood, much work remains to be done in this field.

In a cubic crystal field, the ^6S free ion term transforms as $^6A_1$; no other spin-sextuplet state exists (see Fig 1), so that all *d–d* transitions are spin-forbidden and hence rather weak;

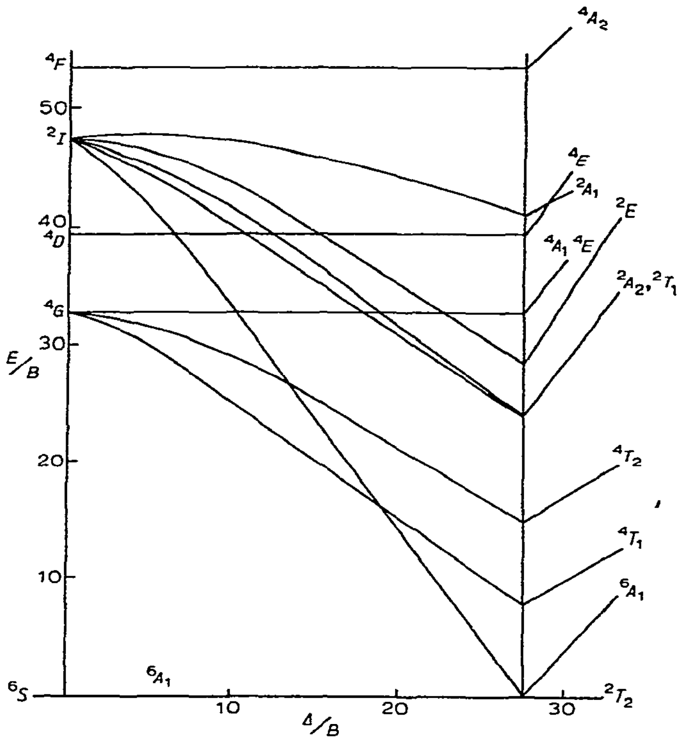


Fig 1 Semiquantitative energy-level diagram for the Fe^{3+} ion in an octahedral field, with $B \simeq 1100$ cm^{-1}, $C/B \simeq 4$ 5 (after Y Tanabe and S Sugano *J Phys Soc Jap* 9 (1954) 753)

(typically, extinction coefficients $\epsilon \simeq 0.01 - 0$ 1 in octahedral systems) These bands are probably made possible by admixture of spin-quartet character into the ground state via spin–orbit coupling Certain states originating from the $^4F(^4A_2)$, $^4D(^4E)$ and $^4G(^4E, {}^4A_1)$ free ion terms are independent of 10*Dq* this gives an unusually direct measure of the nephelauxetic effect

Despite this however, certain problems arise and high-spin Fe^{3+} *d–d* spectra are generally more difficult to assign than those of the isoelectronic Mn^{2+} complexes The main reason for this is that charge transfer absorption occurs at lower energy in the ferric complexes, and often most of the *d*-*d* bands are obscured No definite assignment of the *d–d* bands in the electronic spectrum of the hexaquo ion seems yet to have been made, owing to the ready formation of hydroxy complexes The best results we have are probably those of Holt and Dingle[44] for the $[Fe(urea)_6]^{3+}$ ion (see p. 193) although even these authors felt disinclined to make definite assignments

Few data are available for $S = 3/2$ systems, many transitions are spin-allowed so that extinction coefficients in the range 1–100 may be expected, especially as there is likely to be a good deal of enhancement through overlap with charge transfer bands

When $^2T_2$ becomes the ground state we expect some spin-allowed transitions. Ewald et al.[15] have examined the spectra in the visible and UV regions of a number of iron–sulphur complexes. They obtain reasonable $10Dq$ values of ca. 20,000–25,000 cm^{-1} although the ϵ values (up to 10^3) are unusually high. However, we know little at present about the effects of charge transfer transitions mixing with "d–d" bands so that their assignments are probably correct.

(iii) Electron paramagnetic resonance (EPR)

(a) S = 5/2

Whilst most early EPR work on high spin systems was concerned with the elucidation of the quartic terms in the spin Hamiltonian for virtually cubic systems, we find that many of the parameters in the complete spin Hamiltonian[16,17], viz.

$$H = \beta g H\cdot S + D[S_z^2 - 35/12] + E[S_x^2 - S_y^2] + \left(\frac{a}{180} + b\right)[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2$$
$$- 6S(S+1) + 3S^2(S+1)^2] + \frac{a}{48}[S_+^4 + S_-^4] + A\,S\cdot I$$

may be neglected for D values $\geqslant$ ca. 0.01 cm^{-1}. The terms in a and b are only really important in near-cubic fields whilst we usually neglect the hyperfine term because of the low abundance of ^{57}Fe ($I = 1/2$, abundance 2.2%). We therefore rewrite the spin Hamiltonian as

$$H = \beta g H\cdot S + D[S_z^2 - 35/12] + E[S_x^2 - S_y^2]$$

where D is the 'out-of-plane' zero field splitting parameter and E the 'in-plane' zero field splitting parameter. The real g value is generally taken[18] to be very close to 2.00.

Real and effective g values. At this stage it is very convenient to define the difference between real and effective g values. This is necessary for systems where $S > 1/2$, where it is often expedient to refer to features of the spectra by g_{eff} values rather than field values. For high-spin Fe^{3+} at X-band frequencies (9.3 GHz) signals are often found which can be analysed in terms of $g_\perp$ ca. 1100 gauss and $g_\parallel$ ca. 3300 gauss. Taking a fictitious spin Hamiltonian with $S = 1/2$, we define

$$g_{\text{eff}} = \frac{h\nu}{\beta H_{\text{res}}}$$

so that this signal can be described in terms of the *effective* g values $g_\perp \simeq 6$, $g_\parallel \simeq 2$. In fact, this type of signal arises from D (large) ($\geqslant$ ca. 0.2 cm^{-1}), λ ($= E/D$) $\simeq 0$ in the spin Hamiltonian, corresponding to a strong trigonal or tetragonal distortion[19]. (It is important to note that real g values are independent of microwave frequency whilst "effective" g values are frequency-dependent.)

Likewise, a nearly isotropic resonance is sometimes found ca 1500 gauss at X-band and is described as $g_{\text{eff}} \simeq 4.3$, arising [19] from $D >$ ca 0.2 cm^{-1}, $\lambda \simeq 1/3$. Because of its isotropic nature and statistical effects it generally appears much more intensely than other transitions and usually dominates the spectrum. For near-cubic systems ($D \simeq$ 0.001–0.05 cm^{-1}, $\lambda \simeq 0$) five transitions appear, centred on $g \simeq 2.00$, these are $|5/2\rangle \rightarrow |3/2\rangle$, $|3/2\rangle \rightarrow |1/2\rangle$, $|1/2\rangle \rightarrow |-1/2\rangle$, $|-1/2\rangle \rightarrow |-3/2\rangle$ and $|-3/2\rangle \rightarrow |-5/2\rangle$ transitions. Much of the EPR behaviour of high-spin d^5 systems is summarised in Dowsing and Gibson's paper [20].

(b) S = 3/2

The spin Hamiltonian is

$$H = \beta g H S + D[S_z^2 - 15/12] + E[S_x^2 - S_y^2]$$

Typically for D large and λ ca. 0, effective values $g_\perp \simeq 4$, $g_\parallel \simeq 2$ are obtained as in the case [18] of distorted Cr$^{\text{III}}$ complexes such as Cr(acac)$_3$. However, few data are available.

(c) S = 1/2

The theory has been developed by Bleaney and O'Brien and modified by Griffith[21] a simple spin Hamiltonian of the form

$$H = \beta[g_x H_x . S_x + g_y H_y S_y + g_z H_z S_z]$$

is taken and a low-symmetry perturbation considered to split the one-hole real functions $\zeta(xy)$, $\eta(xz)$ and $\xi(yz)$ so that their energies are Δ, $-\nu/2$ and $\nu/2$ respectively. Taking the form of the ground doublet to be

$$\chi = A|1^+\rangle + B|\zeta_1^-\rangle + C|-1^+\rangle$$

$$\chi' = A|-1^-\rangle - B|\zeta_1^+\rangle + C|1^-\rangle$$

where A, B and C are the coefficients of the wave functions of the ground doublet, from the interaction of these states with the magnetic field, the g values are obtained

$$g_x = 2[2AC - B^2 + kB(C-A)\sqrt{2}]$$

$$g_y = 2[2AC + B^2 + kB(C+A)\sqrt{2}]$$

$$g_z = 2[A^2 - B^2 + C^2 + k(A^2 - C^2)]$$

and

$$A^2 + B^2 + C^2 = 1$$

where k is the orbital reduction factor. The values of V and Δ are related[21] to the coefficients A, B and C and hence V and Δ may be obtained. This, of course, is a slightly modified crystal field approach and makes no allowance for interaction with charge-transfer states or configurations such as $t_{2g}^4 e_g$. The general effect of not including these terms is that inflated k values (often > 1.0) are obtained. A molecular orbital approach would be

TABLE 1

Reported principal values of the g-tensor for low-spin iron(III) complexes

Complex	$\lvert g_1 \rvert$	$\lvert g_2 \rvert$	$\lvert g_3 \rvert$	Medium [c]	Ref
$(Ph_4P)_3[Fe(S_2C_2(CN)_2)_3]$	2 225	2 114	1 986	a	199, 219
$Fe(S_2COEt)_3$	2 193	2 143	1 992	b	199
$Fe(S_2CSEt)_3$	2 178	2 131	1 998	b	199
$Fe(S_2CPh)_3$	2 155	2 094	2 008	c	199
$Fe(MeCSCHCSMe)_3$	2 14	2 09	2 01	a	213
$Fe(MeCSCHCOMe)_3$	2 341	2 182	1 930	d	199
$Fe(PhCSCHCOPh)_3$	2 330	2 171	1 950	e	199
$Fe(PhCSCHCOMe)_3$	2 333	2 175	1 933	e	199
$Fe(MeCSCHCOPh)_3$	2 308	2 177	1 938	e	199
$Fe(S_2CNMe_2)_3$	2 111	2 076	2 015	f	197
$[Fe(py)_2(S_2C_2(CN)_2)_2]^{-}$ [d]	2 13 [a]		1 99 [b]	g	199
$KBa[Fe(S_2C_2O_2)_3]\cdot 6H_2O$	2 13 [a]		1 99 [b]	a	199
$Fe(bipy)_3(PF_6)_3$	2 61 [a]		1 61 [b]	i	149
$Fe(4,4'\text{-dmb})_3(PF_6)_3$	2 64 [a]		1 38 [b]	f	149
$Fe(5,5'\text{-dmb})_3(PF_6)_3$	2 60 [a]		1 60 [b]	f	149
$Fe(phen)_3(PF_6)_3$	2 69 [a]		1 19 [b]	f	149
$K_3Fe(CN)_6$	2 35	2 10	0 92	f	21

[a] $g_\perp$

[b] $g_\parallel$

[c] The following abbreviations are used a, solid b, $CHCl_3$, c PhMe d, CH_2Cl_2, e C_6H_6, f, Co^{III} analogue, g, py (all solvents frozen)

[d] The following abbreviations for ligands are used py = pyridine bipy = 2,2-bipyridyl 4 4 -dmb = 4,4 -dimethylbipy, 5,5'-dmb = 5 5'-dimethylbipy, phen = 1, 10-phenanthroline

preferred but so little is known about the excited states that this is not at present possible Assignments of the electronic spectra are a prerequisite Principal g values for low-spin iron(III) complexes are listed in Table 1

(iv) Mossbauer spectroscopy

A convenient expression for the isomer shift, δ, is

$$\delta = \text{const}\ \frac{\delta r}{r}\left[\lvert\chi(0)\rvert^2_{\text{absorber}} - \lvert\chi(0)\rvert^2_{\text{source}}\right]$$

where δr is the difference in radii between the excited and ground states and the terms in $\chi(0)$ refer to the S-electron density at the nucleus

S-electron density depends upon both oxidation state and co-ordination number, in fact, a concept of "partial isomer shift", whereby the total isomer shift may be regarded as the sum of the partial isomer shifts for the donor atoms (for the same oxidation state of the metal) has been developed[22] (see also ref 149) A second parameter frequently obtained from Mossbauer spectra is the quadrupole splitting, Δ or ΔE This occurs when there is an electric field gradient (EFG) at the nucleus, there exist both 'valence' and 'lattice' contributions to the EFG, the former arising from an uneven electron distribution. Thus, neglecting lattice contributions, octahedral high spin Fe^{3+} ($t_{2g}^3 e_g^2$) should give rise to no quadrupole splitting, whilst octahedral low-spin Fe^{3+} (t_{2g}^5) should exhibit such splitting

