

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

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### GLOSSARY OF SYMBOLS

|                    |  |        |                          |
|--------------------|--|--------|--------------------------|
| $\mu_{\text{eff}}$ | effective magnetic moment (in Bohr magnetons, B M) | $H$    | Hamiltonian operator     |
| $\nu$              | vibrational stretching mode                        | $M_s$  | spin quantum number      |
| $\delta$           | 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 |

\* 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<sup>1</sup> and in the treatises by Gmelin<sup>2</sup>, Mellor<sup>3</sup> and Pascal<sup>4</sup>. 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  $\text{Fe}^{3+}$  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<sup>1-4</sup> referred to earlier, Colton and Canterford's splendid book<sup>5</sup> 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<sup>6</sup> whilst numerous books and review volumes have dealt with magnetism and electronic spectra. At a simpler level, Greenwood's review<sup>7</sup> is probably still the best simple introduction to Mössbauer spectra. No really good simple introduction to EPR exists although Goodman and Raynor have assembled<sup>8</sup> an excellent combination of theoretical and experimental data and together with a suitable text such as that by Atkins

and Symons<sup>9</sup> this constitutes a reasonable introduction to EPR

### (i) Magnetism

The ferric ion has five 3d electrons so that it is evident that  $t_{2g}^3 e_g^2$  ( $S = 5/2$ ),  $t_{2g}^4 e_g^1$  ( $S = 3/2$ ) and  $t_{2g}^5$  ( $S = 1/2$ ) ground states might arise. In fact, the  $t_{2g}^4 e_g^1$  configuration cannot be the ground term in an octahedral or tetrahedral ligand field<sup>10</sup> 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  $\text{Fe}_2\text{O}_3$  can cause significant deviations) or to possible dimer formation, where antiferromagnetic interaction can lead to low  $\mu_{\text{eff}}$  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.<sup>12</sup>

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<sup>13</sup> has calculated the variation of  $\mu_{\text{eff}}$  with temperature as a function of the axial field, also making allowance for covalency. Figgis and co-workers have, however, more recently shown<sup>14</sup> 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  $[\text{Fe}(\text{S}_2\text{C}_2\text{O}_2)_3]^{3-}$  (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;

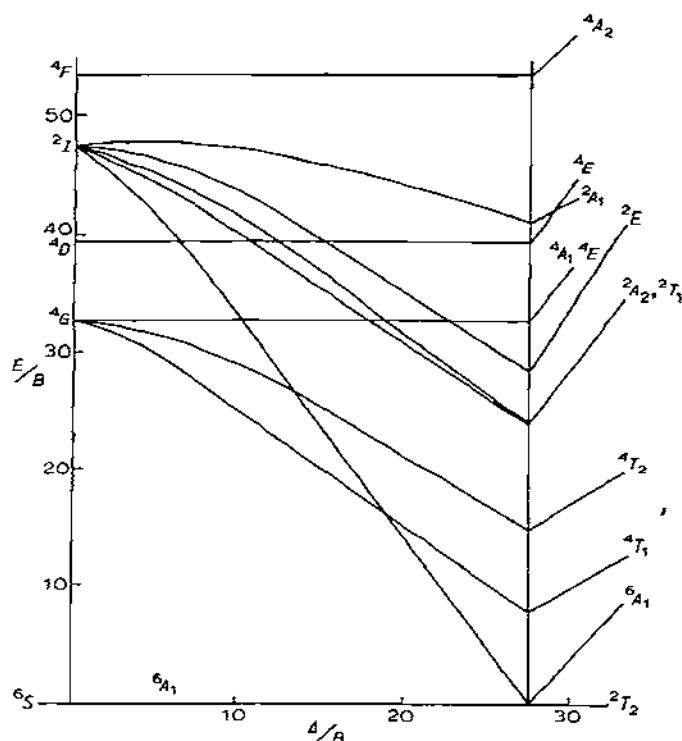


Fig. 1. Semi-quantitative energy-level diagram for the  $\text{Fe}^{3+}$  ion in an octahedral field, with  $B \approx 1100 \text{ cm}^{-1}$ ,  $C/B \approx 4.5$  (after Y. Tanabe and S. Sugano *J. Phys. Soc. Jap.* 9 (1954) 753).

(typically, extinction coefficients  $\epsilon \approx 0.01 - 0.1$  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  $10Dq$ ; this gives an unusually direct measure of the nephelauxetic effect.

Despite this, however, certain problems arise and high-spin  $\text{Fe}^{3+}$   $d-d$  spectra are generally more difficult to assign than those of the isoelectronic  $\text{Mn}^{2+}$  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<sup>44</sup> for the  $[\text{Fe}(\text{urea})_6]^{3+}$  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.<sup>15</sup> 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  $\text{cm}^{-1}$  although the  $\epsilon$  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<sup>16,17</sup>, viz

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

may be neglected for  $D$  values  $\geq$  ca. 0.01  $\text{cm}^{-1}$ . 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  $^{57}\text{Fe}$  ( $I = 1/2$ , abundance 2.2%). We therefore rewrite the spin Hamiltonian as

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

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<sup>18</sup> 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  $g_{\text{eff}}$  values rather than field values. For high-spin  $\text{Fe}^{3+}$  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  $g_{\perp} \approx 6$ ,  $g_{\parallel} \approx 2$ . In fact, this type of signal arises from  $D$  (large) ( $\geq$  ca. 0.2  $\text{cm}^{-1}$ ),  $\lambda (= E/D) \approx 0$  in the spin Hamiltonian, corresponding to a strong trigonal or tetragonal distortion<sup>19</sup>. (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  $g_{\text{eff}} \approx 4.3$ , arising<sup>19</sup> from  $D > \text{ca } 0.2 \text{ cm}^{-1}$ ,  $\lambda \approx 1/3$ . 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 ( $D \approx 0.001\text{--}0.05 \text{ cm}^{-1}$ ,  $\lambda \approx 0$ ) five transitions appear, centred on  $g \approx 2.00$ , these are  $\{5/2 \rightarrow 3/2\}$ ,  $\{3/2 \rightarrow 1/2\}$ ,  $\{1/2 \rightarrow -1/2\}$ ,  $\{-1/2 \rightarrow -3/2\}$  and  $\{-3/2 \rightarrow -5/2\}$  transitions. Much of the EPR behaviour of high-spin  $d^5$  systems is summarised in Dowsing and Gibson's paper<sup>20</sup>

(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  $\lambda$  ca. 0, effective values  $g_{\perp} \approx 4$ ,  $g_{\parallel} \approx 2$  are obtained as in the case<sup>18</sup> of distorted  $\text{Cr}^{\text{III}}$  complexes such as  $\text{Cr}(\text{acac})_3$ . However, few data are available

(c)  $S = 1/2$

The theory has been developed by Bleaney and O'Brien and modified by Griffith<sup>21</sup> 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  $\xi(xy)$ ,  $\eta(xz)$  and  $\xi(yz)$  so that their energies are  $\Delta$ ,  $-\nu/2$  and  $\nu/2$  respectively. Taking the form of the ground doublet to be

$$\chi = A|1^+\rangle + B|\xi_1^-\rangle + C|-1^+\rangle$$

$$\chi' = A|-1^-\rangle - B|\xi_1^+\rangle + C|1^-\rangle$$

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  $\Delta$  are related<sup>21</sup> to the coefficients  $A$ ,  $B$  and  $C$  and hence  $V$  and  $\Delta$  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  $t_{2g}^3 e_g$ . 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 I

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

| Complex   | $ g_1 $           | $ g_2 $ | $ g_3 $           | Medium <sup>c</sup> | Ref      |
|---|-------------------|---------|-------------------|---------------------|----------|
| (Ph <sub>4</sub> P) <sub>3</sub> [Fe(S <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub> ) <sub>3</sub> ] | 2.225             | 2.114   | 1.986             | a                   | 199, 219 |
| Fe(S <sub>2</sub> COEt) <sub>3</sub>  | 2.193             | 2.143   | 1.992             | b                   | 199      |
| Fe(S <sub>2</sub> CSEt) <sub>3</sub>  | 2.178             | 2.131   | 1.998             | b                   | 199      |
| Fe(S <sub>2</sub> CPh) <sub>3</sub>   | 2.155             | 2.094   | 2.008             | c                   | 199      |
| Fe(MeCSCHCSMe) <sub>3</sub>   | 2.14              | 2.09    | 2.01              | a                   | 213      |
| Fe(MeCSCHCOMe) <sub>3</sub>   | 2.341             | 2.182   | 1.930             | d                   | 199      |
| Fe(PhCSCHCOPh) <sub>3</sub>   | 2.330             | 2.171   | 1.950             | e                   | 199      |
| Fe(PhCSCHCOMe) <sub>3</sub>   | 2.333             | 2.175   | 1.933             | e                   | 199      |
| Fe(MeCSCHCOPh) <sub>3</sub>   | 2.308             | 2.177   | 1.938             | e                   | 199      |
| Fe(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub>  | 2.111             | 2.076   | 2.015             | f                   | 197      |
| [Fe(py) <sub>2</sub> (S <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub> ) <sub>2</sub> ] <sup>-d</sup>  | 2.13 <sup>d</sup> |         | 1.99 <sup>b</sup> | g                   | 199      |
| KBa[Fe(S <sub>2</sub> C <sub>2</sub> O <sub>2</sub> ) <sub>3</sub> ]·6H <sub>2</sub> O                | 2.13 <sup>d</sup> |         | 1.99 <sup>b</sup> | a                   | 199      |
| Fe(bipy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>   | 2.61 <sup>a</sup> |         | 1.61 <sup>b</sup> | i                   | 149      |
| Fe(4,4'-dmb) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>   | 2.64 <sup>a</sup> |         | 1.38 <sup>b</sup> | f                   | 149      |
| Fe(5,5'-dmb) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>   | 2.60 <sup>a</sup> |         | 1.60 <sup>b</sup> | f                   | 149      |
| Fe(phen) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>   | 2.69 <sup>d</sup> |         | 1.19 <sup>b</sup> | f                   | 149      |
| K <sub>3</sub> Fe(CN) <sub>6</sub>  | 2.35              | 2.10    | 0.92              | f                   | 21       |

<sup>a</sup>  $g_{\perp}$ <sup>b</sup>  $g_{\parallel}$ <sup>c</sup> The following abbreviations are used: a, solid; b, CHCl<sub>3</sub>; c, PhMe; d, CH<sub>2</sub>Cl<sub>2</sub>; e, C<sub>6</sub>H<sub>6</sub>; f, Co<sup>III</sup> analogue; g, py (all solvents frozen)<sup>d</sup> 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 I.