Experimental results generally bear out these expectations, high-spin species have ΔE values of ca 0–0 5 mm sec^{-1} (generally at the lower end of the range) whilst ΔE values for low-spin systems are frequently as much as 2 mm sec^{-1} A notable exception to this is the $S = 5/2$ system [143] $Fe[N(SiMe_3)_2]_3$ where the quadrupole splitting is 5 12 mm sec^{-1} This may arise from an exceptionally large contribution from the 'valence' part, due to the strong trigonal field, and also the 'valence' and 'lattice' contributions having the same sign

C -COMPLEXES OF OXYGEN-CONTAINING LIGANDS

(i) Monodentate

(a) Water

The salts of the oxyacids $Fe(NO_3)_3 \cdot 9H_2O$, $Fe(ClO_4)_3$ $10H_2O$ and $Fe_2(SO_4)_3$ $10H_2O$ are well known, being obtained from acid solution as pale pink solids The nitrate appears, from EPR results to contain trigonally distorted hexaquo-ferric ions [23] with $D \simeq 0$ 08 cm^{-1} D values up to 0 2 cm^{-1} have been reported [24] for the hexaquo ion in several ferric alums X-ray structural study would be welcomed for a hexaquo complex, Raman study failed to locate $\nu(Fe{-}OH_2)$ in the perchlorate and nitrate complexes

The yellow ferric chloride hexahydrate has been shown [25] to possess the structure *trans*-$[FeCl_2(OH_2)_4]^+Cl^- \cdot 2H_2O$, analogous to $FeCl_2 \cdot 4H_2O$ (ref 26) The far-IR spectrum of this compound has been reported [27] to contain absorption bands at 374–358 cm^{-1} and 305 cm^{-1} (possibly $\nu(Fe{-}OH_2)$ and $\nu(Fe{-}Cl)$ respectively) whilst the Raman spectrum [23] shows bands at 418 cm^{-1} and 298 cm^{-1} ($\nu(Fe{-}OH_2)$) and 255 cm^{-1} ($\nu(Fe{-}Cl)$) The nature of the species present in aqueous solutions of ferric chloride is in some doubt, despite the amount of work done [28–31], solutions dilute in Fe^{3+} and concentrated in HCl contain largely $FeCl_4^-$, but at higher Fe^{3+} concentrations octahedral and polymeric species are present

EPR of $FeCl_3 \cdot 6H_2O$ in $AlCl_3 \cdot 6H_2O$ has been studied [23,32] and interpreted in terms of the spin Hamiltonian parameters $D \simeq 0.15$ cm^{-1} and $\lambda = 0$ It has been suggested [23] that these parameters may be accounted for by the ferric ion having assumed the configuration *trans*-$[Fe(OH_2)_4Cl_2]^+$

Treatment of $FeCl_3 \cdot 6H_2O$ with $SbCl_5$ yields [33] the complex *trans*-$[Fe(OH_2)_4Cl_2]^+SbCl_6^- \cdot 4H_2O$, the crystal structure [34] and Raman spectra [23] have been investigated Another compound is $(NH_4)_2[FeCl_5 \cdot OH_2]$, which forms beautiful red crystals when an aqueous solution of ferric chloride and ammonium chloride is allowed to evaporate slowly The crystal structure has been reported [35] as has that of the indium analogue [36], the EPR spectrum of the diluted iron complex has been interpreted [25] in terms of $D = 0.086$ cm^{-1}, $\lambda = 0.11$, consistent with slightly distorted C_{4v} symmetry Still to be more fully investigated are the mixed halide species [37] $M_2[FeCl_2Br_3{\cdot}OH_2]$ and $M_2[FeCl_3Br_2OH_2]$ (M = Rb, Cs).

Other hydrates include $FeBr_3{\cdot}6H_2O$, about which little is known owing to its tendency to decompose on heating There is, of course, the possibility that it has a structure similar to $FeCl_3{\cdot}6H_2O$ Ferric fluoride forms two hydrates, $FeF_3{\cdot}3H_2O$ and $FeF_3{\cdot}4\frac{1}{2}H_2O$, the trihydrate adopts a nearly regular octahedral structure [38] in which adjacent octahedra share apices in the direction of the c-axis The d–d spectra of ferric bromide and fluoride species in aqueous solution have been studied recently [39], but as with the chloride complexes more work is required to clear up the situation No complex ion $[FeBr_5OH_2]^{2-}$ has been reported, unlike $[InBr_5OH_2]^{2-}$ (refs. 23, 40), a number of ferrifluoride complexes are known which contain water that is possibly coordinated[41] They are of two types $M_2FeF_5\ xH_2O$ (M = Na K, $x = \frac{1}{2}$, M = K, $x = 1$, M = Tl, $x = 3$, M = Ag, $x = 2$) and $MFeF_5\ 7H_2O$ (M = Cd Fe, Co, Ni), the latter probably containing octahedral $M(OH_2)_6^{2+}$ ions Further investigation of these systems by modern spectroscopic methods would be welcome.

(b) Ureas

The complexes $Fe(urea)_6X_3$ ($X = ClO_4$ NO_3, Cl) readily crystallise from aqueous solution [42], EPR results [43] indicate that they contain slightly distorted $[Fe(urea)_6]^{3+}$ ions, in accordance with the polarised single-crystal electronic spectra of $[Fe(urea)_6]^{3+}(ClO_4)_3$, which is reported to be trigonally distorted [44], bands were noted at 12,800, 17,000, 23 030 and 23,320 cm^{-1}. The splitting between the two highest bands coincides with ν(Fe–O) reported for these compounds by two groups of workers [43,45]

The cyclic ureas, ethylene urea (EU) and propylene (PU) form complexes [46] $FeCl_3{\cdot}2EU$ and $FeCl_3{\cdot}2PU$ which may be of the type $[FeL_4Cl_2]^+FeCl_4^-$

(c) Sulphoxides

Most of the work has been concerned with dimethylsulphoxide (DMSO), Cotton and Francis reported[47] the yellow $Fe(ClO_4)_3$ 6DMSO, red-brown $FeBr_3$ 6DMSO, and $FeCl_3$ 2DMSO (yellow) $FeCl_3$ 4DMSO (which is converted into $FeCl_3$ 2DMSO at 50° C) was reported at this time[48] whilst $Fe(NO_3)_3$ 6DMSO has been prepared more recently[49] The 2 1 ferric chloride complex has been shown[50] to possess the structure *trans*-$[Fe(DMSO)_4Cl_2]^+FeCl_4^-$. The hexacoordinate chromophore possesses approximately D_{4h} local symmetry. Johnson and Walton[51] assigned the far-IR spectrum of $Fe(DMSO)_2Cl_3$ on the basis of a pentacoordinate structure, correctly, they assigned the bands at 463 and 290 cm^{-1} to ν(Fe–O) and ν(Fe–Cl) respectively, but ignored ν_3 of $FeCl_4^-$ at 377 cm^{-1} A more recent study of DMSO complexes has confirmed[43] the assignment of ν(Fe–O) whilst EPR spectra have shown that the hexakis-DMSO Fe^{3+} ions are slightly distorted from effective O_h symmetry, in accordance with the predictions of Berney and Weber[52] 2 1 complexes of ferric chloride with tetrahydrothiophen oxide[53] and diphenylsulphoxide[54] have also been prepared, these are thought to possess similar structures to the DMSO analogue

(d) Pyridine N-oxides

A number of complexes of pyridine *N*-oxide itself have been prepared, the first being $Fe(pyO)_6(ClO_4)_3$ where IR spectra and conductance results [55,56] indicated the formula $[Fe(pyO)_6]^{3+}(ClO_4)_3$, ν(Fe–O) being assigned at 385 cm^{-1} in the far-IR $Fe(pyO)_2Cl_3$ was first reported at about the same time [57], this complex affords an example of how an incorrect structure can be assigned on the basis of incomplete data Purely upon the basis of cryoscopic measurements, a monomeric, pentacoordinate structure was assigned Later workers [58] suggested the formulation $[Fe(pyO)_2Cl_2]^+Cl^-$, based upon an incorrect interpretation of the far-IR spectrum As a result of examining the far-IR, Raman, and electronic spectra, most recent work [59] assigned it the structure *trans*-$[Fe(pyO)_4Cl_2]^+(FeCl_4)^-$, similar to that adopted by $Fe(DMSO)_2Cl_3$ (ref 50) This evidence was supported with the observation that the complex is a 1 1 electrolyte in nitrobenzene and that, on treatment with methanolic lithium perchlorate, a complex $[Fe(pyO)_4Cl_2]^+ ClO_4^-{\cdot}H_2O$ was formed The ferric bromide complex $Fe(pyO)_2Br_3$ was also prepared whilst a monomeric chloro complex $Fe(pyO)_3Cl_3$ could also be isolated from ethereal solution $Fe(pyO)_3(NCS)_3$ was first reported slightly earlier [60] and two nitrate complexes, $Fe(pyO)_6(NO_3)_3{\cdot}2H_2O$ and $Fe(pyO)_4(NO_3)_3{\cdot}H_2O$ have been made [59] The latter is believed to contain two monodentate nitrate groups

Consistent assignment of ν(Fe–O) can be made [59] to infrared bands in the region 320–380 cm^{-1}, but the non-observation of Raman bands assignable to ν_{sym}(Fe–O) in the hexakis-(pyO) complexes has led to the suggestion that the $[Fe(pyO)_6]^{3+}$ ion is very distorted, a theory supported by the observation of a strong signal with g_{eff} ca 4 3 in the X-band EPR spectra of the 6 1 nitrate and perchlorate complexes The spin-Hamiltonian parameters $D = 0.36$ cm^{-1}, $\lambda = 0\ 233$ have been assigned to the $[Fe(pyO)_6]^{3+}$ ion in the perchlorate complex [59]

A series of complexes of the type $[Fe(4\text{-}RC_5H_4NO)_6](ClO_4)_3$ have been studied [61] (R = OMe, Me, H, Cl, or NO_2), ν(Fe–O) being assigned to bands ca 400 cm^{-1} in the IR, μ_{eff} values lay in the range 5 97 – 6 07 B M

(e) Amides and related ligands

Dimethylformamide (DMF) readily complexes with iron(III), EPR and vibrational studies on $Fe(DMF)_6(ClO_4)_3$ imply [43] that the complex is structurally very similar to the dimethylsulphoxide analogues The ligand phenazone (pn) (Ph$\overline{\text{N}\cdot\text{CO}\cdot\text{CH C(Me)N}}\cdot$Me) coordinates via a carbonyl oxygen, and complexes $Fe(pn)_6(ClO_4)_3$, $[Fe(pn)_6]^{3+}(FeX_4^-)_3$ (X = Cl, Br) and $Fe(pn)_3(NCS)_3$ are known [62] Far-IR Raman, and EPR results support these structures [43] Yet another example of a complex containing a FeL_6^{3+} ion is $Fe(HMPA)_6(ClO_4)_3$ (HMPA = hexamethylphosphoramide $OP(NMe_2)_3$), reported by Donoghue and Drago [63], the reported magnetic moment is 6 25 B M , which seems rather high The hexakis complex of trimethylphosphate with ferric perchlorate has $\mu_{eff} = 6\ 04$ B M , and is a 1 3 electrolyte in nitrobenzene [64], electronic spectral measurements imply that this hexacoordinate species is also present in solution With *N,N*-dimethylacetamide

(DMA) the complexes $Fe(DMA)_6(ClO_4)_3$, $Fe(DMA)_2Cl_3$ and $Fe(DMA)_2Cl_3 \cdot 2H_2O$ are formed [65], the anhydrous chloride complex is a 1:1 electrolyte in DMA and thus is probably $[Fe(DMA)_4Cl_2]^+FeCl_4^-$. ε-Caprolactam ($\overline{HN \cdot (CH_2)_5 C}=O$) forms complexes[66] Fe(caprolactam)$_6$$(ClO_4)_3$ and Fe(caprolactam)$_2$$Cl_3$ which are, respectively, 1:3 and 1:1 electrolytes in nitromethane and thus are probably of the usual $(FeL_6)^{3+}(ClO_4^-)_3$ and $(FeCl_4Cl_2)^+(FeCl_4)^-$ types.

(j) Phosphine and arsine oxides

Compared to the ligands discussed earlier, where six ligand molecules can coordinate to the metal ion, at most only four phosphine oxide ligands can coordinate to the ferric ion. $Fe(Ph_3PO)_4(ClO_4)_3$ was first prepared from alcoholic solution by Bannister and Cotton[67] whilst $Fe(Ph_3PO)_2Cl_3$ was later prepared from benzene solution [68]. $Fe(Ph_3AsO)_4(ClO_4)_3$ was originally prepared by a slightly more indirect method from ferric nitrate, sodium perchlorate and triphenylarsine oxide in ethanol [69] although it may be prepared by the direct reaction of ferric perchlorate and the ligand [70]. $Fe(Ph_3AsO)_2Cl_3$ was prepared by a similar reaction to that utilised for the Ph_3PO analogue. Phillips and Tyree suggested [69] that the triphenyl arsine oxide complexes should be formulated $[Fe(Ph_3AsO)_4]^{3+}(ClO_4)_3$ and $[Fe(Ph_3AsO)_4Cl_2]^+FeCl_4^-$, as a result of conductance measurements. There is no evidence [70] in the IR spectra of either of the above perchlorate complexes for perchlorate coordination, but in $Fe(Bu^n{}_3PO)_4(ClO_4)_3$, two perchlorate groups are thought to coordinate [71]. This reflects the lessened steric effect of *n*-alkyl compared with phenyl groups. Far-IR assignments were $\nu(Fe{-}OPBu^n{}_3)$ at 440 cm^{-1} and $\nu(Fe{-}OClO_3)$ at 315 cm^{-1}.

Further studies of the triphenyl phosphine and arsine oxide systems have been made recently [70] utilising Raman, IR and EPR spectroscopy in re-examining the perchlorate and chloride complexes, and in characterising the complexes FeL_2Br_3, $FeL_2(NO_3)_3$ and $Fe(Ph_3PO)_2(NCS)_3$. The perchlorate complexes gave the ($g_\perp = 6, g_\parallel = 2$) type of EPR spectrum and were thus assigned square-planar rather than tetrahedral structures. For the phosphine oxide complex, $D = 0.84$ cm^{-1}, $\lambda = 0.005$ and for the arsenic analogue, $D = 1.05$ cm^{-1}, $\lambda = 0$. IR data indicated that the nitrate complexes did not contain 'ionic' nitrate groups, and the EPR results suggested a trigonal-bipyramidal structure with monodentate nitrates (D_{3h}). At the X-band, the EPR signals were of the ($g_\perp = 6, g_\parallel = 2$) type with a slight splitting in the $g = 6$ resonance; this was interpreted in terms of the signal reflecting the overall rather than the local symmetry. The D values are ca. 0.6 cm^{-1} and λ values ca. 0.05. $Fe(Ph_3PO)_2(NCS)_3$ was thought to have a similar structure; the D value of 0.07 cm^{-1} compared to 0.55 cm^{-1} for the nitrate analogue shows that the trigonal distortion is quite small here, reflecting the similar Dq values that NCS^- and Ph_3PO create.

The halide complexes evidently possess the *trans*-$[Fe(Ph_3RO)_4X_2]^+(FeX_4^-)$ structure: the characteristic vibrational fundamentals of the FeX_4^- ions were noted in both the far-IR and Raman spectra and the EPR spectra exhibited ($g_{eff} = 2$) resonances from the FeX_4 ions and ($g_\perp = 6$) resonances from the hexacoordinate chromophores. In the ions $[Fe(Ph_3RO)_4X_2]^+$, for R = P, X = Cl then $D = 0.63$, $\lambda = 0.01$ and for X = Br, $D = 1.20$ cm^{-1}, $\lambda = 0$, for R = As, X = Cl, $D = 0.55$ cm^{-1}, $\lambda = 0.01$ and for X = Br, $D = 1.50$ cm^{-1}, $\lambda = 0$

Although ν(Fe—O) may be assigned to a band of medium-to-strong intensity in the IR spectra of the arsine oxide complexes in the region 400—435 cm^{-1}, no such consistent assignment is possible for the phosphine oxide complexes. This is a good example of the limitations of far-IR spectroscopy as a stereochemical tool

It would be interesting to study the effects of small alkyl groups, unlike Fe(pyO)$_3$Cl$_3$ (ref 59) no complex Fe(Ph$_3$PO)$_3$Cl$_3$ can be prepared[70], it appears, however, that alkyl substituents are less stereochemically demanding than phenyl groups[71]

(g) Miscellaneous

FeCl$_3$·Et$_2$O and related systems were prepared many years ago [72] but little is known about them. 1 1 adducts of ferric chloride with benzophenone and acetophenone are known [7 whilst with benzanthrone, C$_{17}$H$_{10}$O, FeX$_3$ benzathrone complexes (X = Cl, Br) have been reported [74], μ_{eff} values being 5.73 B M (X = Cl) and 6 02 B M. (X = Br)

The dark brown ethoxide Fe(OEt)$_3$ has been prepared from FeCl$_3$ and NaOEt in ethanol [7 or from ferric chloride in ether—benzene on treatment with excess ammonia [76] Fe(OMe)$_3$ is also known The magnetic properties of these systems, which are high-spin with abnormally large Curie—Weiss constants, have been interpreted [77,78] in terms of a trinuclear structure involving FeO$_4$ tetrahedra.

The alcoholates FeCl$_3$·2ROH (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i) have been reported [79,80], they are prepared from ferric chloride and the appropriate alcohol in benzene

(ii) Bi- and ter-dentate ligands

Iron(III) forms three complexes with acetylacetone (acac), of which Fe(acac)$_3$ is the best known It is readily prepared as red crystals by the reaction of aqueous ferric chloride with urea and excess acetylacetone The crystal structure [81] shows that the ferric ion is at the centre of a nearly perfect octahedron of oxygen atoms The ferric tris(tropolonate) complex, Fe(C$_7$H$_5$O$_2$)$_3$ contains a much more distorted octahedron [82], as one might expect from the more rigid nature of the ligand

Single-crystal magnetic susceptibility measurements [83] on Fe(acac)$_3$ have determined D to be −0 11 ± 0 04 cm^{-1} whilst ν(Fe—O) has been assigned to far-IR bands at 434 and 300 cm^{-1} with the aid of metal isotope substitution [84,85] Single-crystal electronic spectra have also been reported [86]

Fe(acac)$_2$Cl and Fe(acac)Cl$_2$ can be prepared either by refluxing the appropriate quantities of FeCl$_3$ and acac in benzene [87], or by reaction of the stoichiometric amounts of FeCl$_3$ and Fe(acac)$_3$. Fe(acac)$_2$Cl has been shown [88] to possess a slightly distorted square-pyramidal structure, with the Fe atom raised 0 51 Å above the basal plane. The Mössbauer parameters are [89] δ = 0 60 mm sec^{-1} and ΔE = 1 mm sec^{-1}, for Fe(acac)Cl$_2$, ΔE is [90] 0.44 mm sec^{-1}

Fowles et al. [91] have reported complexes of 1,4-dioxan which include FeCl$_3$·dioxan, this may have a polymeric structure involving bridging dioxans and hence pentacoordinate ferric iron *d–d* bands occur at 12.0, 15.2, 17.1, 19.0, 24.6, 30.0, 37 0 and 45.0 (x 10^3) cm^{-1}, it is, however, not improbable that the structure is $[Fe(dioxan)_2Cl_2]^+(FeCl_4)^-$ because of the richness of *d–d* bands and also since ν(Fe–Cl) was noted at 380 cm^{-1}, which is high for ν(Fe–Cl) in a five-coordinate environment but correct for $(FeCl_4)^-$. An earlier report [92] concerned this compound and two others, $FeCl_3(dioxan)_2 \cdot 2H_2O$ and $FeCl_3 \cdot (dioxan)_3 \cdot HCl$, which are not well defined

More recently, the 1 1 complex of ferric chloride with dimethoxyethane ($C_4H_{10}O_2$) was reported [93], this possibly involves pentacoordinate iron(III), ν(Fe–Cl) being assigned to bands at 355 and 375 cm^{-1} and *d–d* bands occurring at 11.0, 14 4, 23 0, 28.4, 31 5 and 36.0 (x 10^3) cm^{-1}.

Walmsley and Tyree [94] have investigated some complexes formed with liquids of the type $R_2PO \cdot CH_2 \cdot POR_2$ (where R = Bu^n (L_1) or Pr^nO (L_2)) preparing $[Fe(L_1)_3]^{3+}(FeCl_4^-)_3$, $[Fe(L_1)_3]^{3+}(ClO_4)_3$ and $[Fe(L_2)_2Cl_2]^+(FeCl_4)^-$ all of which have μ_{eff} values of ca. 6 1 B.M at ambient temperatures. A related complex, $[Fe(OMPA)_3]^{3+}(FeCl_4^-)_3$ (OMPA = octamethylpyrophosphoramide, $(Me_2N)_2OPOPO(NMe_2)_2$) was reported by Joesten and Nykerk who found it to be a 1 3 electrolyte in nitrobenzene [95] They report μ_{eff} to be 12 8 B M., evidently this is not μ_{eff} per Fe, which would seem to be 6 4 B.M , which is still very high.

The complex $[Fe(bipyO_2)_3](ClO_4)_3 \cdot 3H_2O$ ($bipyO_2$ = 2,2′-bipyridyl-2,2′-dioxide) has μ_{eff} = 6 13 B M at room temperature [96] whilst ν(Fe–O) has been assigned [97] to far-IR bands at 408 and 377 cm^{-1}

2,2′,2″-Terpyridine-1,1′,1″-trioxide ($terpyO_3$) is a terdentate ligand. Reiff and Baker [98] have prepared the complexes $Fe(terpyO_3)Cl_3$ and $Fe(terpyO_3)_2(ClO_4)_3$, which are both high-spin Because of the stereochemical requirements of the ligand, the ferric chloride complex should adopt the meridional configuration

(iii) Mixed O,N donors

Some of the most interesting complexes of this kind of donor are formed by salen (*N,N′*-ethylenebis(salicylideneiminato)) and related ligands, the first examples being prepared by Pfeiffer and Tsumaki [99] Two forms of Fe(salen)Cl have been isolated, one being monomeric and having a molecule of nitromethane in the lattice [100] whilst the other is dimeric [101]. The monomers follow Curie–Weiss behaviour, with μ_{eff} values of 5.7–6 0 B M at 300°K and θ values of 2–6° whilst the dimers have moments which drop from 5.1–5 4 B.M. at 300°K to 3.6–3.9 B M at 77°K (ref. 102) The latter results have been interpreted in terms of a binuclear spin-free iron(III) model, with *J* values of 6 5 –8 cm^{-1} Mossbauer spectra have been recorded for a number of these systems [103], as a result of this, certain reclassifications were suggested. The pentacoordinate monomers generally give smaller isomer shifts than the dimers, as one might expect More recently, adducts of the type $Fe(salen) \cdot RCO_2$ have been studied [104], these exhibited similar magnetic behaviour to the other systems, so it appears that both monomers and dimers exist here too

Further examples of complexes involving O,N donors are provided by complexes of *N*-substituted salicylaldimines (salHNR) which give complexes $FeCl_3(salNHR)_2$ (probably five-coordinate $[FeCl(salHNR)_2]^{2+}Cl_2^-$), octahedral $Fe(salNR)_3$ and $Fe(salNR)_2X$ (X = Cl, Br) which may be also five-coordinate[105]. The terdentate ligand derived from *N*-(2-hydroxylphenyl) salicylaldimine (LH_2) gives complexes FeLX (X = Cl, Br) with μ_{eff} values of 5.0 ± 0.05 B.M. at 295°K, so that they are probably dimeric[106]. On refluxing these in pyridine, complexes $FeLX(py)_3$ are obtained, which have 'normal' moments of 6.0 ± 0.05 B.M. and are thus probably monomers, with one mole of lattice pyridine.

N,N-Dimethylethylenediamine *N*-oxide gives a rather unstable brown complex[107], $Fe(Me_2NO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3(ClO_4)_3$, which is a 1:3 electrolyte and has μ_{eff} = 5.80 B.M.; the ligand is presumably bidentate.

(iv) Acids

One of the conspicuous gaps in our knowledge of coordination compounds concerns amino acid complexes; considering the importance of amino acids in biological systems, too little attention has been paid to their metal complexes. We discuss complexes of both carboxylic and amino acids in this section.

(a) Carboxylates

Generally, iron(III), like chromium(III), does not form monomeric carboxylates; instead, species based on a triangular Fe_3O chromophore are formed. The magnetism of a number of these systems has been investigated in both the solid state and solution[108], and interpreted in terms of antiferromagnetic behaviour.

A complex $[Fe(en)(OH)_2(PhCO_2)]$ has been isolated[109] and the magnetic behaviour (μ_{eff}^{296} = 2.74 B.M.; μ_{eff}^{95} = 2.32 B.M.) interpreted on the basis of a spin-equilibrium. The complex may not be monomeric, however.

The red crystalline $FeCl(MeCO_2)_2$ is reported to be formed from the reaction of anhydrous $FeCl_3$ with anhydrous acetic acid; the dark brown bromide analogue is known, as is[110] $FeCl(HCO_2)_2 \cdot 3/2\,H_2O$). Are these monomers?

By extracting a mixture of $Fe(MeCO_2)_2$ and $[Fe_3(MeCO_2)_8OH]$ with acetic acid[111], a dark compound $Fe_2(MeCO_2)_5$ was obtained; this is presumably dimeric. Starke[112] has reported that reaction of formic or acetic acid with iron, in methanol in the presence of oxygen, produces species $Fe(RCO_2)(OMe)_2$.