#### (iv) Mossbauer spectroscopy

A convenient expression for the isomer shift,  $\delta$ , is

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

where  $\delta r$  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<sup>22</sup> (see also ref. 149). A second parameter frequently obtained from Mossbauer spectra is the quadrupole splitting,  $\Delta$  or  $\Delta E$ . 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  $\text{Fe}^{3+}$  ( $t_{2g}^3 e_g^2$ ) should give rise to no quadrupole splitting, whilst octahedral low-spin  $\text{Fe}^{3+}$  ( $t_{2g}^5$ ) should exhibit such splitting.

Experimental results generally bear out these expectations, high-spin species have  $\Delta E$  values of ca. 0–0.5 mm sec<sup>-1</sup> (generally at the lower end of the range) whilst  $\Delta E$  values for low-spin systems are frequently as much as 2 mm sec<sup>-1</sup>. A notable exception to this is the  $S = 5/2$  system  $^{143}\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$  where the quadrupole splitting is 5.12 mm sec<sup>-1</sup>. 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  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Fe}(\text{ClO}_4)_3 \cdot 10\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$  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<sup>23</sup> with  $D \approx 0.08 \text{ cm}^{-1}$ .  $D$  values up to  $0.2 \text{ cm}^{-1}$  have been reported<sup>24</sup> for the hexaquo ion in several ferric alums. X-ray structural study would be welcomed for a hexaquo complex, Raman study failed to locate  $\nu(\text{Fe}-\text{OH}_2)$  in the perchlorate and nitrate complexes.

The yellow ferric chloride hexahydrate has been shown<sup>25</sup> to possess the structure  $\text{trans-}[\text{FeCl}_2(\text{OH}_2)_4]^+ \text{Cl}^- \cdot 2\text{H}_2\text{O}$ , analogous to  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (ref. 26). The far-IR spectrum of this compound has been reported<sup>27</sup> to contain absorption bands at  $374\text{--}358 \text{ cm}^{-1}$  and  $305 \text{ cm}^{-1}$  (possibly  $\nu(\text{Fe}-\text{OH}_2)$  and  $\nu(\text{Fe}-\text{Cl})$  respectively) whilst the Raman spectrum<sup>23</sup> shows bands at  $418 \text{ cm}^{-1}$  and  $298 \text{ cm}^{-1}$  ( $\nu(\text{Fe}-\text{OH}_2)$ ) and  $255 \text{ cm}^{-1}$  ( $\nu(\text{Fe}-\text{Cl})$ ). The nature of the species present in aqueous solutions of ferric chloride is in some doubt, despite the amount of work done<sup>28-31</sup>, solutions dilute in  $\text{Fe}^{3+}$  and concentrated in HCl contain largely  $\text{FeCl}_4^-$ , but at higher  $\text{Fe}^{3+}$  concentrations octahedral and polymeric species are present.

EPR of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  has been studied<sup>23,32</sup> and interpreted in terms of the spin Hamiltonian parameters  $D \approx 0.15 \text{ cm}^{-1}$  and  $\lambda = 0$ . It has been suggested<sup>23</sup> that these parameters may be accounted for by the ferric ion having assumed the configuration  $\text{trans-}[\text{Fe}(\text{OH}_2)_4\text{Cl}_2]^+$ .

Treatment of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{SbCl}_5$  yields<sup>33</sup> the complex  $\text{trans-}[\text{Fe}(\text{OH}_2)_4\text{Cl}_2]^+ \text{SbCl}_6^- \cdot 4\text{H}_2\text{O}$ , the crystal structure<sup>34</sup> and Raman spectra<sup>23</sup> have been investigated. Another compound is  $(\text{NH}_4)_2[\text{FeCl}_5 \cdot \text{OH}_2]$ , 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<sup>35</sup> as has that of the indium



analogue<sup>36</sup>, the EPR spectrum of the diluted iron complex has been interpreted<sup>25</sup> in terms of  $D = 0.086 \text{ cm}^{-1}$ ,  $\lambda = 0.11$ , consistent with slightly distorted  $C_{4v}$  symmetry. Still to be more fully investigated are the mixed halide species<sup>37</sup>  $M_2[\text{FeCl}_2\text{Br}_3 \cdot \text{OH}_2]$  and  $M_2[\text{FeCl}_3\text{Br}_2\text{OH}_2]$  ( $M = \text{Rb}, \text{Cs}$ ).

Other hydrates include  $\text{FeBr}_3 \cdot 6\text{H}_2\text{O}$ , 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  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Ferric fluoride forms two hydrates,  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{FeF}_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , the trihydrate adopts a nearly regular octahedral structure<sup>38</sup> 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<sup>39</sup>, but as with the chloride complexes more work is required to clear up the situation. No complex ion  $[\text{FeF}_5\text{OH}_2]^{2-}$  has been reported, unlike  $[\text{InBr}_5\text{OH}_2]^{2-}$  (refs. 23, 40), a number of ferrifluoride complexes are known which contain water that is possibly coordinated<sup>41</sup>. They are of two types  $M_2\text{FeF}_5 \cdot x\text{H}_2\text{O}$  ( $M = \text{Na}, \text{K}, x = \frac{1}{2}$ ,  $M = \text{K}, x = 1$ ,  $M = \text{Tl}, x = 3$ ,  $M = \text{Ag}, x = 2$ ) and  $M\text{FeF}_5 \cdot 7\text{H}_2\text{O}$  ( $M = \text{Cd}, \text{Fe}, \text{Co}, \text{Ni}$ ), the latter probably containing octahedral  $M(\text{OH}_2)_6^{2+}$  ions. Further investigation of these systems by modern spectroscopic methods would be welcome.

#### (b) Ureas

The complexes  $\text{Fe}(\text{urea})_6\text{X}_3$  ( $X = \text{ClO}_4, \text{NO}_3, \text{Cl}$ ) readily crystallise from aqueous solution<sup>42</sup>, EPR results<sup>43</sup> indicate that they contain slightly distorted  $[\text{Fe}(\text{urea})_6]^{3+}$  ions, in accordance with the polarised single-crystal electronic spectra of  $[\text{Fe}(\text{urea})_6]^{3+}(\text{ClO}_4)_3$ , which is reported to be trigonally distorted<sup>44</sup>, bands were noted at 12,800, 17,000, 23,030 and 23,320  $\text{cm}^{-1}$ . The splitting between the two highest bands coincides with  $\nu(\text{Fe}-\text{O})$  reported for these compounds by two groups of workers<sup>43,45</sup>.

The cyclic ureas, ethylene urea (EU) and propylene (PU) form complexes<sup>46</sup>  $\text{FeCl}_3 \cdot 2\text{EU}$  and  $\text{FeCl}_3 \cdot 2\text{PU}$  which may be of the type  $[\text{FeL}_4\text{Cl}_2]^+ \text{FeCl}_4^-$ .

#### (c) Sulphoxides

Most of the work has been concerned with dimethylsulphoxide (DMSO), Cotton and Francis reported<sup>47</sup> the yellow  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{DMSO}$ , red-brown  $\text{FeBr}_3 \cdot 6\text{DMSO}$ , and  $\text{FeCl}_3 \cdot 2\text{DMSO}$  (yellow),  $\text{FeCl}_3 \cdot 4\text{DMSO}$  (which is converted into  $\text{FeCl}_3 \cdot 2\text{DMSO}$  at  $50^\circ \text{C}$ ) was reported at this time<sup>48</sup> whilst  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{DMSO}$  has been prepared more recently<sup>49</sup>. The 2:1 ferric chloride complex has been shown<sup>50</sup> to possess the structure *trans*- $[\text{Fe}(\text{DMSO})_4\text{Cl}_2]^+ \text{FeCl}_4^-$ . The hexacoordinate chromophore possesses approximately  $D_{4h}$  local symmetry. Johnson and Walton<sup>51</sup> assigned the far-IR spectrum of  $\text{Fe}(\text{DMSO})_2\text{Cl}_3$  on the basis of a pentacoordinate structure, correctly, they assigned the bands at 463 and 290  $\text{cm}^{-1}$  to  $\nu(\text{Fe}-\text{O})$  and  $\nu(\text{Fe}-\text{Cl})$  respectively, but ignored  $\nu_3$  of  $\text{FeCl}_4^-$  at 377  $\text{cm}^{-1}$ . A more recent study of DMSO complexes has confirmed<sup>43</sup> the assignment of  $\nu(\text{Fe}-\text{O})$  whilst EPR spectra have shown that the hexakis-DMSO  $\text{Fe}^{3+}$  ions are slightly distorted from effective  $O_h$  symmetry, in accordance with the predictions of Berney and Weber<sup>52</sup>. 2:1 complexes of ferric chloride with tetrahydrothiophen oxide<sup>53</sup> and diphenylsulphoxide<sup>54</sup> 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  $\text{Fe}(\text{pyO})_6(\text{ClO}_4)_3$  where IR spectra and conductance results<sup>55,56</sup> indicated the formula  $[\text{Fe}(\text{pyO})_6]^{3+}(\text{ClO}_4)_3$ ,  $\nu(\text{Fe}-\text{O})$  being assigned at  $385\text{ cm}^{-1}$  in the far-IR.  $\text{Fe}(\text{pyO})_2\text{Cl}_3$  was first reported at about the same time<sup>57</sup>, 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<sup>58</sup> suggested the formulation  $[\text{Fe}(\text{pyO})_2\text{Cl}_2]^+\text{Cl}^-$ , 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<sup>59</sup> assigned it the structure *trans*- $[\text{Fe}(\text{pyO})_4\text{Cl}_2]^+(\text{FeCl}_4)^-$ , similar to that adopted by  $\text{Fe}(\text{DMSO})_2\text{Cl}_3$  (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  $[\text{Fe}(\text{pyO})_4\text{Cl}_2]^+\text{ClO}_4^-\cdot\text{H}_2\text{O}$  was formed. The ferric bromide complex  $\text{Fe}(\text{pyO})_2\text{Br}_3$  was also prepared whilst a monomeric chloro complex  $\text{Fe}(\text{pyO})_3\text{Cl}_3$  could also be isolated from ethereal solution.  $\text{Fe}(\text{pyO})_3(\text{NCS})_3$  was first reported slightly earlier<sup>60</sup> and two nitrate complexes,  $\text{Fe}(\text{pyO})_6(\text{NO}_3)_3\cdot 2\text{H}_2\text{O}$  and  $\text{Fe}(\text{pyO})_4(\text{NO}_3)_3\cdot\text{H}_2\text{O}$  have been made<sup>59</sup>. The latter is believed to contain two monodentate nitrate groups.