However, more simple complexes are formed with oxalate and related ions. $M_3Fe(oxalate)_3{\cdot}nH_2O$ (M = Li, Na, n = 0; M = K, n = 3) are typical. The structure of the potassium salt has been determined[113]; the six oxygen atoms coordinated to the iron atom form an approximately octahedral array, the O—Fe—O angles averaging ca. 85°. Single-crystal magnetic susceptibility measurements have determined *D*, the zero-field splitting parameter, to be −0.55 cm^{-1}, reflecting the strong trigonal field[83]. Little investigation seems to have been made of complexes[114] of the type $Fe(D\text{-tartrate})_3 \cdot 5H_2O$ where interesting possibilities arise.

(b) Amino acid complexes

The amino acid DL-methionine [$MeS(CH_2)_2CH(NH_2)CO_2H$] forms a tris-complex with iron(III) having $\mu_{eff} = 5.63$ B.M.; it was suggested [115] that coordination occurs via the amine and carboxylate functions. More recently, it has been found that reaction between Fe^{3+} and L-cysteine in alcohol gives labile red, blue, and violet complexes [116]. The violet complex was found to be Fe(cysteine)$_3\cdot 2H_2O$; it is initially produced at −78° as a green complex which changes irreversibly into the purple complex on raising the temperature. Electronic spectral, ORD and CD measurements indicated the blue species to be a 1:1 complex, the red species to be a 1:2 complex and the violet species 1:3, all involving S,O-coordination. It was suggested that the unstable green complex is an isomer of the violet tris-complex, having S,N-coordination. Röder and Bayer have reported [117] the EPR spectrum of an iron(III)–cysteine complex of unspecified composition, having $g_\perp = 2.33$, $g_\parallel = 1.94$; evidently it is an ($S = 1/2$) species, involving considerable axial distortion.

Iron salts give a deep purple colour with thioglycollic acid in ammoniacal solution; no stable iron(III) complex exists, but the species present is thought to contain only ferric iron [118]. EPR measurements on frozen solutions might be of value here.

(c) Complexes of EDTA and related ligands

Two types of EDTA coordination have been discovered by X-ray diffraction studies; in the complexes Rb[Fe(EDTA)H_2O]$\cdot H_2O$ and Li[Fe(EDTA)H_2O]$\cdot 2H_2O$, ferric ions are surrounded by a hexadentate EDTA molecule and a water molecule, in what may be regarded as a distorted pentagonal-bipyramidal configuration [119]. In Fe(HEDTA)$\cdot H_2O$, one carboxylic group is protonated, and thus does not coordinate, so that the ethylenediaminetetraacetic acid group is pentadentate; a water molecule completes the distorted octahedral coordination of the metal [120].

The EPR spectrum of Fe(HEDTA)$\cdot H_2O$, doped into the isostructural Ga analogue, has been investigated [121]; at 110°K, the spectra were interpreted in terms of the parameters $D = 0.69$ cm^{-1}, $\lambda = 0.267$ (on cooling further, λ appears to increase). The EPR of Fe^{3+} doped into a NH_4^+[Co(EDTA)$\cdot H_2O$] host has been reported [122] and interpreted [123] in terms of the parameters $D = 0.769$ cm^{-1}, $\lambda = 0.307$.

The complexes (NH_4)[Fe(EDTA)OH_2] and [Fe(EDTAH)]$\cdot xH_2O$ ($0 < x < 1$) have been found [124] to be high-spin ($S = 5/2$) over the range 90–291°K.

Cohen and Hoard have described [125] the structure of the complex Ca[Fe(DCTA)(OH_2)]$\cdot 8H_2O$ (DCTA = *trans*-1,2-diaminocyclohexane-*N,N'*-tetraacetate) where the ferric ion is heptacoordinate as in the EDTA analogue.

D. COMPLEXES OF NITROGEN-DONOR LIGANDS

(i) Monodentate

(a) Thiocyanate and cyanate

Reaction of Fe(NCS)$_3$ and alkylammonium thiocyanates in alcohol leads to the formation of the hexakis salts $(R_4N^+)_3[Fe(NCS)_6]^{3-}$ In the electronic spectrum of the tetramethylammonium salt, d–d bands are noted at 10,640 cm^{-1} and 17,500 cm^{-1}, most of the spectrum being obscured by the usual Fe–NCS charge-transfer absorption[126] Far-IR absorptions assignable to ν(Fe–NCS) were noted[127] at 298sh, 272 and 233 cm^{-1}, in the ethyl analogue, others[128] assign ν(Fe–NCS) at 270 cm^{-1} and δ(Fe–NCS) at 98 cm^{-1} Iron(III)–thiocyanate complexes are all probably *N*-bonded, the occurrence of a medium intensity band at ca 470 cm^{-1} in the IR being regarded as diagnostic of this[129].

$(Ph_4As)^+[Fe(NCO)_4]$ has been prepared from AgNCO and $FeCl_4^-$ in acetone[130], ν(Fe–NCO) was assigned to a far-IR band at 410 cm^{-1} The coordination is presumably tetrahedral and thus it is likely to be *N*-bonded The high-spin complex $[Fe(N_3)_5]^{2-}$ has been reported, the structure of the tetraphenylarsonium salt shows the ferric ion to have near-D_{3h} local symmetry Equatorial Fe–N distances, at 1 963–1 971 Å, are shorter than the axial Fe–N distance[261], presumably due to ligand–ligand repulsion

(b) Ammonia

No simple complexes exist in aquous solution, addition of ammonia to ferric salts merely precipitating the hydrous oxide However, treatment of anhydrous ferric chloride[131] and ferric bromide[132] with ammonia gas produces the very hygroscopic, unstable complexes $FeCl_3 \cdot 6NH_3$ and $FeBr_3 \cdot 6NH_3$, about which very little is known

(c) Pyridine

A larger number of basic complexes have been isolated, as well as species of the type $(pyH)^+(FeCl_4)^-$ and $(pyH^+)_3(Fe_2Cl_9)^{3-}$ (refs 133, 134) The latter complexes have all been shown[135] to contain $FeCl_4^-$ ions On the other hand, some genuine pyridine complexes have been made $Fe(py)_3(NCS)_3$ and $Fe(quinoline)_3(NCS)_3$ were prepared as iridescent crystals from alcoholic solution[136] A reinvestigation of the pyridine complex[137] led to far-IR assignments of ν(Fe–NCS) at 300 cm^{-1} and ν(Fe–py) at 249 cm^{-1}, the paucity of far-IR bands suggests that this is the *fac*-isomer

The complex $Fe(py)_4Cl_3$ was also prepared by refrigerating a dilute solution of anhydrous ferric chloride in pyridine[133,134], it forms very hygroscopic red crystals A more recent investigation[138] suggests that it is *fac*-$Fe(py)_3Cl_3 \cdot py$, the spin Hamiltonian parameters are $D \simeq 0\ 164$ cm^{-1}, $\lambda = 0\ 100$ whilst ν(Fe–Cl) is assigned to 300 and 250 cm^{-1} and ν(Fe–N) at 233 and ca 200 cm^{-1} Whilst no characterisable product could be obtained from the reaction of $FeBr_3$ and pyridine, the parameters $D = 0\ 665$ cm^{-1}, $\lambda = 0\ 033$ were obtained from $In(Fe)py_3Br_3$ implying a *fac* structure

Spectrophotometric studies of $FeCl_3$ in pyridine[139] suggest that three species are present, $FeCl_4^-$, an uncharged species $[Fe(py)_nCl_3]$ and a metastable species of low Cl^- Fe^{3+} ratio, possibly $[Fe(py)_4Cl_2]^+$

(d) Pyrazoles

In an early study[140] of the complexing ability of pyrazole, a complex $Fe(pyrazole)_4Cl_3$ was reported It was claimed, purely on the basis of halogen analysis, that this was the correct formula for a complex which could not, however, be obtained in a pure state More recent investigation[138] has shown that this is in fact $Fe(pyrazole)_3Cl_3$, EPR spectra (D =

0.24 cm^{-1}, λ = 0.13), far-IR and Raman results imply it is in fact the *fac*-isomer. A similar complex Fe(3-methylpyrazole)$_3$Cl$_3$ may be isolated, this has more Raman and far-IR bands than the pyrazole analogue, and in view of the EPR data (D ca. 0.90 cm^{-1}, λ = 0.31), a meridional structure was assigned. The ligands pyrazine and pyrimidine are potentially polydentate, the complex Fe(pyrazine)$_{5/2}$Cl$_3$ is thought to be dimeric, whilst Fe(pyrimidine)$_2$Cl$_3$ is probably a polymer[138].

(e) Fe[N(SiMe$_3$)$_2$]$_3$

This compound exhibits a number of interesting features, first prepared by Burger and Wannagat[141], the crystal structure shows that the iron atom is three-coordinate[142]. The FeN$_3$ and FeNSi$_2$ units are planar, and the symmetry of the environment of the iron atom may be regarded as D_{3h}, although the molecule has only D_3 symmetry overall.

A preliminary study of the magnetic and spectroscopic properties of this complex showed that it obeyed the Curie–Weiss law to liquid nitrogen temperatures (μ_{eff} = 5.91 B.M., θ = −10°). The isomer shift in the Mossbauer spectrum is of the order expected for a tercoordinate Fe^{3+} ion (δ = 0.43 mm sec^{-1} relative to nitroprusside) but the quadrupole splitting is extremely large (ΔE = 5.12 mm sec^{-1}) and this has not yet been explained. The EPR spectra at X-band (9.3 GHz) and Q-band (36.0 GHz) were interpreted in terms of the parameters D = 1.00 cm^{-1}, λ = 0. Crystal field calculations in D_{3h} symmetry afford the d orbital sequence e' +12370, a' −6980, e'' −8800 cm^{-1}, implying strong interaction in the xy plane[143].

(ii) Bidentate (and other) ligands

Much preparative work has been carried out with the ligands 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy). Addition of these ligands to aqueous solutions of ferric salts leads to the formation of brown hydroxy-bridged dimers of the type[144] [(phen)$_2$Fe(OH)$_2$Fe(phen)$_2$]$^{4+}$. However if the tris-complexes of Fe^{2+} are first prepared, they can be smoothly oxidised to the blue [Fe(phen)$_3$]$^{3+}$ and [Fe(bipy)$_3$]$^{3+}$ complex ions[145]. These systems are low-spin: the magnetic moments[146,147], Mossbauer parameters[149,158] (Table 2) and EPR spectra[150] (Table 1) have been obtained. Figgis[146] interprets the variation of magnetic susceptibility with temperature in terms of an axial field of ca. 400–600 cm^{-1}. On the other hand, the EPR spectra are interpreted[150] in terms of a distortion of 800–1200 cm^{-1} and postulate an E ground term, in contradiction to the inferences of Figgis. The limitations of the simple crystal field approach is revealed by the magnitude of k, the orbital reduction factor calculated, 0.93–1.07: this results from the neglect of factors such as configuration interaction.

Other low-spin systems[147] are of the type [Fe(bipy)$_2$(CN)$_2$]$^+$ClO$_4^-$ expected to be *cis* (C_{2v}), which exhibit a quadrupole splitting in the Mossbauer spectrum comparable to that of the tris-complex[149]. Susceptibility results have also been reported[148], μ_{eff} values of 2.40–2.00 B.M. were noted over the range 295–79°K and were interpreted in terms of a low-symmetry field of ca. 500 cm^{-1} and a k value of 0.9–1.0. EPR results would be welcome

Reaction of ferric chloride in dilute HCl with phenanthroline gives [149] a complex $Fe_2phen_3Cl_6$ whilst similar reactions in acetic acid lead [151] to $Fe_2phen_2Cl_6 \cdot \frac{1}{2}MeCO_2H$. This latter complex is part of a series $[Fe(phen)_2Cl_2]^+X^-$ $n$$MeCO_2H$ ($X = ClO_4$, $n = 1$, $X = Cl$, $n = 2$, $X = FeCl_4^-$, $n = 0.5$). A complex $Fe(phen)Cl_3$ was originally [152] formulated as $[Fe(phen)_2Cl_2]^+$ $[FeCl_4]^-$ as it gave a perchlorate $[Fe(phen)_2Cl_2]^+ClO_4^-$. Later studies [149] indicated that this complex (which could be isolated in two crystalline modifications) is probably a chloro-bridged dimer $Fe_2(phen)_3Cl_6$ is thought to be $[Fe(phen)_2Cl_2]^+[Fe(phen)Cl_4]^-$; on treatment with methanolic $LiClO_4$, $[Fe(phen)_2Cl_2]^+ClO_4^-$ is obtained, whilst reaction with tetraethylammonium chloride yields $[Et_4N]^+[Fe(phen)Cl_4]$, which can also be prepared directly from $(Et_4N)^+(FeCl_4)^-$ and phen in acetone. Clearly more work on these systems is desirable.