Consistent assignment of  $\nu(\text{Fe}-\text{O})$  can be made<sup>59</sup> to infrared bands in the region  $320\text{--}380\text{ cm}^{-1}$ , but the non-observation of Raman bands assignable to  $\nu_{\text{sym}}(\text{Fe}-\text{O})$  in the hexakis-(pyO) complexes has led to the suggestion that the  $[\text{Fe}(\text{pyO})_6]^{3+}$  ion is very distorted, a theory supported by the observation of a strong signal with  $g_{\text{eff}}$  ca. 4.3 in the X-band EPR spectra of the 6:1 nitrate and perchlorate complexes. The spin-Hamiltonian parameters  $D = 0.36\text{ cm}^{-1}$ ,  $\lambda = 0.233$  have been assigned to the  $[\text{Fe}(\text{pyO})_6]^{3+}$  ion in the perchlorate complex<sup>59</sup>.

A series of complexes of the type  $[\text{Fe}(4\text{-RC}_5\text{H}_4\text{NO})_6](\text{ClO}_4)_3$  have been studied<sup>61</sup> ( $\text{R} = \text{OMe}$ ,  $\text{Me}$ ,  $\text{H}$ ,  $\text{Cl}$ , or  $\text{NO}_2$ ),  $\nu(\text{Fe}-\text{O})$  being assigned to bands ca.  $400\text{ cm}^{-1}$  in the IR,  $\mu_{\text{eff}}$  values lay in the range  $5.97\text{--}6.07\text{ B M}$ .

*(e) Amides and related ligands*

Dimethylformamide (DMF) readily complexes with iron(III), EPR and vibrational studies on  $\text{Fe}(\text{DMF})_6(\text{ClO}_4)_3$  imply<sup>43</sup> that the complex is structurally very similar to the dimethylsulphoxide analogues. The ligand phenazone (pn)  $(\text{PhN}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{Me})\text{N}\cdot\text{Me})$  coordinates via a carbonyl oxygen, and complexes  $\text{Fe}(\text{pn})_6(\text{ClO}_4)_3$ ,  $[\text{Fe}(\text{pn})_6]^{3+}$  ( $\text{FeX}_4^-$ )<sub>3</sub> ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) and  $\text{Fe}(\text{pn})_3(\text{NCS})_3$  are known<sup>62</sup>. Far-IR, Raman, and EPR results support these structures<sup>43</sup>. Yet another example of a complex containing a  $\text{FeL}_6^{3+}$  ion is  $\text{Fe}(\text{HMPA})_6(\text{ClO}_4)_3$  (HMPA = hexamethylphosphoramide  $\text{OP}(\text{NMe}_2)_3$ ), reported by Donoghue and Drago<sup>63</sup>, the reported magnetic moment is  $6.25\text{ B M}$ , which seems rather high. The hexakis complex of trimethylphosphate with ferric perchlorate has  $\mu_{\text{eff}} = 6.04\text{ B M}$ , and is a 1:3 electrolyte in nitrobenzene<sup>64</sup>, electronic spectral measurements imply that this hexacoordinate species is also present in solution. With *N,N*-dimethylacetamide

(DMA) the complexes  $\text{Fe}(\text{DMA})_6(\text{ClO}_4)_3$ ,  $\text{Fe}(\text{DMA})_2\text{Cl}_3$  and  $\text{Fe}(\text{DMA})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  are formed<sup>65</sup>, the anhydrous chloride complex is a 1:1 electrolyte in DMA and thus is probably  $[\text{Fe}(\text{DMA})_4\text{Cl}_2]^+[\text{FeCl}_4]^-$ .  $\epsilon$ -Caprolactam ( $\text{HN}(\text{CH}_2)_5\text{C}=\text{O}$ ) forms complexes<sup>66</sup>  $\text{Fe}(\text{caprolactam})_6(\text{ClO}_4)_3$  and  $\text{Fe}(\text{caprolactam})_2\text{Cl}_3$  which are, respectively, 1:3 and 1:1 electrolytes in nitromethane and thus are probably of the usual  $(\text{FeL}_6)^{3+}(\text{ClO}_4)_3$  and  $(\text{FeCl}_4\text{Cl}_2)^+(\text{FeCl}_4)^-$  types.

*(f) 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.  $\text{Fe}(\text{Ph}_3\text{PO})_4(\text{ClO}_4)_3$  was first prepared from alcoholic solution by Bannister and Cotton<sup>67</sup> whilst  $\text{Fe}(\text{Ph}_3\text{PO})_2\text{Cl}_3$  was later prepared from benzene solution.<sup>68</sup>  $\text{Fe}(\text{Ph}_3\text{AsO})_4(\text{ClO}_4)_3$  was originally prepared by a slightly more indirect method from ferric nitrate, sodium perchlorate and triphenylarsine oxide in ethanol<sup>69</sup> although it may be prepared by the direct reaction of ferric perchlorate and the ligand.<sup>70</sup>  $\text{Fe}(\text{Ph}_3\text{AsO})_2\text{Cl}_3$  was prepared by a similar reaction to that utilised for the  $\text{Ph}_3\text{PO}$  analogue. Phillips and Tyree suggested<sup>69</sup> that the triphenyl arsine oxide complexes should be formulated  $[\text{Fe}(\text{Ph}_3\text{AsO})_4]^{3+}(\text{ClO}_4)_3$  and  $[\text{Fe}(\text{Ph}_3\text{AsO})_4\text{Cl}_2]^+[\text{FeCl}_4]^-$ , as a result of conductance measurements. There is no evidence<sup>70</sup> in the IR spectra of either of the above perchlorate complexes for perchlorate coordination, but in  $\text{Fe}(\text{Bu}^n_3\text{PO})_4(\text{ClO}_4)_3$ , two perchlorate groups are thought to coordinate.<sup>71</sup> This reflects the lessened steric effect of *n*-alkyl compared with phenyl groups. Far-IR assignments were  $\nu(\text{Fe}-\text{OPBu}^n_3)$  at  $440\text{ cm}^{-1}$  and  $\nu(\text{Fe}-\text{OClO}_3)$  at  $315\text{ cm}^{-1}$ .

Further studies of the triphenyl phosphine and arsine oxide systems have been made recently<sup>70</sup> utilising Raman, IR and EPR spectroscopy in re-examining the perchlorate and chloride complexes, and in characterising the complexes  $\text{FeL}_2\text{Br}_3$ ,  $\text{FeL}_2(\text{NO}_3)_3$  and  $\text{Fe}(\text{Ph}_3\text{PO})_2(\text{NCS})_3$ . The perchlorate complexes gave the ( $g_1 = 6, g_2 = 2$ ) type of EPR spectrum and were thus assigned square-planar rather than tetrahedral structures. For the phosphine oxide complex,  $D = 0.84\text{ cm}^{-1}$ ,  $\lambda = 0.005$  and for the arsenic analogue,  $D = 1.05\text{ cm}^{-1}$ ,  $\lambda = 0.1$ . 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 ( $g_1 = 6, g_2 = 2$ ) 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.  $0.6\text{ cm}^{-1}$  and  $\lambda$  values ca.  $0.05$ .  $\text{Fe}(\text{Ph}_3\text{PO})_2(\text{NCS})_3$  was thought to have a similar structure; the  $D$  value of  $0.07\text{ cm}^{-1}$  compared to  $0.55\text{ cm}^{-1}$  for the nitrate analogue shows that the trigonal distortion is quite small here, reflecting the similar  $Dq$  values that  $\text{NCS}^-$  and  $\text{Ph}_3\text{PO}$  create.

The halide complexes evidently possess the *trans*- $[\text{Fe}(\text{Ph}_3\text{RO})_4\text{X}_2]^+[\text{FeX}_4]^-$  structure; the characteristic vibrational fundamentals of the  $\text{FeX}_4^-$  ions were noted in both the far-IR and Raman spectra and the EPR spectra exhibited ( $g_{\text{eff}} = 2$ ) resonances from the  $\text{FeX}_4^-$  ions and ( $g_1 = 6$ ) resonances from the hexacoordinate chromophores. In the ions  $[\text{Fe}(\text{Ph}_3\text{RO})_4\text{X}_2]^+$ , for  $\text{R} = \text{P}$ ,  $\text{X} = \text{Cl}$  then  $D = 0.63$ ,  $\lambda = 0.01$  and for  $\text{X} = \text{Br}$ ,  $D = 1.20\text{ cm}^{-1}$ ,  $\lambda = 0$ ; for  $\text{R} = \text{As}$ ,  $\text{X} = \text{Cl}$ ,  $D = 0.55\text{ cm}^{-1}$ ,  $\lambda = 0.01$  and for  $\text{X} = \text{Br}$ ,  $D = 1.50\text{ cm}^{-1}$ ,  $\lambda = 0$ .