$Fe(en)_3Cl_3$ has been prepared by direct reaction in absolute alcohol [153], it is low-spin, as might be expected if the ethylenediamines are chelating. The electronic spectrum was analysed in terms of the parameters $B = 500$, $C = 2000$, $Dq = 1950\ cm^{-1}$, B is reduced to about 50% of the free ion value

2-(2′-Pyridyl)imidazole (pyimH) and 2-(2′-pyridyl)benzimidazole (pybeimH) form low-spin tris-complexes [154] $Fe(pyimH)_3(ClO_4)_3$ and $Fe(pybeimH)_3Cl_3$ as well as an 'inner' complex $Fe(pyim)_3 \cdot \frac{1}{2}H_2O$

Two terpyridyl complexes have been reported [155], $Fe(terpy)Cl_3$ and $Fe(terpy)_2(ClO_4)_3$, as in the case of the analogous phenanthroline complex, the perchlorate had to be prepared from the iron(II) complex. The chloride complex should be meridional, as $InCl_3 \cdot terpy$ is thought to be [156]

One class of complexes which is rather hard to classify is the isocyanide complexes reported over 60 years ago [157]. $FeCl_3 \cdot 2EtNC$, $FeCl_3 \cdot 3EtNC$ and $FeCl_3 \cdot 3PhNC$ were obtained initially as oils from ether, eventually yellow crystals were obtained. No further work seems to have been reported on these complexes

A rather exotic example of a ferric complex with only nitrogen-donor ligands is a hepta-coordinate complex whose structure has been reported by Fleischer and Hawkinson [159], a pentadentate macrocycle and two *N*-bonded thiocyanates make up the coordination sphere, where Fe—N(macro) = 2 23 ± 0 05 Å and Fe—NCS = 2.01 ± 0 02 Å. This is one of a series of complexes [160] which are of the general form $[FeBX_2]^+Y^-$, where B = 2,13-dimethyl-3, 6,9,12,18-penta-azabicyclo[12,3,1]octadeca-1(18)2,12,14,16-pentaene, where X = Cl, Br, I or NCS, and Y = ClO_4, BF_4 or NCS They are $S = 5/2$ systems which are 1:1 electrolytes — of especial interest is the Fe^{III}—I linkage, one of the few known Further study of this type of system would be interesting

E COMPLEXES OF HALIDES

The species considered in this section are those which contain only halide ions coordinated to iron(III), other ferric halide complexes are discussed in other sections, especially in sect. C

TABLE 2

Mossbauer parameters and magnetic moments [a]

	Temp	δ (mm sec^{-1}) [b]	ΔE (mm sec^{-1})	μ_{eff} (B M) [c]
$Fe(phen)_3(ClO_4)_3 \cdot 3H_2O$	80	0.36	1.71	2.40
$Fe(bipy)_3(ClO_4)_3 \cdot 3H_2O$	80	0.32	1.80	2.40
$[Fe(bipy)_2(CN)_2]ClO_4$	300	0.24	1.63	2.34 (294)
				2.01 (81)
$[Fe(phen)_2(CN)_2]ClO_4$				2.42 (300)
				2.03 (80)
$[Fe(phen)_2Cl_2]^+[Fe(phen)Cl_4]^-$	80	0.63	0.05	
$[Et_4N]^+[Fe(phen)Cl_4]^-$	80	0.65	0.05	5.87
$[Fe(phen)_2Cl_2]^+ClO_4^-$	80	0.65	0.05	5.91
$Fe(en)_3Cl_3$	77	0.40	1.36	2.45 (285)
				2.17 (80)
$Fe(terpy)Cl_3$	80	ca 0.71	0.54	5.85
$Fe(terpy)_2(ClO_4)_3$	80	ca 0.33	3.43	2.16 (286)
				1.91 (78)
$Fe(pyimH)_3(ClO_4)_3$				2.47 (295)
$Fe(pyim)_3 \cdot \frac{1}{2}H_2O$				2.52 (295)

[a] Data from refs 146, 148, 149, 151, 153 and 158

[b] Relative to sodium nitroprusside

[c] At ca 300°K unless otherwise stated

The tetrachloroferrate ion occurs in a number of complexes; the essentially tetrahedral nature of the ion has been confirmed by crystallographic investigation, although it is usually slightly distorted In $(Ph_4As)^+(FeCl_4)^-$ the Cl—Fe—Cl angles are [161] 107° and 114.5° whilst in $[Fe(DMSO)_4Cl_2]^+(FeCl_4)^-$ they are [162] 108.2° and 112.2°. Similar values have been reported for $Na^+FeCl_4^-$ (ref 163) and $(PCl_4)^+(FeCl_4)^-$ (ref 164) Mössbauer studies have also been made [135,165], reported isomer shifts are 0.45 mm sec^{-1} for $(FeCl_4)^-$ and 0.51 mm sec^{-1} for $(FeBr_4)^-$ Ginsberg and Robin [135] showed that salts of the type $(pyH^+)_3(Fe_2Cl_9)^{3-}$ are in fact composed of $(FeCl_4)^-$ ions, but they did prove that one form of $Cs_3Fe_2Cl_9$ ~~does in~~ fact contain dimeric $(Fe_2Cl_9)^{3-}$ units The assignments of the *d–d* bands in the electronic spectrum of the tetrahaloferrate ions is still the subject of uncertainty as fine structure has been found at low temperatures [135] unsuspected by others [166]

The mixed tetrahaloferrate ions also exist, $FeCl_3Br^-$ and $FeBr_3Cl^-$ were prepared by Kraus and Heidlberg [37] and re-examined by Clausen and Good [167] who treated an alcoholic solution of the appropriate ferric halide with a tetraalkylammonium halide. $FeCl_2Br_2^-$ has also been isolated [167] from bromine oxidation of alcoholic $FeCl_2$, followed by addition of

TABLE 3

Vibrational fundamentals [168] for $FeCl_4^-$ and $FeBr_4^-$ (in cm^{-1})

	$FeCl_4^-$	$FeBr_4^-$
ν_1	330	200
ν_2	114	
ν_3	378	285
ν_4	137	95

the alkylammonium halide The Mossbauer spectra [167] show a gradual increase in isomer shift as chloride is replaced by bromide, no quadrupole splitting was seen The far-IR spectra showed ν(Fe–Cl) in the region 350–390 cm^{-1} and ν(Fe–Br) in the region 260–300 cm^{-1}, a number of unassignable bands were, however, noted Fundamentals for $FeCl_4^-$ and $FeBr_4^-$ are tabulated [168] in Table 3

No anionic pentachlorides or bromides have been reported but some pentafluorides are known In the case of indium(III) both $InCl_4^-$ and $InCl_5^{2-}$ can be obtained, depending upon the choice of conditions (especially solvent), so that it is possible that the unsolvated $FeCl_5^{2-}$ ion might be obtained

In contrast, the stable anionic species for fluoride ion is [41] FeF_6^{3-}, ν(Fe–F) has been assigned in the 450–500 cm^{-1} in the IR [169,170] A number of tetra- and penta-fluorides have been prepared, but these are probably polymers with fluoride bridges, M_3FeF_6 (M = NH_4, Li, Na) have μ_{eff} values of 5 80–5.95 B M at room temperature whilst $CsFeF_4$ and K_2FeF_5 have moments of ca 4 8 B M (ref 171) These 'low' moments may reflect antiferromagnetic interaction via bridging fluorines. On heating $(NH_4)_3FeF_6$ to 140°C, NH_4FeF_4 is formed [172] A detailed study [173] of M_3FeF_6 systems (M = Li, Na, K, Rb, Cs, Ag, Tl and NH_4) showed that they contained FeF_6^{3-} octahedra, having Curie–Weiss magnetic behaviour to liquid nitrogen temperature ν(Fe–F) was assigned at 450–500 cm^{-1} and δ(F–Fe–F) at 270–350 cm^{-1} in the far-IR A recent EPR study [174] has been made of the FeF_6^{3-} ion in aqueous solution showing the strength of fluoride coordination to iron, the expected seven-line spectrum was obtained, characterised by g_{iso} = 2 0036 and a_F ca 23 0 gauss

It is evident from the value of the isomer shift (0 69–0 71 mm sec^{-1}) in the Mossbauer spectra [135,165] of $FeCl_3$ and $FeBr_3$ that the ferric ion is hexacoordinate, but it was not until recently that the $FeCl_6^{3-}$ ion was isolated and characterised. It is precipitated from solution [175] by large cations such as $[Co(NH_3)_6]^{3+}$ There is controversy over the electronic spectral assignments, early workers [176] assign a band at 18,730 cm^{-1} to $^6A_1 \rightarrow {}^4T_2$ and a band at 22,080 cm^{-1} to $^6A_1 \rightarrow {}^4A_1, {}^4E$ (this is probably a charge-transfer band) whilst others [31] assign bands at 9100, 11,550 and 13,150 cm^{-1} to $^6A_1 \rightarrow {}^4A_1$, $^6A_1 \rightarrow {}^4T_2$ and $^6A_1 \rightarrow {}^4A_1, {}^4E$ respectively, giving Dq values which appear rather low. More recently [177], these transitions have been ascribed to bands at 8900, 12,800 and 18,000 cm^{-1}, giving $10Dq$

values in accordance with theory [178] and are consistent with the *d–d* bands of $Cs_3Fe_2Cl_9$ at 9800, 13,600 and 17.900 cm^{-1} The reported isomer shift [165,179] for $FeCl_6^{3-}$ is ca. 0.75 mm sec^{-1} ; the absence of a quadrupole splitting implies near octahedral symmetry. The low-energy vibrational spectrum of $(FeCl_6)^{3-}$ has been investigated [179 180], $\nu_3(\nu_{as}Fe{-}Cl)$ occurs in the range 248–257 cm^{-1}. $\nu_4(\delta Cl{-}Fe{-}Cl)$ at 181 cm^{-1} and $\nu_1(\nu_{sym}Fe{-}Cl)$ at 283 cm^{-1}. One expects that $(FeBr_6)^{3-}$ would be more unstable, owing to steric factors, it might be formed in melts No iodide complexes are known

F COMPLEXES OF SULPHUR DONORS

Most of the recent interest in ferric complexes in due to the possibility of obtaining "spin-equilibria" complexes, especially with sulphur-containing ligands In this section the dithiocarbamate system, doyen of "spin-equilibria" compounds, will be dealt with first, followed by discussion of the other systems Metal complexes of sulphur-containing ligands have been reviewed generally by Livingstone [181], McCleverty [182] and Coucouvanis[183] Magnetic moments and Mossbauer parameters for some of these complexes are presented in Tables 4 and 5.

(a) Dithiocarbamates

These black solids were initially prepared by Delépine [184,185], but it was Cambi et al [186–190] who studied a wide range of these compounds at 84, 194, 291 and 350°K. They found that room temperature moments varied between 2 3 and 5 9 B M per ferric ion, depending upon the nature of the substituent R in $(R_2NCS_2)_3Fe$ Furthermore, the variation of susceptibility with temperature involved complete departure from Curie–Weiss behaviour, the moments generally tended towards "low-spin" values as the temperature was lowered Despite all the inherent limitations in research at this period, Cambi presented what is still regarded as the correct interpretation of the results, in the words of Martin and co-workers[191], Cambi's interpretation of this rather confusing and novel behaviour in terms of "a thermal equilibrium between two magnetically isomeric forms" (currently termed "low-" and "high-spin", $S = 1/2$, $S = 5/2$) was "remarkably perceptive" Martin and his co-workers initially studied a series of *N,N*-disubstituted dialkyldithiocarbamates in both the solid state and solution, finding that the anomalous magnetism persisted in benzene and chloroform. so that, together with mol wt determinations, it was established that the magnetic phenomena were not due to antiferromagnetic (whether inter- or intra-molecular) effects. It was found that four of the nineteen complexes then studied exhibited discrepancies between the solid and solution magnetochemistry results These were explained [191] as being due to the relaxation of lattice forces in solution which "impress distortions on the FeS_6 octahedra in the solid state". The magnetic effects were rationalised in terms of a thermal equilibrium between the two possible ground states, $^2T_2$ and $^6A_1$, with the $^2T_2$ state being the ground state and the $^6A_1$ state being increasingly populated as the temperature rose [192].

The most recent publication from these workers [15] discussed magnetic measurements made over a range of temperatures and pressures, ΔV, the volume difference between the

TABLE 4

Magnetic moments of some low-spin complexes of S-donors

Complex	μ_{eff} (B.M.)	Temperature (°K)	Ref
$Fe(S_2CNBu^n{}_2)_3$	2.46	300	207
$Fe(S_2CSEt)_3$	2.19	109	205
	2.57	301	
$Fe(S_2CPh)_3$	2.11	103	209
	2.26	295	
$Fe(S_2COMe)_3$	2.11	91	15
	2.45	293	
$Fe(MeCSCHCSMe)_3$	1.73	100	213
	2.00	293	
$KBa[Fe(S_2C_2O_2)_3]\cdot 6H_2O$	2.04	100	215
	2.28	297	
$(Ph_4P)_3[Fe(S_2C_2(CN)_2)_3]$	2.50	293	218
	2.25	94	
$(Ph_4P)_2[Fe(S_2C_2(CN)_2)_2(S_2CNMe_2)]^{2-}$	2.53	ca. 290	
$(Ph_4P)_2[Fe(S_2C_2(CN)_2)_2(S_2CNEt_2)]^{2-}$	2.60	ca. 290	222
$(Ph_4P)[Fe(S_2C_2(CN)_2)(S_2CNEt_2)_2]^{-}$	2.36	ca. 290	
$(Ph_4P)_3[Fe(S_2C{:}C(CN)_2)(S_2C_2(CN)_2)_2]^{3-}$	2.50	ca. 290	

two states, was found to correspond to a contraction of ca. 0.1 Å in the Fe–S bond on passing from high-spin to low-spin behaviour. The only published crystal structure is of $Fe(S_2CNBu^n{}_2)_3$, where the configuration of the six sulphur atoms around the iron atom is intermediate between trigonal prismatic and trigonal antiprismatic [193]. The sulphurs may be regarded as being at the corners of two parallel equilateral triangles, which are rotated by 32° from the trigonal prismatic configuration.

The Mossbauer spectra of a number of these compounds have been studied by several workers [194–197], the observed quadrupole splittings typically lay in the range 0.4–0.7 mm sec^{-1}. It is important to note that only a single spectrum is noted at all temperatures, that is, not one that can be analysed as a superimposition of spectra from both high- and low-spin species. This means that the relaxation time from one spin state to another is shorter than the lifetime of the ^{57}Fe excited state, and hence the isomer shift and quadrupole splitting are functions of the proportions of high- and low-spin species at that temperature. Attempts to observe EPR signals in the undiluted compounds were unsuccessful [197,198] but Rickards et al. [197] diluted $Fe(S_2CNMe_2)_3$ with the diamagnetic Co^{3+} analogue, and at 4.2°K obtained $g_1 = 2.111$, $g_2 = 2.076$, and $g_3 = 2.015$. Both the EPR parameters and the small Mossbauer quadrupole splittings (this complex is almost entirely low-spin at 4.2°K) have

TABLE 5

Mossbauer parameters for low-spin iron(III) complexes with S-donors

Complex	δ (mm sec^{-1})^a	ΔE (mm sec^{-1})	Temp (°K)	Ref
$Fe(S_2CPh)_3$	-0.10^b	1.87	ca 300	209
$Fe(MeCSCHCSMe)_3$	0.46	1.84	293	213
	0.55	1.90	83	
	0.54	1.96	42	
$(Ph_4P)_3[Fe(S_2C_2(CN)_2)_3]$	0.59	1.57	190	220
	0.65	1.69	77	
$Fe(PhCSCHCOPh)_3$	0.60	1.90	80	234
$Fe(MeCSCHCOMe)_3$	0.52	0.24	80	234
$Fe(MeCSCHCOPh)_3$	0.61	1.91	80	234
$Fe(PhCSCHCOMe)_3$	0.58	1.68	80	234
$Fe(S_2CNMe_2)_3$	0.42	0.71	77	196

[a] Relative to nitroprusside

[b] Relative to ^{57}Co in Pt

been taken to imply little deviation from O_h microsymmetry. The weakness of this correlation (and those for other Fe–S complexes of known structure [199]) with structural results is probably a consequence of neglecting factors such as configuration interaction [199], bearing in mind the proximity of the Dq values for many of these systems to the 'crossover' region, it is easy to see how this may come about. For a more complete description of the magnetic phenomena in the dithiocarbamate systems, the reader is referred to a recent review[200].

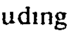
On treatment of the tris(dialkyldithiocarbamates) with small quantities of concentrated hydrohalic acid, complexes of the formula $FeX(S_2CNR)_2$ (X = Cl, Br, I) are obtained. Crystallographic study [201] has shown that the configuration about the iron atom is distorted square-pyramidal, with the iron atom slightly raised out of the S_4 basal plane. The magnetic behaviour in both the solid state and solution [12] has shown that there are three unpaired electrons ($S = 3/2$), whilst bands in the far-IR spectra of $FeX(S_2CNEt_2)_2$ (X = Cl, Br) at 353, 309 and 225 cm^{-1} are assigned as ν(Fe–S), (Fe–Cl) and (Fe–Br) respectively. EPR results [12,202] give $g_\perp \simeq 4, g_\parallel \simeq 2$ at X-band, consistent with a $S = 3/2$ ion with an appreciable zero-field splitting. Mossbauer results on solid samples [203] indicate a large quadrupole splitting ($\Delta E \simeq 2.8$ mm sec^{-1}) but a low Q.S. has been noted [204] in DMF at 77°K ($\Delta E = 0.70$ mm sec^{-1}), a value similar to that noted for the tris(dithiocarbamates), and interpreted in terms of solvation and hence hexacoordination. Rapid removal of DMF from these solutions gives a product having a four-line Mossbauer spectrum, it was suggested that partial dimerisation had taken place.

It is clear that whilst an $S = 3/2$ system is not possible in a regular octahedral or tetrahedral field[10] under the point group C_{4v} a ground state $^4A_2$ can be obtained

It is not surprising, therefore, that many workers have studied the magnetic and spectroscopic properties of iron(III)–sulphur complexes in the years following the discoveries of Martin and his co-workers

(b) Xanthates and similar systems

The xanthates $Fe(ROCS_2)_3$ and thioxanthates $Fe(RSCS_2)_3$ are readily prepared from ferric chloride and the sodium salt of the ligand All the xanthates, except the ethylxanthate, are virtually pure low-spin [15] but the thioxanthates appear to be examples of a spin-equilibrium system [205] The alkylthioxanthate complexes readily eliminate CS_2 to form the dimeric diamagnetic complexes $[Fe(SR)(S_2CSR)_2]_2$, where there are two mercaptide and two thioxanthate bridges [206 207] $Fe(Bu^tSCS_2)_3$ is more stable than the other thioxanthates and no evidence of dimer formation was found, this is ascribable to steric factors The structure of $Fe(S_2COEt)_3$ has been determined [208] like $Fe(S_2CNBu^n)_3$, it contains a very distorted arrangement of six sulphurs about the iron atom (although the distortion is less marked)

The dithiobenzoate, $Fe(S_2CPh)_3$ is rather more stable than the foregoing systems, and is prepared from ferric chloride and sodium dithiobenzoate, being purified by recrystallisation from apolar solvents the usual method for such systems Attempts to prepare $FeCl(S_2CPh)_2$ analogous to the dithiocarbamate systems, were unsuccessful [209] Coucouvanis and Lippard [210] prepared the similar (also low-spin) system $Fe(p\text{-tolCS}_2)_3$ in the course of studying the reactions of ferric chloride with $Zn(p\text{-tolCS}_3)_2$, when the complexes $Fe(p\text{-tolCS}_3)_2(p\text{-tolCS}_2)$ and $Fe(p\text{-tolCS}_3)(p\text{-tolCS}_2)_2$ were also obtained The crystal structure of the last-named complex shows that the coordination of the iron is octahedral, including an FeC linkage All these complexes are low-spin, with room temperature magnetic moments of 2 2–2 5 B M

When an aqueous solution containing acetylacetone and $FeCl_3$ is treated with H_2S, the violet $Fe(MeCS\cdot CHCS\cdot Me)_2Cl_4$ is produced [211]. The crystal structure [212] shows the complex to be composed of $(MeCSCHCSMe)^+$ and $FeCl_4^-$ ions, upon dithionite or borohydride reduction, the red-brown complex $Fe(MeCSCHCSMe)_3$ is formed The g values [213] of 2 14, 2 09 and 2 01 are typical of low-spin iron(III) complexes [199], Mossbauer and magnetic results are in accord with this The structure, determined by X-ray methods, shows that the octahedron of six sulphurs around the iron atom is only slightly distorted [213], the quadrupole splitting of ca 1.90 mm sec^{-1} is rather large, however

(c) Dithiooxalates

The dithiooxalate ion binds to metals via sulphur, Dwyer and Sargeson first synthesized the $[Fe(S_2C_2O_2)_3]^{3-}$ ion [214] and found μ_{eff} to be 2 95 B M This is very high for a low-spin d^5 ion, and the authors ascribe part of this value to the presence of high-spin impurities Later workers [215] prepared samples of $KBa[Fe(S_2C_2O_2)_3]$ $6H_2O$ having a magnetic moment of 2 28 B.M , by studying the Co^{III} and Cr^{III} analogues, they showed that whilst dithiooxalate does not lead to exceptional Dq values, it does reduce the separation of the energy levels of the metal ion by a considerable amount, making sulphur ligands *appear* to be 'strong' ligands in the spectrochemical sense. The Ph_4As^+ salt is also low-spin, but the $(Ph_3P)_2M^+$ salts (M = Cu, Ag) are *high*-spin [216], it was suggested that the metal M binds to two C=O groups and reduces *Dq* sufficiently for the change in spin state. Treatment of $[Fe(S_2C_2O_2)_3]^{3-}$ with I_2 leads to the formation of $[FeI(S_2C_2O_2)_2]^{3-}$, whose reported magnetic moment at room temperature is 4.03 B.M., this is quite consistent with its being an ($S = 3/2$) system (cf. the monohalobis(dithiocarbamates)). The EPR spectrum has not been reported, we anticipate it being of the ($g_\perp = 4, g_\parallel = 2$) variety at X-band. On refluxing a CH_2Cl_2 solution of $[Fe(S_2C_2O_2)_3]^{3-}$, $[Fe_2(S_2C_2O_2)_5]^{4-}$, of unknown structure, is formed.

(d) Dicyano-1,2-dithiolenes and related ligands

There has been much interest in the structures of complexes of *cis*-dicyano-1,2-dithiolene $[(S_2C_2(CN)_2)^{2-}]$ complexes. The environment of the vanadium ion in $(Me_4N)_2[V(S_2C_2(CN)_2)_3]$ is that of a very distorted octahedron of sulphurs [217]. $(Ph_4P)_3[Fe(S_2C_2(CN)_2)_3]$ is prepared from $FeCl_3 \cdot 6H_2O$ and excess $Na_2S_2C_2(CN)_2$, in the absence of air, as a dark red solid [218], it is readily oxidised to the dianionic species in solution (this can be reduced back to the iron(III) complex with sulphite, for example) but is quite stable in the solid state. This is low-spin and the EPR spectrum [219] is quite typical of an ($S = 1/2$) species. it should however, be noted that the separation of the t_{2g} levels originally suggested [219] is incorrect [199]. The Mossbauer spectrum [220], [221] shows a large quadrupole splitting (ca. 1.6 mm sec^{-1}) interpreted in terms of a considerable distortion from cubic symmetry. In view of the controversy surrounding the assignment of meaningful oxidation states to the metal ion in such complexes, it is worth noting that on reducing $[Fe(S_2C_2(CN)_2)_3]^{2-}$ to the tri-anionic species, the isomer shift increases from 0.50 to 0.65 mm sec^{-1}, indicating that the unpaired electron has entered an orbital of largely metallic (presumably *3d*) character [220].

Recently [222], the mixed 1,1- 1,2-dithiolene complexes have been prepared by treating the complexes $[Fe(S_2C_2(CN)_2)_2]^-$ with 1,1-dithiolene ligand, followed by sulphite reduction. Thus $(Ph_4P)_3[Fe\{L{-}L\}(S_2C_2(CN)_2)_2]$ (where L–L = e.g. $S_2C{:}C(CN)_2$, $S_2C{:}N(CN)$) were obtained. They are low-spin, having room temperature moments of ca. 2.5 B.M. at room temperature, however, no EPR or Mössbauer data are yet available.

The complexes of the type $[Fe(S_2C_2(CN)_2)_2]^-$ are in fact dimeric in the solid state, the environment of the iron atom being pentacoordinate [223],[224]. In solution, however, the magnetic behaviour is typical of an ($S = 3/2$) species so that solvated monomers are probably formed. A number of solid complexes of the type $[FeL(S_2C_2(CN)_2)_2]^-$, where L = e.g. pyridine, have been prepared [225] which exhibit $S = 3/2$ magnetic behaviour in both the solid state and solution, when L = e.g. PPh_3, bipy, phen, the behaviour is typical of an ($S = 1/2$) ion. The shift of g_{av} away from the free-electron value in the ($S = 1/2$) species may be correlated with the decline in Lewis basicity of the donor [199]. Balch [226] has very recently reported more adducts of the type $[Fe(L^{n-})(S_2C_2X_2)_2]^{(n+1)-}$ (X = CN, CF_3, L = Ph_3PO, Ph_3AsO, pyO, py, Cl, Br) which exhibit $S = 3/2$ magnetic behaviour (μ_{eff} = 3.90–4.02 B.M. at 296° K).