Although  $\nu(\text{Fe}-\text{O})$  may be assigned to a band of medium-to-strong intensity in the IR spectra of the arsine oxide complexes in the region  $400-435\text{ cm}^{-1}$ , 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  $\text{Fe}(\text{pyO})_3\text{Cl}_3$  (ref. 59) no complex  $\text{Fe}(\text{Ph}_3\text{PO})_3\text{Cl}_3$  can be prepared<sup>70</sup>, it appears, however, that alkyl substituents are less stereochemically demanding than phenyl groups<sup>71</sup>.

#### (g) Miscellaneous

$\text{FeCl}_3 \cdot \text{Et}_2\text{O}$  and related systems were prepared many years ago<sup>72</sup> but little is known about them. 1:1 adducts of ferric chloride with benzophenone and acetophenone are known<sup>73</sup> whilst with benzanthrone,  $\text{C}_{17}\text{H}_{10}\text{O}$ ,  $\text{FeX}_3$  benzathrone complexes ( $\text{X} = \text{Cl}, \text{Br}$ ) have been reported<sup>74</sup>,  $\mu_{\text{eff}}$  values being 5.73 B.M. ( $\text{X} = \text{Cl}$ ) and 6.02 B.M. ( $\text{X} = \text{Br}$ ).

The dark brown ethoxide  $\text{Fe}(\text{OEt})_3$  has been prepared from  $\text{FeCl}_3$  and  $\text{NaOEt}$  in ethanol<sup>75</sup> or from ferric chloride in ether-benzene on treatment with excess ammonia<sup>76</sup>.  $\text{Fe}(\text{OMe})_3$  is also known. The magnetic properties of these systems, which are high-spin with abnormally large Curie-Weiss constants, have been interpreted<sup>77-78</sup> in terms of a trinuclear structure involving  $\text{FeO}_4$  tetrahedra.

The alcoholates  $\text{FeCl}_3 \cdot 2\text{ROH}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i$ ) have been reported<sup>79,80</sup>, they are prepared from ferric chloride and the appropriate alcohol in benzene.

#### (ii) Bi- and ter-dentate ligands

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

Single-crystal magnetic susceptibility measurements<sup>83</sup> on  $\text{Fe}(\text{acac})_3$  have determined  $D$  to be  $-0.11 \pm 0.04\text{ cm}^{-1}$  whilst  $\nu(\text{Fe}-\text{O})$  has been assigned to far-IR bands at 434 and  $300\text{ cm}^{-1}$  with the aid of metal isotope substitution<sup>84,85</sup>. Single-crystal electronic spectra have also been reported<sup>86</sup>.

$\text{Fe}(\text{acac})_2\text{Cl}$  and  $\text{Fe}(\text{acac})\text{Cl}_2$  can be prepared either by refluxing the appropriate quantities of  $\text{FeCl}_3$  and acac in benzene<sup>87</sup>, or by reaction of the stoichiometric amounts of  $\text{FeCl}_3$  and  $\text{Fe}(\text{acac})_3$ .  $\text{Fe}(\text{acac})_2\text{Cl}$  has been shown<sup>88</sup> to possess a slightly distorted square-pyramidal structure, with the Fe atom raised  $0.51\text{ \AA}$  above the basal plane. The Mössbauer parameters are<sup>89</sup>  $\delta = 0.60\text{ mm sec}^{-1}$  and  $\Delta E = 1\text{ mm sec}^{-1}$ , for  $\text{Fe}(\text{acac})\text{Cl}_2$ ,  $\Delta E$  is<sup>90</sup>  $0.44\text{ mm sec}^{-1}$ .

Fowles et al.<sup>91</sup> have reported complexes of 1,4-dioxan which include  $\text{FeCl}_3 \cdot \text{dioxan}$ , 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 ( $\times 10^3$ )  $\text{cm}^{-1}$ , it is, however, not improbable that the structure is  $[\text{Fe}(\text{dioxan})_2\text{Cl}_2]^+(\text{FeCl}_4)^-$  because of the richness of  $d-d$  bands and also since  $\nu(\text{Fe}-\text{Cl})$  was noted at 380  $\text{cm}^{-1}$ , which is high for  $\nu(\text{Fe}-\text{Cl})$  in a five-coordinate environment but correct for  $(\text{FeCl}_4)^-$ . An earlier report<sup>92</sup> concerned this compound and two others,  $\text{FeCl}_3(\text{dioxan})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot (\text{dioxan})_3 \cdot \text{HCl}$ , which are not well defined.

More recently, the 1:1 complex of ferric chloride with dimethoxyethane ( $\text{C}_4\text{H}_{10}\text{O}_2$ ) was reported<sup>93</sup>, this possibly involves pentacoordinate iron(III),  $\nu(\text{Fe}-\text{Cl})$  being assigned to bands at 355 and 375  $\text{cm}^{-1}$  and  $d-d$  bands occurring at 11.0, 14.4, 23.0, 28.4, 31.5 and 36.0 ( $\times 10^3$ )  $\text{cm}^{-1}$ .

Walmsley and Tyree<sup>94</sup> have investigated some complexes formed with liquids of the type  $\text{R}_2\text{PO} \cdot \text{CH}_2 \cdot \text{POR}_2$  (where  $\text{R} = \text{Bu}^n (\text{L}_1)$  or  $\text{Pr}^n\text{O} (\text{L}_2)$ ) preparing  $[\text{Fe}(\text{L}_1)_3]^{3+}(\text{FeCl}_4)^-$ ,  $[\text{Fe}(\text{L}_1)_3]^{3+}(\text{ClO}_4)^-$  and  $[\text{Fe}(\text{L}_2)_2\text{Cl}_2]^+(\text{FeCl}_4)^-$  all of which have  $\mu_{\text{eff}}$  values of ca. 6.1 B.M. at ambient temperatures. A related complex,  $[\text{Fe}(\text{OMPA})_3]^{3+}(\text{FeCl}_4)^-$  (OMPA = octamethylpyrophosphoramidate,  $(\text{Me}_2\text{N})_2\text{OPOPO}(\text{NMe}_2)_2$ ) was reported by Joesten and Nykerk who found it to be a 1:3 electrolyte in nitrobenzene<sup>95</sup>. They report  $\mu_{\text{eff}}$  to be 12.8 B.M., evidently this is not  $\mu_{\text{eff}}$  per Fe, which would seem to be 6.4 B.M., which is still very high.

The complex  $[\text{Fe}(\text{bipyO}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$  ( $\text{bipyO}_2 = 2,2'$ -bipyridyl-2,2'-dioxide) has  $\mu_{\text{eff}} = 6.13$  B.M. at room temperature<sup>96</sup> whilst  $\nu(\text{Fe}-\text{O})$  has been assigned<sup>97</sup> to far-IR bands at 408 and 377  $\text{cm}^{-1}$ .

2,2',2''-Terpyridine-1,1',1''-trioxide ( $\text{terpyO}_3$ ) is a terdentate ligand, Reiff and Baker<sup>98</sup> have prepared the complexes  $\text{Fe}(\text{terpyO}_3)\text{Cl}_3$  and  $\text{Fe}(\text{terpyO}_3)_2(\text{ClO}_4)_3$ , 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<sup>99</sup>. Two forms of  $\text{Fe}(\text{salen})\text{Cl}$  have been isolated, one being monomeric and having a molecule of nitromethane in the lattice<sup>100</sup> whilst the other is dimeric<sup>101</sup>. The monomers follow Curie-Weiss behaviour, with  $\mu_{\text{eff}}$  values of 5.7–6.0 B.M. at 300°K and  $\theta$  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  $\text{cm}^{-1}$ . Mossbauer spectra have been recorded for a number of these systems<sup>103</sup>, 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  $\text{Fe}(\text{salen}) \cdot \text{RCO}_2$  have been studied<sup>104</sup>, 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 salicylaldehydes (salHNR) which give complexes  $\text{FeCl}_3(\text{salHNR})_2$  (probably five-coordinate  $[\text{FeCl}(\text{salHNR})_2]^{2+}\text{Cl}_2^-$ ), octahedral  $\text{Fe}(\text{salNR})_3$  and  $\text{Fe}(\text{salNR})_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) which may be also five-coordinate.<sup>105</sup> The terdentate ligand derived from *N*-(2-hydroxyphenyl) salicylaldehyde ( $\text{LH}_2$ ) gives complexes  $\text{FeLX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with  $\mu_{\text{eff}}$  values of  $5.0 \pm 0.05$  B.M. at 295°K, so that they are probably dimeric.<sup>106</sup> On refluxing these in pyridine, complexes  $\text{FeLX}(\text{py})_3$  are obtained, which have 'normal' moments of  $6.0 \pm 0.05$  B.M. and are thus probably monomers, with one mole of lattice pyridine.

*N,N*-Dimethylethylenediamine *N*-oxide gives a rather unstable brown complex<sup>107</sup>,  $\text{Fe}(\text{Me}_2\text{NO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_3(\text{ClO}_4)_3$ , which is a 1:3 electrolyte and has  $\mu_{\text{eff}} = 5.80$  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  $\text{Fe}_3\text{O}$  chromophore are formed. The magnetism of a number of these systems has been investigated in both the solid state and solution<sup>108</sup>, and interpreted in terms of antiferromagnetic behaviour.

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

The red crystalline  $\text{FeCl}(\text{MeCO}_2)_2$  is reported to be formed from the reaction of anhydrous  $\text{FeCl}_3$  with anhydrous acetic acid, the dark brown bromide analogue is known, as is<sup>110</sup>  $\text{FeCl}(\text{HCO}_2)_2 \cdot 3/2 \text{H}_2\text{O}$ . Are these monomers?

By extracting a mixture of  $\text{Fe}(\text{MeCO}_2)_2$  and  $[\text{Fe}_3(\text{MeCO}_2)_8\text{OH}]$  with acetic acid<sup>111</sup>, a dark compound  $\text{Fe}_2(\text{MeCO}_2)_5$  was obtained, this is presumably dimeric. Starke<sup>112</sup> has reported that reaction of formic or acetic acid with iron, in methanol in the presence of oxygen, produces species  $\text{Fe}(\text{RCO}_2)(\text{OMe})_2$ .

However, more simple complexes are formed with oxalate and related ions.  $\text{M}_3\text{Fe}(\text{oxalate})_3 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Li}, \text{Na}, n = 0, \text{M} = \text{K}, n = 3$ ) are typical. The structure of the potassium salt has been determined<sup>113</sup>; 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  $-0.55 \text{ cm}^{-1}$ , reflecting the strong trigonal field<sup>83</sup>. Little investigation seems to have been made of complexes<sup>114</sup> of the type  $\text{Fe}(\text{D-tartrate})_3 \cdot 5\text{H}_2\text{O}$  where interesting possibilities arise.

*(b) Amino acid complexes*

The amino acid DL-methionine  $[\text{MeS}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}]$  forms a tris-complex with iron(III) having  $\mu_{\text{eff}} = 5.63 \text{ B.M.}$ , it was suggested<sup>115</sup> that coordination occurs via the amine and carboxylate functions. More recently, it has been found that reaction between  $\text{Fe}^{3+}$  and L-cysteine in alcohol gives labile red, blue, and violet complexes<sup>116</sup>. The violet complex was found to be  $\text{Fe}(\text{cysteine})_3 \cdot 2\text{H}_2\text{O}$ , it is initially produced at  $-78^\circ$  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<sup>117</sup> 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 thioglycolic acid in ammoniacal solution; no stable iron(III) complex exists, but the species present is thought to contain only ferric iron<sup>118</sup>. 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  $\text{Rb}[\text{Fe}(\text{EDTA})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$  and  $\text{Li}[\text{Fe}(\text{EDTA})\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ , ferric ions are surrounded by a hexadentate EDTA molecule and a water molecule, in what may be regarded as a distorted pentagonal-bipyramidal configuration<sup>119</sup>. In  $\text{Fe}(\text{HEDTA}) \cdot \text{H}_2\text{O}$ , one carboxylic group is protonated, and thus does not coordinate, so that the ethylenediamine-tetraacetic acid group is pentadentate, a water molecule completes the distorted octahedral coordination of the metal<sup>120</sup>.

The EPR spectrum of  $\text{Fe}(\text{HEDTA}) \cdot \text{H}_2\text{O}$ , doped into the isostructural Ga analogue, has been investigated<sup>121</sup>, at  $110^\circ\text{K}$ , the spectra were interpreted in terms of the parameters  $D = 0.69 \text{ cm}^{-1}$ ,  $\lambda = 0.267$  (on cooling further,  $\lambda$  appears to increase). The EPR of  $\text{Fe}^{3+}$  doped into a  $\text{NH}_4^+[\text{Co}(\text{EDTA}) \cdot \text{H}_2\text{O}]$  host has been reported<sup>122</sup> and interpreted<sup>123</sup> in terms of the parameters  $D = 0.769 \text{ cm}^{-1}$ ,  $\lambda = 0.307$ .

The complexes  $(\text{NH}_4)[\text{Fe}(\text{EDTA})\text{OH}_2]$  and  $[\text{Fe}(\text{EDTAH})] \cdot x\text{H}_2\text{O}$  ( $0 < x < 1$ ) have been found<sup>124</sup> to be high-spin ( $S = 5/2$ ) over the range  $90\text{--}291^\circ\text{K}$ .

Cohen and Hoard have described<sup>125</sup> the structure of the complex  $\text{Ca}[\text{Fe}(\text{DCTA})(\text{OH}_2)] \cdot 8\text{H}_2\text{O}$  (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

*(1) Monodentate**(a) Thiocyanate and cyanate*

Reaction of  $\text{Fe}(\text{NCS})_3$  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  $10,640\text{ cm}^{-1}$  and  $17,500\text{ cm}^{-1}$ , most of the spectrum being obscured by the usual  $Fe-NCS$  charge-transfer absorption<sup>126</sup>. Far-IR absorptions assignable to  $\nu(Fe-NCS)$  were noted<sup>127</sup> at  $298\text{ sh}$ ,  $272$  and  $233\text{ cm}^{-1}$ , in the ethyl analogue, others<sup>128</sup> assign  $\nu(Fe-NCS)$  at  $270\text{ cm}^{-1}$  and  $\delta(Fe-NCS)$  at  $98\text{ cm}^{-1}$ . Iron(III)-thiocyanate complexes are all probably  $N$ -bonded, the occurrence of a medium intensity band at ca  $470\text{ cm}^{-1}$  in the IR being regarded as diagnostic of this<sup>129</sup>.

$(Ph_4As)^+[Fe(NCO)_4]^-$  has been prepared from  $AgNCO$  and  $FeCl_4^-$  in acetone<sup>130</sup>,  $\nu(Fe-NCO)$  was assigned to a far-IR band at  $410\text{ cm}^{-1}$ . The coordination is presumably tetrahedral and thus it is likely to be  $N$ -bonded. The high-spin complex  $[Fe(N_3)_6]^{2-}$  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  $1.963-1.971\text{ \AA}$ , are shorter than the axial  $Fe-N$  distance<sup>261</sup>, presumably due to ligand-ligand repulsion.

#### (b) Ammonia

No simple complexes exist in aqueous solution, addition of ammonia to ferric salts merely precipitating the hydrous oxide. However, treatment of anhydrous ferric chloride<sup>131</sup> and ferric bromide<sup>132</sup> 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<sup>135</sup> to contain  $FeCl_4^-$  ions. On the other hand, some genuine pyridine complexes have been made.  $Fe(py)_3(NCS)_3$  and  $Fe(\text{quinoline})_3(NCS)_3$  were prepared as iridescent crystals from alcoholic solution<sup>136</sup>. A reinvestigation of the pyridine complex<sup>137</sup> led to far-IR assignments of  $\nu(Fe-NCS)$  at  $300\text{ cm}^{-1}$  and  $\nu(Fe-py)$  at  $249\text{ cm}^{-1}$ , 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<sup>133, 134</sup>, it forms very hygroscopic red crystals. A more recent investigation<sup>138</sup> suggests that it is *fac*- $Fe(py)_3Cl_3 \cdot py$ , the spin Hamiltonian parameters are  $D \approx 0.164\text{ cm}^{-1}$ ,  $\lambda = 0.100$  whilst  $\nu(Fe-Cl)$  is assigned to  $300$  and  $250\text{ cm}^{-1}$  and  $\nu(Fe-N)$  at  $233$  and ca  $200\text{ cm}^{-1}$ . Whilst no characterisable product could be obtained from the reaction of  $FeBr_3$  and pyridine, the parameters  $D = 0.665\text{ cm}^{-1}$ ,  $\lambda = 0.033$  were obtained from  $In(Fe)py_3Br_3$  implying a *fac* structure.

Spectrophotometric studies of  $FeCl_3$  in pyridine<sup>139</sup> 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<sup>140</sup> of the complexing ability of pyrazole, a complex  $Fe(\text{pyrazole})_4Cl_3$  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<sup>138</sup> has shown that this is in fact  $Fe(\text{pyrazole})_3Cl_3$ . EPR spectra ( $D =$



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

(e)  $\text{Fe[N(SiMe}_3)_2]_3$

This compound exhibits a number of interesting features, first prepared by Burger and Wannagat<sup>141</sup>, the crystal structure shows that the iron atom is three-coordinate<sup>142</sup>. The  $\text{FeN}_3$  and  $\text{FeNSi}_2$  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 ( $\mu_{\text{eff}} = 5.91 \text{ B.M.}$ ,  $\theta = -10^\circ$ ). The isomer shift in the Mossbauer spectrum is of the order expected for a tercoordinate  $\text{Fe}^{3+}$  ion ( $\delta = 0.43 \text{ mm sec}^{-1}$  relative to nitroprusside) but the quadrupole splitting is extremely large ( $\Delta E = 5.12 \text{ mm sec}^{-1}$ ) 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  $D = 1.00 \text{ cm}^{-1}$ ,  $\lambda = 0$ . Crystal field calculations in  $D_{3h}$  symmetry afford the  $d$  orbital sequence  $e' + 12370$ ,  $a' - 6980$ ,  $e'' - 8800 \text{ cm}^{-1}$ , implying strong interaction in the  $x_1$  plane.<sup>143</sup>

(n) 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<sup>144</sup>  $[(\text{phen})_2\text{Fe}(\text{OH})_2\text{Fe}(\text{phen})_2]^{4+}$ . However, if the tris-complexes of  $\text{Fe}^{2+}$  are first prepared, they can be smoothly oxidised to the blue  $[\text{Fe}(\text{phen})_3]^{3+}$  and  $[\text{Fe}(\text{bipy})_3]^{3+}$  complex ions.<sup>145</sup> These systems are low-spin; the magnetic moments<sup>146,147</sup>, Mossbauer parameters<sup>149,158</sup> (Table 2) and EPR spectra<sup>150</sup> (Table 1) have been obtained. Figgis<sup>146</sup> interprets the variation of magnetic susceptibility with temperature in terms of an axial field of ca.  $400\text{--}600 \text{ cm}^{-1}$ . On the other hand, the EPR spectra are interpreted<sup>150</sup> in terms of a distortion of  $800\text{--}1200 \text{ cm}^{-1}$  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,  $0.93\text{--}1.07$ ; this results from the neglect of factors such as configuration interaction.