Reaction of $(Bu^n{}_4N)[Fe\{S_2C_2(CF_3)_2\}_2]$ with triphenylphosphine, in the presence of air, leads to the formation of the $S = 3/2$ complex $(Bu^n{}_4N)[Fe(Ph_3PO)\{S_2C_2(CF_3)_2\}_2]$ which has a square-based pyramidal structure, the iron atom being 0.43 Å above the basal plane[262].

The EPR spectra of frozen acetone or dichloromethane solutions of $[Fe(py)(S_2C_2(CN)_2)_2]^-$ are consistent with the presence of an ($S = 3/2$) ion with a definite zero-field splitting, $g_\perp \simeq 3.8$, $g_\parallel \simeq 2$. In frozen pyridine solution, however, a strong $g_\perp = 2.13$, $g_\parallel = 1.99$ resonance is observed, and this has been ascribed to the low-spin $[Fe(py)_2(S_2C_2(CN)_2)_2]^-$. The Mossbauer data[220] for $[Fe(py)(S_2C_2(CN)_2)_2]^-$ ($S = 3/2$, $\delta = 0.59$ mm.sec^{-1}, $\Delta = 2.41$ mm sec^{-1} at 77°K) and $[Fe(phen)(S_2C_2(CN)_2)_2]^-$ ($S = 1/2$, $\delta = 0.57$ mm sec^{-1}, $\Delta = 1.80$ mm sec^{-1} at 77°K) are interesting as they provide evidence for strong distortions of the field about the iron atom.

We have, so far, been concerned with complexes exhibiting, at least partly, $S = 3/2$ or $1/2$ behaviour. The tris-complexes of 1,1-dicyanoethylene-2,2-dithiolene, $[S_2C(CN)_2]^{2-}$, are high-spin ($S = 5/2$)[227,228] with reported moments of 5.89 – 5.95 B.M. At X-band, the EPR spectrum of $(Pr^n{}_4N)_3[Fe(S_2C\,C(CN)_2)_3]$ has $g_\perp \simeq 6$ and $g_\parallel \simeq 2$, implying a nearly octahedral coordination of sulphurs about the ferric ion[199]. This is interesting in view of the fact that the metal–chelate ring is only four-membered, and a greater distortion might have been expected.

(e) Dithiophosphates

The four complexes $Fe(S_2PR_2)_3$ (R = Et, EtO, Ph, PhO) were first prepared by Malatesta and Pizzotti[229] who found that they were high-spin with $\mu_{eff} \simeq 5.9$ B.M., they are rather hygroscopic black solids. Jorgensen[230] re-examined $Fe(S_2P(OEt)_2)_3$ and found that crystals of the iron(III) complex doped into the indium(III) analogue are quite stable. More recently, the temperature dependence of μ_{eff} has been examined[15] for a number of complexes $Fe(S_2OR_2)_3$ (R = MeO, EtO, Pr^nO, and Pr^iO), over the range 96–300°K, μ_{eff} values were in the range 5.61 – 5.85 B.M., showing the complexes to be genuinely high-spin.

(f) S,O donors

'Mixed' donors where one donor atom is sulphur and the other oxygen will now be considered. Fe(2-thiopyridine *N*-oxide)$_3$ has been shown by magnetic measurements[231] and EPR[199] to be high-spin. The related monothio-β-diketonates $Fe(R_1{\cdot}CS{\cdot}CH{\cdot}CO{\cdot}R_2)_3$ (R = e.g. Ph, OEt, CF_3) were prepared by Ho and Livingstone[232,233] who studied the magnetic properties and postulated a 'spin-equilibrium' between $S = 1/2$ and $S = 5/2$ species, with the ($S = 1/2$) form favoured at low temperatures. They showed that μ_{eff} was field-independent, excluding ferromagnetic species, and that the analogous Fe^{II} complexes were not obtainable. Room temperature μ_{eff} values were 2.3 – 5.8 B.M. for their choice of R_1, R_2, for R_1 = *p*-tolyl, $R_2 = CF_3$, μ_{eff} varied from 2.11 B.M. at 83°K to 5.06 B.M. at 378°K.

Fitzsimmons and co-workers[234] studied the Mossbauer spectra and magnetic moments of the four complexes where R_1 or R_2 = Ph or Me. They found similar magnetic behaviour to that found previously[232,233] and, moreover, were able to detect the resonances from the separate spin-isomers in the Mossbauer spectra, in contrast to the dithiocarbamate systems. The high-spin ($S = 5/2$) species are characterised by $\delta \sim 0.75 \pm 0.15$ mm.sec^{-1}, $\Delta E \simeq 0$, whilst the low-spin species have $\delta \sim 0.65 \pm 0.05$ mm sec^{-1}, and ΔE values up to 1.9 mm.sec^{-1}. The individual spin-isomers were also observed in the EPR spectra of the complexes [199], which were obtained in both the solid state and frozen solution over a wide temperature range, showing that the 'spin-equilibrium' is not just a solid state effect The high-spin species were characterised by nearly isotropic signals with $g_{eff} \simeq 4.3$ whilst the $S = 1/2$ species gave spectra closely similar to those of complexes of bidentate S donors. The observation of separate EPR and Mossbauer resonances for the two spin-isomers implies that the relaxation time from one spin-state to another is long compared to both the electron spin relaxation time and to the lifetime of the ^{57}Fe excited state.

(g) Other complexes

Berzelius [235] reported the dark brown $Fe_2(CS_3)_3$ as the product of reaction between $FeCl_3$ and Na_2CS_3, but more recent work would be welcomed on this and $Fe(SEt)_3$, the amorphous red product of the analogous reaction with NaSEt [236]. The latter complex is of especial interest in that a monodentate S donor is involved

The only example of a complex of a Se donor discussed in this work is the red-brown $2FeCl_3 \cdot MeSe(CH_2)_3 \cdot SeMe$ whose reported [237] magnetic moment is 5.34 B M. Two possible structures are (i) a polymer with antiferromagnetic interaction, or (ii) a species of the type $[FeCl_2(MeSe(CH_2)_3SeMe)_2]^+ (FeCl_4)^-$ which would require μ_{eff} for the cation of ca. 4 7 B M Thus it seems the complex is probably a polymer

G COMPLEXES OF PHOSPHOROUS AND ARSENIC DONORS

(i) Monodentate

$FeCl_3 \cdot PPh_3$ and $FeCl_3 \cdot AsPh_3$ were prepared [238] by refluxing $Fe_3(CO)_{12}$ in $CHCl_3$ with the ligand for 12 h, addition of hexane to the concentrated mother-liquors gave an oil which on further treatment with hexane and ethanol gave yellow solids, recrystallisable from ethanol Far-IR assignments were ν(Fe–P) at 525 cm^{-1} and ν(Fe–Cl) at 370 and 320 cm^{-1} A number of amine complexes of reportedly similar stoichiometry were shown to be iron(II) complexes by Birchall [239], who found the Mossbauer spectra of the phosphine and arsine complexes quite consistent with a pseudo-tetrahedral structure For $FeCl_3 \cdot PPh_3$ at 77°K, $\delta = 0.54$ mm sec^{-1} and $\Delta E = 0.21$ mm sec^{-1}, whilst $FeCl_3 \cdot AsPh_3$ gave $\delta = 0.57$ mm sec^{-1}, $\Delta E = 0.23$ mm sec^{-1}

On the other hand, Naldini [240] examined the reactions of triphenylphosphine and triphenylarsine with a number of ferric salts. Ethereal solutions of Ph_3P and Ph_3As reacted with anhydrous $FeCl_3$ to give very dark red crystals of $Fe(Ph_3R)_2Cl_3$ (R = P, As), which gave non-conducting MeCN solutions. A similar reaction occurred with $Fe(NCS)_3$ to give the red $Fe(Ph_3P)_2(NCS)_3$, ethanolic ferric nitrate on treatment with the ligands in ether gave the yellow $Fe(Ph_3R)_2(NO_3)_3$ These were non-electrolytes in nitrobenzene. All of these complexes were high-spin, with μ_{eff} values of 5 75 – 6 14 B M at room temperature Nyholm [241] reported complexes of various tertiary arsines of two types, $FeCl_3(R'R''_2As)_2$ and $(FeCl_3)_2(R'R''_2As)_3$ When R′ = Me, R″ = Ph, both types of complex were isolated, when R′ = *o*-tolyl, R″ = Me, only the former were obtained, and when R′ and R″ = *p*-tolyl or Me, only the latter were isolated The colour of the complexes varied from yellow to brown. Isslieb and Brack [242] isolated the yellow $FeCl_3 \cdot P(C_6H_{11})_3$ from ethanol

(ii) Polydentate donors

With this class of ligand, all those reported involve arsenic as donor, mostly with the ligand diars (*o*-phenylenebisdimethylarsine) Reaction of anhydrous $FeCl_3$ in ethanol or benzene with diars affords the crimson $FeCl_3 \cdot$diars which is in fact [243] $[FeCl_2(diars)_2]^+(FeCl_4)^-$, having μ_{eff} = 4 55 B M per Fe atom Treatment of an acetone solution of the complex with $HClO_4$ affords the red $[Fe(diars)_2Cl_2]^+ClO_4^-$, with μ_{eff} = 2 34 B M [243] [244] the $FeCl_4^-$ ion is of course high-spin

Addition of diars to excess anhydrous $FeBr_3$ in benzene affords the chocolate-brown $FeBr_3 \cdot$diars (μ_{eff} = 4 57 B M per Fe), being $[Fe(diars)_2Br_2]^+(FeBr_4)^-$ On careful hydrolysis, the green $[Fe(diars)_2Br_2]^+Br^-$ is formed (this can also be prepared from a 1 1 ratio of reactants in ethanol) Far-IR assignments are ν(Fe–Cl) at 376 cm^{-1} in $[Fe(diars)_2Cl_2]^+BF_4^-$, ν(Fe–Br) at 292 cm^{-1} in $[Fe(diars)_2Br_2]^+BF_4^-$, and 273 and 306 cm^{-1} in $[Fe(diars)_2Br_2]^+Br^-$ (refs 245, 246)

The 1,2-bis(dimethylarsino)ethylene (edas) complexes $Fe(edas)_3(ClO_4)_3$ and $[Fe(edas)_2Cl_2]^+(FeCl_4)^-$ have been prepared, the former by HNO_3 oxidation of the Fe^{II} analogue, and the latter by direct reaction of the ligand with anhydrous $FeCl_3$ in ethanol [247]

Methyl-bis(3-propane-dimethylarsine)arsine (TAS, $MeAs[(CH_2)_3AsMe_2]_2$) is a terdentate ligand and the deep green complex $Fe(NCS)_3 \cdot$TAS, a non-electrolyte having μ_{eff} = 2 22 B M , has been isolated [248] Reportedly, other ferric halides form analogous complexes Further investigation is merited here

The analogous tetradentate ligand TTA (= $As[(CH_2)_3AsMe_2]_3$) reacts with anhydrous $FeCl_3$ in ethanol to form $[Fe(TTA)Cl_2]^+(FeCl_4)^-$ μ_{eff} per Fe = 4 45 B M , so that μ_{eff} for $[Fe(TTA)Cl_2]^+$ is ca 2 2 B M The chlorines are thought [249] to be *cis*

H. COMPLEXES OF CARBON DONORS

Within this class, we shall discuss two types, those containing cyanide and those containing cyclopentadienyl type ligands

(a) Cyanide

$K_3Fe(CN)_6$ is well known, as are pentacyano species of the type $[Fe(CN)_5X]^{2-}$, where X = e g H_2O, NO_2 : these are all $S = 1/2$ systems

The blue solids formed from reaction of Fe^{III} with $Fe(CN)_6^{4-}$ or Fe^{II} with $Fe(CN)_6^{3-}$ are also familiar, and appear to be based upon a cubic array of iron atoms with CN^- ions along cube edges between them [250] Mössbauer spectra show that these complexes contain discrete ferrous and ferric ions, measurements on $Fe(CN)_6{}^{3-}$ have been made by a number of workers [158,251]. Magnetic measurements over a temperature range [146] on $K_3Fe(CN)_6$ have been interpreted in terms of an orbital reduction factor $k \simeq 0.8$ and an axial field $\Delta = 400$ cm^{-1} EPR results [21] give $k = 0.87$, $\Delta = 220$ cm^{-1}, the g values being $g_x = 2\ 35$, $g_y = 2\ 10$, $g_z = 0\ 915$