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

welcome

Reaction of ferric chloride in dilute HCl with phenanthroline gives <sup>149</sup> a complex  $\text{Fe}_2\text{phen}_3\text{Cl}_6$  whilst similar reactions in acetic acid lead <sup>151</sup> to  $\text{Fe}_2\text{phen}_2\text{Cl}_6 \cdot \frac{1}{2}\text{MeCO}_2\text{H}$ . This latter complex is part of a series  $[\text{Fe}(\text{phen})_2\text{Cl}_2]^+\text{X}^- n\text{MeCO}_2\text{H}$  ( $\text{X} = \text{ClO}_4$ ,  $n = 1$ ,  $\text{X} = \text{Cl}$ ,  $n = 2$ ,  $\text{X} = \text{FeCl}_4^-$ ,  $n = 0.5$ ). A complex  $\text{Fe}(\text{phen})\text{Cl}_3$  was originally <sup>152</sup> formulated as  $[\text{Fe}(\text{phen})_2\text{Cl}_2]^+[\text{FeCl}_4]^-$  as it gave a perchlorate  $[\text{Fe}(\text{phen})_2\text{Cl}_2]^+\text{ClO}_4^-$ . Later studies <sup>149</sup> indicated that this complex (which could be isolated in two crystalline modifications) is probably a chloro-bridged dimer  $\text{Fe}_2(\text{phen})_3\text{Cl}_6$  is thought to be  $[\text{Fe}(\text{phen})_2\text{Cl}_2]^+[\text{Fe}(\text{phen})\text{Cl}_4]^-$ ; on treatment with methanolic  $\text{LiClO}_4$ ,  $[\text{Fe}(\text{phen})_2\text{Cl}_2]^+\text{ClO}_4^-$  is obtained, whilst reaction with tetraethylanmonium chloride yields  $[\text{Et}_4\text{N}]^+[\text{Fe}(\text{phen})\text{Cl}_4]^-$ , which can also be prepared directly from  $(\text{Et}_4\text{N})^+(\text{FeCl}_4)^-$  and phen in acetone. Clearly more work on these systems is desirable.

$\text{Fe}(\text{en})_3\text{Cl}_3$  has been prepared by direct reaction in absolute alcohol <sup>153</sup>, it is low-spin, as might be expected if the ethylenediamines are chelating. The electronic spectrum was analysed in terms of the parameters  $B = 500$ ,  $C = 2000$ ,  $Dq = 1950 \text{ cm}^{-1}$ ,  $B$  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 <sup>154</sup>  $\text{Fe}(\text{pyimH})_3(\text{ClO}_4)_3$  and  $\text{Fe}(\text{pybeimH})_3\text{Cl}_3$  as well as an 'inner' complex  $\text{Fe}(\text{pyim})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$

Two terpyridyl complexes have been reported <sup>155</sup>,  $\text{Fe}(\text{terpy})\text{Cl}_3$  and  $\text{Fe}(\text{terpy})_2(\text{ClO}_4)_3$ , 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  $\text{InCl}_3 \cdot \text{terpy}$  is thought to be <sup>156</sup>

One class of complexes which is rather hard to classify is the isocyanide complexes reported over 60 years ago <sup>157</sup>.  $\text{FeCl}_3 \cdot 2\text{EtNC}$ ,  $\text{FeCl}_3 \cdot 3\text{EtNC}$  and  $\text{FeCl}_3 \cdot 3\text{PhNC}$  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 <sup>159</sup>, a pentadentate macrocycle and two *N*-bonded thiocyanates make up the coordination sphere, where  $\text{Fe}-\text{N}(\text{macro}) = 2.23 \pm 0.05 \text{ \AA}$  and  $\text{Fe}-\text{NCS} = 2.01 \pm 0.02 \text{ \AA}$ . This is one of a series of complexes <sup>160</sup> which are of the general form  $[\text{FeBX}_2]^+\text{Y}^-$ , where  $\text{B} = 2,13\text{-dimethyl-3,6,9,12,18-penta-azabicyclo}[12,3,1]\text{octadeca-1(18)2,12,14,16-pentaene}$ , where  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$  or  $\text{NCS}$ , and  $\text{Y} = \text{ClO}_4$ ,  $\text{BF}_4$  or  $\text{NCS}$ . They are  $S = 5/2$  systems which are 1:1 electrolytes — of especial interest is the  $\text{Fe}^{\text{III}}-\text{I}$  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

Mössbauer parameters and magnetic moments <sup>a</sup>

|   | Temp | $\delta$<br>(mm sec <sup>-1</sup> ) <sup>b</sup> | $\Delta E$<br>(mm sec <sup>-1</sup> ) | $\mu_{\text{eff}}$<br>(B.M.) <sup>c</sup> |
|---|------|--|---------------------------------------|---|
| Fe(phen) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O                     | 80   | 0.36   | 1.71                                  | 2.40                                      |
| Fe(bipy) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O                     | 80   | 0.32   | 1.80                                  | 2.40                                      |
| [Fe(bipy) <sub>2</sub> (CN) <sub>2</sub> ](ClO <sub>4</sub> )                                 | 300  | 0.24   | 1.63                                  | 2.34 (294)                                |
|   |      |  |                                       | 2.01 (81)                                 |
| [Fe(phen) <sub>2</sub> (CN) <sub>2</sub> ](ClO <sub>4</sub> )                                 |      |  |                                       | 2.42 (300)                                |
|   |      |  |                                       | 2.03 (80)                                 |
| [Fe(phen) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> [Fe(phen)Cl <sub>4</sub> ] <sup>-</sup> | 80   | 0.63   | 0.05                                  |   |
| [Et <sub>4</sub> N] <sup>+</sup> [Fe(phen)Cl <sub>4</sub> ] <sup>-</sup>                      | 80   | 0.65   | 0.05                                  | 5.87                                      |
| [Fe(phen) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>           | 80   | 0.65   | 0.05                                  | 5.91                                      |
| Fe(en) <sub>3</sub> Cl <sub>3</sub>   | 77   | 0.40   | 1.36                                  | 2.45 (285)                                |
|   |      |  |                                       | 2.17 (80)                                 |
| Fe(terpy)Cl <sub>3</sub>  | 80   | ca 0.71  | 0.54                                  | 5.85                                      |
| Fe(terpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub>                                       | 80   | ca 0.33  | 3.43                                  | 2.16 (286)                                |
|   |      |  |                                       | 1.91 (78)                                 |
| Fe(py <sub>4</sub> mH) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>                          |      |  |                                       | 2.47 (295)                                |
| Fe(py <sub>4</sub> m) <sub>3</sub> ·½H <sub>2</sub> O   |      |  |                                       | 2.52 (295)                                |

<sup>a</sup> Data from refs. 146, 148, 149, 151, 153 and 158<sup>b</sup> Relative to sodium nitroprusside<sup>c</sup> 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<sub>4</sub>As)<sup>+</sup>(FeCl<sub>4</sub>)<sup>-</sup> the Cl-Fe-Cl angles are <sup>161</sup> 107° and 114.5° whilst in [Fe(DMSO)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>(FeCl<sub>4</sub>)<sup>-</sup> they are <sup>162</sup> 108.2° and 112.2°. Similar values have been reported for Na<sup>+</sup>FeCl<sub>4</sub><sup>-</sup> (ref. 163) and (PCl<sub>4</sub>)<sup>+</sup>(FeCl<sub>4</sub>)<sup>-</sup> (ref. 164). Mössbauer studies have also been made <sup>136, 165</sup>, reported isomer shifts are 0.45 mm sec<sup>-1</sup> for (FeCl<sub>4</sub>)<sup>-</sup> and 0.51 mm sec<sup>-1</sup> for (FeBr<sub>4</sub>)<sup>-</sup>. Ginsberg and Robin <sup>135</sup> showed that salts of the type (pyH<sup>+</sup>)<sub>3</sub>(Fe<sub>2</sub>Cl<sub>9</sub>)<sup>3-</sup> are in fact composed of (FeCl<sub>4</sub>)<sup>-</sup> ions, but they did prove that one form of Cs<sub>3</sub>Fe<sub>2</sub>Cl<sub>9</sub> does in fact contain dimeric (Fe<sub>2</sub>Cl<sub>9</sub>)<sup>3-</sup> 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 <sup>135</sup> unsuspected by others <sup>166</sup>.

The mixed tetrahaloferrate ions also exist, FeCl<sub>3</sub>Br<sup>-</sup> and FeBr<sub>3</sub>Cl<sup>-</sup> were prepared by Kraus and Heidberg <sup>37</sup> and re-examined by Clausen and Good <sup>167</sup> who treated an alcoholic solution of the appropriate ferric halide with a tetraalkylammonium halide. FeCl<sub>2</sub>Br<sub>2</sub><sup>-</sup> has also been isolated <sup>167</sup> from bromine oxidation of alcoholic FeCl<sub>2</sub>, followed by addition of

TABLE 3

Vibrational fundamentals<sup>168</sup> for  $\text{FeCl}_4^-$  and  $\text{FeBr}_4^-$  (in  $\text{cm}^{-1}$ )

|         | $\text{FeCl}_4^-$ | $\text{FeBr}_4^-$ |
|---------|-------------------|-------------------|
| $\nu_1$ | 330               | 200               |
| $\nu_2$ | 114               |                   |
| $\nu_3$ | 378               | 285               |
| $\nu_4$ | 137               | 95                |

the alkylammonium halide. The Mossbauer spectra<sup>167</sup> show a gradual increase in isomer shift as chloride is replaced by bromide, no quadrupole splitting was seen. The far-IR spectra showed  $\nu(\text{Fe}-\text{Cl})$  in the region  $350-390\text{ cm}^{-1}$  and  $\nu(\text{Fe}-\text{Br})$  in the region  $260-300\text{ cm}^{-1}$ , a number of unassignable bands were, however, noted. Fundamentals for  $\text{FeCl}_4^-$  and  $\text{FeBr}_4^-$  are tabulated<sup>168</sup> in Table 3.

No anionic pentachlorides or bromides have been reported but some pentafluorides are known. In the case of indium(III) both  $\text{InCl}_4^-$  and  $\text{InCl}_5^{2-}$  can be obtained, depending upon the choice of conditions (especially solvent), so that it is possible that the unsolvated  $\text{FeCl}_5^{2-}$  ion might be obtained.

In contrast, the stable anionic species for fluoride ion is  $^{41}\text{FeF}_6^{3-}$ ,  $\nu(\text{Fe}-\text{F})$  has been assigned in the  $450-500\text{ cm}^{-1}$  in the IR.<sup>169,170</sup> A number of tetra- and penta-fluorides have been prepared, but these are probably polymers with fluoride bridges,  $\text{M}_3\text{FeF}_6$  ( $\text{M} = \text{NH}_4$ ,  $\text{Li}$ ,  $\text{Na}$ ) have  $\mu_{\text{eff}}$  values of  $5.80-5.95\text{ B.M.}$  at room temperature whilst  $\text{CsFeF}_4$  and  $\text{K}_2\text{FeF}_5$  have moments of ca.  $4.8\text{ B.M.}$  (ref. 171). These 'low' moments may reflect antiferromagnetic interaction via bridging fluorines. On heating  $(\text{NH}_4)_3\text{FeF}_6$  to  $140^\circ\text{C}$ ,  $\text{NH}_4\text{FeF}_4$  is formed.<sup>172</sup> A detailed study<sup>173</sup> of  $\text{M}_3\text{FeF}_6$  systems ( $\text{M} = \text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ,  $\text{Ag}$ ,  $\text{Tl}$  and  $\text{NH}_4$ ) showed that they contained  $\text{FeF}_6^{3-}$  octahedra, having Curie-Weiss magnetic behaviour to liquid nitrogen temperature.  $\nu(\text{Fe}-\text{F})$  was assigned at  $450-500\text{ cm}^{-1}$  and  $\delta(\text{F}-\text{Fe}-\text{F})$  at  $270-350\text{ cm}^{-1}$  in the far-IR. A recent EPR study<sup>174</sup> has been made of the  $\text{FeF}_6^{3-}$  ion in aqueous solution showing the strength of fluoride coordination to iron, the expected seven-line spectrum was obtained, characterised by  $g_{\text{iso}} = 2.0036$  and  $a_{\text{F}} \text{ ca. } 23.0\text{ gauss}$ .

It is evident from the value of the isomer shift ( $0.69-0.71\text{ mm sec}^{-1}$ ) in the Mossbauer spectra<sup>135,165</sup> of  $\text{FeCl}_3$  and  $\text{FeBr}_3$  that the ferric ion is hexacoordinate, but it was not until recently that the  $\text{FeCl}_6^{3-}$  ion was isolated and characterised. It is precipitated from solution<sup>175</sup> by large cations such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . There is controversy over the electronic spectral assignments, early workers<sup>176</sup> assign a band at  $18,730\text{ cm}^{-1}$  to  $^6A_1 \rightarrow ^4T_2$  and a band at  $22,080\text{ cm}^{-1}$  to  $^6A_1 \rightarrow ^4A_1, ^4E$  (this is probably a charge-transfer band) whilst others<sup>31</sup> assign bands at  $9100$ ,  $11,550$  and  $13,150\text{ cm}^{-1}$  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<sup>177</sup>, these transitions have been ascribed to bands at  $8900$ ,  $12,800$  and  $18,000\text{ cm}^{-1}$ , giving  $10Dq$

values in accordance with theory<sup>178</sup> and are consistent with the  $d-d$  bands of  $\text{Cs}_3\text{Fe}_2\text{Cl}_9$  at 9800, 13,600 and 17,900  $\text{cm}^{-1}$ . The reported isomer shift<sup>165,179</sup> for  $\text{FeCl}_6^{3-}$  is ca. 0.75  $\text{mm sec}^{-1}$ ; the absence of a quadrupole splitting implies near octahedral symmetry. The low-energy vibrational spectrum of  $(\text{FeCl}_6)^{3-}$  has been investigated<sup>179,180</sup>,  $\nu_3(\nu_{\text{as}}\text{Fe}-\text{Cl})$  occurs in the range 248–257  $\text{cm}^{-1}$ ,  $\nu_4(\delta\text{Cl}-\text{Fe}-\text{Cl})$  at 181  $\text{cm}^{-1}$  and  $\nu_1(\nu_{\text{sym}}\text{Fe}-\text{Cl})$  at 283  $\text{cm}^{-1}$ . One expects that  $(\text{FeBr}_6)^{3-}$  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 is 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<sup>181</sup>, McCleverty<sup>182</sup> and Coucouvanis<sup>183</sup>. 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<sup>184,185</sup>, but it was Cambi et al.<sup>186–190</sup> 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  $(\text{R}_2\text{NCS}_2)_3\text{Fe}$ . 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<sup>191</sup>, 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<sup>191</sup> as being due to the relaxation of lattice forces in solution which "impress distortions on the  $\text{FeS}_6$  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<sup>192</sup>.

The most recent publication from these workers<sup>15</sup> discussed magnetic measurements made over a range of temperatures and pressures,  $\Delta V$ , the volume difference between the

TABLE 4

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

| Complex   | $\mu_{\text{eff}}$<br>(B.M.) | Temperature<br>(°K) | Ref |
|---|------------------------------|---------------------|-----|
| $\text{Fe}(\text{S}_2\text{CNBu}''_2)_3$  | 2.46                         | 300                 | 207 |
| $\text{Fe}(\text{S}_2\text{CSEt})_3$  | 2.19                         | 109                 | 205 |
|   | 2.57                         | 301                 |     |
| $\text{Fe}(\text{S}_2\text{CPh})_3$   | 2.11                         | 103                 | 209 |
|   | 2.26                         | 295                 |     |
| $\text{Fe}(\text{S}_2\text{COMe})_3$  | 2.11                         | 91                  | 15  |
|   | 2.45                         | 293                 |     |
| $\text{Fe}(\text{MeCSCHCSMe})_3$  | 1.73                         | 100                 | 213 |
|   | 2.00                         | 293                 |     |
| $\text{KBa}[\text{Fe}(\text{S}_2\text{C}_2\text{O}_2)_3] \cdot 6\text{H}_2\text{O}$                                       | 2.04                         | 100                 | 215 |
|   | 2.28                         | 297                 |     |
| $(\text{Ph}_4\text{P})_3[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_3]$   | 2.50                         | 293                 | 218 |
|   | 2.25                         | 94                  |     |
| $(\text{Ph}_4\text{P})_2[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2(\text{S}_2\text{CNMe}_2)]^{2-}$                   | 2.53                         | ca 290              |     |
| $(\text{Ph}_4\text{P})_2[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2(\text{S}_2\text{CNEt}_2)]^{2-}$                   | 2.60                         | ca 290              | 222 |
| $(\text{Ph}_4\text{P})[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)(\text{S}_2\text{CNEt}_2)_2]^-$                        | 2.36                         | ca 290              |     |
| $(\text{Ph}_4\text{P})_3[\text{Fe}(\text{S}_2\text{C}_2\text{C}(\text{CN})_2)(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{3-}$ | 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  $\text{Fe}(\text{S}_2\text{CNBu}''_2)_3$ , where the configuration of the six sulphur atoms around the iron atom is intermediate between trigonal prismatic and trigonal antiprismatic<sup>193</sup>. 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<sup>194–197</sup>, the observed quadrupole splittings typically lay in the range 0.4–0.7 mm sec<sup>-1</sup>. 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 <sup>57</sup>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<sup>197,198</sup> but Rickards et al.<sup>197</sup> diluted  $\text{Fe}(\text{S}_2\text{CNMe}_2)_3$  with the diamagnetic  $\text{Co}^{3+}$  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   | $\delta$<br>(mm sec <sup>-1</sup> ) <sup>a</sup> | $\Delta E$<br>(mm sec <sup>-1</sup> ) | Temp<br>(°K) | Ref |
|---|--|---------------------------------------|--------------|-----|
| Fe(S <sub>2</sub> CPh) <sub>3</sub>   | -0.10 <sup>b</sup>                               | 1.87                                  | ca 300       | 209 |
| Fe(MeCSCHCSMe) <sub>3</sub>   | 0.46   | 1.84                                  | 293          | 213 |
|   | 0.55   | 1.90                                  | 83           |     |
|   | 0.54   | 1.96                                  | 42           |     |
| (Ph <sub>4</sub> P) <sub>3</sub> [Fe(S <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub> ) <sub>3</sub> ] | 0.59   | 1.57                                  | 190          | 220 |
|   | 0.65   | 1.69                                  | 77           |     |
| Fe(PhCSCHCOPh) <sub>3</sub>   | 0.60   | 1.90                                  | 80           | 234 |
| Fe(MeCSCHCOMe) <sub>3</sub>   | 0.52   | 0.24                                  | 80           | 234 |
| Fe(MeCSCHCOPh) <sub>3</sub>   | 0.61   | 1.91                                  | 80           | 234 |
| Fe(PhCSCHCOMe) <sub>3</sub>   | 0.58   | 1.68                                  | 80           | 234 |
| Fe(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub>  | 0.42   | 0.71                                  | 77           | 196 |

<sup>a</sup> Relative to nitroprusside<sup>b</sup> Relative to <sup>57</sup>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<sup>199</sup>) with structural results is probably a consequence of neglecting factors such as configuration interaction<sup>199</sup>, 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<sup>200</sup>.