For $K_3Fe(CN)_6$, reportedly having a monoclinic unit cell ($C_{2h}^5 - P2_{1/c}$), ν_{as}(Fe—CN) has been assigned [252] to an IR band near 520 cm^{-1}, and δ(Fe—CN) near 400 cm^{-1} Raman studies in solution [253] give results rather similar, although ν(Fe—CN) has been assigned at rather lower energy

More work might be carried out in the field of cyanide complexes, as this relatively simple ligand affords complexes where π-bonding and delocalisation should be readily studied Crystallographic data would also be welcomed

(b) Cyclopentadienyl and related ligands

Oxidation of ferrocene yields the ferricinium ion, $[Fe(\pi\text{-}C_5H_5)_2]^+$, which contains one unpaired electron and may be formally regarded as a ferric complex It seems that $[Fe(\pi\text{-}C_5H_5)_2]I_3$ contains a planar ferricinium ion [254], although the X-ray study was complicated by disorder

There has been controversy concerning the ground state in these systems, which might be $(a_{1g}{}^1)^2(e_{2g}{}^{\pm})^3$ or $(e_{2g}{}^{\pm})^4(a_{1g}{}^1)^1$ in D_{5d} symmetry, and, until recently, no definite EPR data were available

Some carborane systems have been synthesised [256 256] such as $[Fe(B_9C_2H_{11})_2]^-$ and $[(\pi\text{-}C_5H_5)Fe(B_9C_2H_{11})]$ Crystallographic study [257] of the latter complex showed that both the 'carbollide' and cyclopentadienyl ligands were π-bonded, the former having two carbon and three boron atoms bonded to the iron atom, the rings were eclipsed, in contrast to ferrocene

Maki and Berry [258] examined the EPR of a number of iron(III)—carborane systems at 85°K, and found signals that could be described in terms of an axially symmetric g-tensor (see Table 6) and a certain amount of delocalisation Comparison with theoretical predictions indicated the ground state to be $(a_{1g}{}^1)^2(e_{2g}{}^{\pm})^3$

Recent EPR studies on highly purified samples of $[Fe(\pi\text{-}C_5H_5)_2]^+$ salts gave similar spectra at 77°K, implying a similar ground-state configuration These workers ascribe the previous non-observation of spectra at 77°K to the extensive line-broadening effect of small quantities of impurity [259] Prins [260] has also investigated the EPR spectra of some ferricinium systems His spectrum from $\{Fe(\pi\text{-}C_5H_5)_2\}^+ I_3{}^-$ is not as well resolved as those of Horsfield and Wasserman [259], it may account for some differences between the reported g values (see Table 6), but it does appear that anion or solvent perturbations also are important His results are in general concordance with other workers, the energy levels are $a_{1g}{}^2 \lesssim e_{2g}{}^3 < {}^*e_{1g}$ The calculated separation between the $|M_J| = 5/2$ and $|M_J| = 3/2$ levels is 800 cm^{-1} in the ferricinium ion, this small splitting is undoubtedly responsible for the short relaxation times above 77°K.

TABLE 6

Values of g for ferricinium-type systems

Compound	$g_\perp$	$g_\parallel$	Medium
$[Fe(B_9C_2H_{11})_2]^-$	3.94	1.532	Glass (1:1 DMF CHCl$_3$)
$[Fe(B_9H_9C_2Me_2)_2]^-$	2.79	1.711	Glass (1:1 DMF CHCl$_3$)
$[(\pi\text{-}C_5H_5)Fe(B_9C_2H_{11})]$	3.58	1.778	Glass (1:1 DMF CHCl$_3$)
$[Fe(B_9H_9C_2HPh)_2]^-$	3.57	1.799	Glass (1:1 DMF CHCl$_3$)
$[Fe(B_9H_9C_2HPh)_2]^-$	3.70	1.725	Powder
$[Fe(\pi\text{-}C_5H_5)_2]^+$	3.28	1.87	Single crystal
(trichloroacetate)$^-$	3.26	1.86	Powder
	3.35	1.85	Glass (CH_2Cl_2)
$[Fe(\pi\text{-}C_5H_5)_2]^+$(picrate)$^-$	3.15	1.82	Powder
$[Fe(\pi\text{-}C_5H_5)_2]^+Cl^-$	3.20	1.90	Glass (H_2O)
$Fe(\pi\text{-}C_5H_5)_2^+I_3^-$	4.35	1.26	Glass (DMF)
$Fe(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4\cdot CH_3)^+$	4.17	1.47	Glass (DMF)
$Fe(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4\cdot C_6H_5)^+$	3.98	1.58	Glass (DMF)
$Fe(\pi\text{-}C_5H_4\cdot CH_3)_2^+$	3.83	1.67	Glass (DMF)
$Fe(\pi\text{-}C_5H_4\cdot C_4H_9)_2^+$	3.88	1.68	Glass (DMF)
$Fe(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4\cdot C_6H_5CO)^+$	3.69	1.73	Glass (DMF)
$Fe(\pi\text{-}C_5H_4\cdot C_6H_5)_2^+$	3.63	1.74	Glass (H_2SO_4)
$Fe(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4\cdot CH_3CO)^+$	3.62	1.76	Glass (DMF)

There is obviously much scope here for work on complexes containing σ-bonded carbon. An obvious reaction which could be tried is that of a benzyl Grignard with ferric chloride, in the hope of obtaining $Fe(CH_2Ph)_3$ or a related compound

I CONCLUSION

Rather limited X-ray data are available (see Appendix) but it is clear that most Fe^{III} complexes involve approximately octahedral coordination.

Ferric iron readily complexes with oxygen donor ligands and with halides (except I^-, because of the redox reaction $Fe^{3+} + I^- \rightarrow Fe^{2+} + \frac{1}{2} I_2$) Its affinity for monodentate nitrogen donors is limited, the most stable ones seem to be those where Cl is also present in the co-ordination sphere. Fe—S complexes are also very important, although they often decompose readily.

Very little has been done with other donor atoms, and this remains a major omission The isolation, and more important, characterisation of further stable phosphine complexes would be a major step forward.

Much of the work performed so far has been of a very haphazard nature, complexes have generally prepared with the sole object of comparison with other ions, so that general trends are obscured, and there is a need for a systematic approach

Since the high-spin d^5 ion has no crystal-field stabilization energy, investigation of unusual coordination numbers (especially pentacoordinate species) might prove rewarding; investigation of interactions between ferric salts and amino acids or nucleotide bases could be interesting from the biological angle

Generally speaking, there is much scope for both experimental and theoretical work in the field One example of this lies in the field of electronic spectra, where, in $S = 5/2$ systems, opportunity is afforded for calculating the D value from the electronic spectra and comparing it with the value obtained from EPR or single crystal susceptibility measurements The D value is related [19] to the splitting of the lowest $^4T_1$ state by the equation

$$D = \frac{\zeta^2}{10}\left[2/E_z - \frac{1}{E_x} - \frac{1}{E_y}\right]$$

where ζ is the spin–orbit coupling constant and E_x, E_y, E_z the energies of the components of the $^4T_1$ state relative to the $^6A_1$ ground state

Likewise, the interpretation of the electronic spectra of the low-spin complexes would be an important step towards an a M.O scheme which would account for the binding in these complexes, as well as for the Mossbauer and EPR parameters

ACKNOWLEDGEMENTS

The reviewer wishes to thank Dr. Peter Thornton (Queen Mary College, London) for helpful comments upon the manuscript, and Dr. John Gibson (Imperial College, London) who introduced him to ferric complexes He is indebted to the Science Research Council for financial support

APPENDIX

Crystallographic data for iron(III) complexes

	d(Fe–X) (Å)	Space group	|Z|	Chromophore	Ref
β-FeF$_3$·3H$_2$O	1.94(O), 1.94(F)	$P4/n$	2	F$_4$O$_2$	38
[Fe(OH$_2$)$_4$Cl$_2$]$^+$Cl$^-$·2H$_2$O	2.07(O), 2.30(Cl)	$C2/m$	2	O$_4$Cl$_2$	25
[Fe(OH$_2$)$_4$Cl$_2$]$^+$SbCl$_6^-$·4H$_2$O	2.08(O), 2.36(Cl)	$P4/mmm$	2	O$_4$Cl$_2$	34
(NH$_4$)$_2$[FeCl$_5$(OH$_2$)]	2.08(O), 2.35–2.41(Cl)	$Pnma$	4	OCl$_5$	35
[Fe(Me$_2$SO)$_4$Cl$_2$]$^+$·FeCl$_4^-$	2.07(O), 2.37(Cl) 2.162(FeCl$_4^-$)	$I4_1/a$	4	O$_4$Cl$_2$ Cl$_4$	50, 162
(Ph$_4$As)$^+$FeCl$_4^-$	2.19(Cl)	$I\bar{4}$	2	Cl$_4$	161
Na$^+$FeCl$_4^-$	2.180–2.218(Cl)	$P2_12_12_1$	4	Cl$_4$	163
PCl$_4^+$FeCl$_4^-$	2.182–2.187(Cl)	$Pbcm$ or $Pbc2_1$	4	Cl$_4$	164
Fe(acac)$_3$	1.986–2.004(O)	$Pbca$	8	O$_6$	81
Fe(acac)$_2$Cl	1.95(O), 2.213(Cl)	$P2_1/n$	4	O$_4$Cl	88
K$_3$Fe(oxalate)$_3$·3H$_2$O	2.01–2.06(O)	$P2_1/c$	4	O$_6$	113
Fe(tropolonate)$_3$	2.008(O)	$R\bar{3}c$	6	O$_6$	82
[Fe(EDTAH)OH$_2$]	1.93–2.03(O), 2.07(OH$_2$) 2.19–2.25(N)	$P2_1/c$	4	N$_2$O$_4$	120
Rb[Fe(EDTA)OH$_2$]·H$_2$O	1.974–2.085(O), 2.106(OH$_2$) 2.312–2.322(N)	$P2/a$	4	N$_2$O$_5$	119
Li[Fe(EDTA)OH$_2$]·H$_2$O	1.938–2.128(O), 2.107(OH$_2$) 2.304–2.346(N)	$Pbca$	8	N$_2$O$_5$	119
Ca[Fe(DCTA)OH$_2$]·8H$_2$O	2.017–2.092(O), 2.09(OH$_2$) 2.29(N)	$C2/c$	4	N$_2$O$_5$	125
Fe(salen)Cl·(CH$_3$NO$_2$)$_x$ ^{d}	1.879–1.885(O), 2.238(Cl) 2.064–2.099(N)	$Pn2_1a$	2	O$_2$N$_2$Cl	100
[Fe{(NSiMe$_3$)$_2$}$_3$]	1.918(N)	$P\bar{3}1c$	2	N$_3$	142

$[\mathrm{Fe(B)(NCS)_2}]^+(\mathrm{ClO_4})^-$ [b]	2 23 ± 0 05(N, macro) 2 01 ± 0 02(NCS)	$P2_1/b$	4	N_7	159
$\mathrm{Fe(S_2CNBu^n{}_2)_3}$	2 413–2 426(S)	$C2/c$	4	S_6	193
$\mathrm{FeCl(S_2CNEt_2)_2}$	2 32(S), 2 27(Cl)	$P2_1/c$	4	S_4Cl	201
$\mathrm{Fe(S_2COEt)_3}$	2 308–2 326(S)	$R\bar{3}$	6	S_6	208
$\mathrm{Fe(MeCSCHCSMe)_3}$	2 220–2 264(S)	$C2/c$	4	S_6	213
$[\mathrm{Fe(S_2CSEt)_2(SEt)_2}]_2$	2 34(terminal S) 2 22 (bridging SEt) 2 28 (bridging S_2CSEt)	$P2_1/c$	4	S_6 [c]	206, 207
$[\mathrm{Fe(S_2C{\cdot}}p\text{-}\mathrm{tol)_2(S_3C{\cdot}}p\text{-}\mathrm{tol)}]$	2 19–2 35(S)	$P2_1/c$	4	S_6	210
$(\pi\text{-}\mathrm{C_5H_5})\mathrm{Fe}(\pi\text{-}\mathrm{B_9C_2H_{11}})$	2 07(C, C_5H_5) 2 04(C, $C_2B_9H_{11}$) 2 09(B)	$P2_1/c$	4	C_7B_3 [d]	257
$\mathrm{(Ph_4As)_2[Fe(N_3)_5]}$	1 963–2 041	$C2/c$	4	N_5	261
$\mathrm{K_2NaFeI_6}$	1 910	$Fm3m$	4	I_6	262
$\mathrm{(Bu^n{}_4N)[Fe(Ph_3PO)\{S_2C_2(CF_3)_2\}_2]}$	2 199–2 239(S) 1 957(O)	$P2_1/c$	4	S_4O	263

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[a] $0 < \lambda < 1$

[b] B = pentadentate macrocycle (see text)

[c] Dimer

[d] 'Sandwich' compound, coordinated to one C_5 ring and one C_2B_3 'ring'

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