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<sup>201</sup> 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<sup>12</sup> 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<sup>-1</sup> are assigned as  $\nu(Fe-S)$ ,  $\nu(Fe-Cl)$  and  $\nu(Fe-Br)$  respectively. EPR results<sup>12,202</sup> give  $g_{\perp} \approx 4$ ,  $g_{\parallel} \approx 2$  at X-band, consistent with a  $S = 3/2$  ion with an appreciable zero-field splitting. Mossbauer results on solid samples<sup>203</sup> indicate a large quadrupole splitting ( $\Delta E \approx 2.8$  mm sec<sup>-1</sup>) but a low  $Q S$  has been noted<sup>204</sup> in DMF at 77°K ( $\Delta E = 0.70$  mm sec<sup>-1</sup>), 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 tetra-

hedral field<sup>10</sup> 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<sup>15</sup> but the thioxanthates appear to be examples of a spin-equilibrium system<sup>205</sup>. 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<sup>206–207</sup>.  $Fe(Bu^tSCS_2)_3$  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<sup>208</sup> like  $Fe(S_2CNBu^t)_3$ , 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<sup>209</sup>. Coucouvanis and Lippard<sup>210</sup> prepared the similar (also low-spin) system  $Fe(p\text{-tol}CS_2)_3$  in the course of studying the reactions of ferric chloride with  $Zn(p\text{-tol}CS_3)_2$ , when the complexes  $Fe(p\text{-tol}CS_3)_2(p\text{-tol}CS_2)$  and  $Fe(p\text{-tol}CS_3)(p\text{-tol}CS_2)_2$  were also obtained. The crystal structure of the last-named complex shows that the coordination of the iron is octahedral, including an  $Fe\text{---}S\text{---}S\text{---}C$  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<sup>211</sup>. The crystal structure<sup>212</sup> shows the complex to be composed of  $(MeCSCHCSMe)^+$  and  $FeCl_4^{2-}$  ions; upon dithionite or borohydride reduction, the red-brown complex  $Fe(MeCSCHCSMe)_3$  is formed. The  $g$  values<sup>213</sup> of 2.14, 2.09 and 2.01 are typical of low-spin iron(III) complexes<sup>199</sup>; 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<sup>213</sup>; the quadrupole splitting of  $c_d$   $1.90\text{ mm sec}^{-1}$  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<sup>214</sup> and found  $\mu_{eff}$  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<sup>215</sup> prepared samples of  $KBa[Fe(S_2C_2O_2)_3] \cdot 6H_2O$  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  $\text{Ph}_3\text{As}^+$  salt is also low-spin, but the  $(\text{Ph}_3\text{P})_2\text{M}^+$  salts ( $\text{M} = \text{Cu}, \text{Ag}$ ) are *high-spin*<sup>216</sup>, it was suggested that the metal  $\text{M}$  binds to two  $\text{C}=\text{O}$  groups and reduces  $Dq$  sufficiently for the change in spin state. Treatment of  $[\text{Fe}(\text{S}_2\text{C}_2\text{O}_2)_3]^{3-}$  with  $\text{I}_2$  leads to the formation of  $[\text{Fe}(\text{S}_2\text{C}_2\text{O}_2)_2]^{3-}$ , 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 ( $g_1 = 4, g_2 = 2$ ) variety at X-band. On refluxing a  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{Fe}(\text{S}_2\text{C}_2\text{O}_2)_3]^{3-}$ ,  $[\text{Fe}_2(\text{S}_2\text{C}_2\text{O}_2)_5]^{4-}$ , 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  $[\text{S}_2\text{C}_2(\text{CN})_2]^{2-}$  complexes. The environment of the vanadium ion in  $(\text{Me}_4\text{N})_2[\text{V}(\text{S}_2\text{C}_2(\text{CN})_2)_3]$  is that of a very distorted octahedron of sulphurs<sup>217</sup>.  $(\text{Ph}_4\text{P})_3[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_3]$  is prepared from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and excess  $\text{Na}_2\text{S}_2\text{C}_2(\text{CN})_2$ , in the absence of air, as a dark red solid<sup>218</sup>, 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<sup>219</sup> is quite typical of an ( $S = 1/2$ ) species; it should, however, be noted that the separation of the  $t_{2g}$  levels originally suggested<sup>219</sup> is incorrect<sup>199</sup>. The Mossbauer spectrum<sup>220, 221</sup> shows a large quadrupole splitting (ca. 1.6 mm sec<sup>-1</sup>) 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  $[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$  to the tri-anionic species, the isomer shift increases from 0.50 to 0.65 mm sec<sup>-1</sup>, indicating that the unpaired electron has entered an orbital of largely metallic (presumably  $3d$ ) character<sup>220</sup>.

Recently<sup>222</sup>, the mixed 1,1'-1,2-dithiolene complexes have been prepared by treating the complexes  $[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  with 1,1'-dithiolene ligand, followed by sulphite reduction. Thus  $(\text{Ph}_4\text{P})_3[\text{Fe}\{\text{L-L}\}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$  (where  $\text{L-L} = \text{e.g. S}_2\text{C}(\text{CN})_2, \text{S}_2\text{C}(\text{N}(\text{CN}))$ ) were obtained. They are low-spin, having room temperature moments of ca. 2.5 B.M. at room temperature, however, no EPR or Mossbauer data are yet available.

The complexes of the type  $[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  are in fact dimeric in the solid state, the environment of the iron atom being pentacoordinate<sup>223, 224</sup>. 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  $[\text{FeL}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ , where  $\text{L} = \text{e.g. pyridine}$ , have been prepared<sup>225</sup> which exhibit  $S = 3/2$  magnetic behaviour in both the solid state and solution, when  $\text{L} = \text{e.g. PPh}_3, \text{bipy}, \text{phen}$ , 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<sup>199</sup>. Balch<sup>226</sup> has very recently reported more adducts of the type  $[\text{Fe}(\text{L}^{n-})(\text{S}_2\text{C}_2\text{X}_2)_2]^{(n+1)-}$  ( $\text{X} = \text{CN}, \text{CF}_3$ ,  $\text{L} = \text{Ph}_3\text{PO}, \text{Ph}_3\text{AsO}, \text{pyO}, \text{py}, \text{Cl}, \text{Br}$ ) which exhibit  $S = 3/2$  magnetic behaviour ( $\mu_{eff} = 3.90\text{--}4.02$  B.M. at 296° K).

Reaction of  $(\text{Bu}^n_4\text{N}) [\text{Fe} \{ \text{S}_2\text{C}_2(\text{CF}_3)_2 \}_2]$  with triphenylphosphine, in the presence of air, leads to the formation of the  $S = 3/2$  complex  $(\text{Bu}^n_4\text{N}) [\text{Fe}(\text{Ph}_3\text{PO}) \{ \text{S}_2\text{C}_2(\text{CF}_3)_2 \}_2]$  which has a square-based pyramidal structure, the iron atom being 0.43 Å above the basal plane<sup>262</sup>

The EPR spectra of frozen acetone or dichloromethane solutions of  $[\text{Fe}(\text{py})(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  are consistent with the presence of an ( $S = 3/2$ ) ion with a definite zero-field splitting,  $g_{\perp} \approx 3.8$ ,  $g_{\parallel} \approx 2$ . 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  $[\text{Fe}(\text{py})_2(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ . The Mossbauer data<sup>220</sup> for  $[\text{Fe}(\text{py})(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  ( $S = 3/2$ ,  $\delta = 0.59 \text{ mm} \cdot \text{sec}^{-1}$ ,  $\Delta = 2.41 \text{ mm} \cdot \text{sec}^{-1}$  at 77°K) and  $[\text{Fe}(\text{phen})(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  ( $S = 1/2$ ,  $\delta = 0.57 \text{ mm} \cdot \text{sec}^{-1}$ ,  $\Delta = 1.80 \text{ mm} \cdot \text{sec}^{-1}$  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,  $[\text{S}_2\text{C}(\text{CN})_2]^{2-}$ , are high-spin ( $S = 5/2$ )<sup>227,228</sup> with reported moments of 5.89 – 5.95 B.M. At X-band, the EPR spectrum of  $(\text{Pr}^n_4\text{N})_3 [\text{Fe}(\text{S}_2\text{C}(\text{CN})_2)_3]$  has  $g_{\perp} \approx 6$  and  $g_{\parallel} \approx 2$ , implying a nearly octahedral coordination of sulphurs about the ferric ion<sup>199</sup>. 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

#### (c) Dithiophosphates

The four complexes  $\text{Fe}(\text{S}_2\text{PR}_2)_3$  ( $\text{R} = \text{Et}, \text{EtO}, \text{Ph}, \text{PhO}$ ) were first prepared by Malatesta and Pizzotti<sup>229</sup> who found that they were high-spin with  $\mu_{\text{eff}} \approx 5.9 \text{ B.M.}$ , they are rather hygroscopic black solids. Jorgensen<sup>230</sup> re-examined  $\text{Fe}(\text{S}_2\text{P}(\text{OEt})_2)_3$  and found that crystals of the iron(III) complex doped into the indium(III) analogue are quite stable. More recently, the temperature dependence of  $\mu_{\text{eff}}$  has been examined<sup>15</sup> for a number of complexes  $\text{Fe}(\text{S}_2\text{OR}_2)_3$  ( $\text{R} = \text{MeO}, \text{EtO}, \text{Pr}^n\text{O}, \text{and Pr}^i\text{O}$ ), over the range 96–300°K,  $\mu_{\text{eff}}$  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.  $\text{Fe}(2\text{-thiopyridine } N\text{-oxide})_3$  has been shown by magnetic measurements<sup>231</sup> and EPR<sup>199</sup> to be high-spin. The related monothio- $\beta$ -diketonates  $\text{Fe}(\text{R}_1\text{-CS-CH-CO-R}_2)_3$  ( $\text{R} = \text{e.g. Ph, OEt, CF}_3$ ) were prepared by Ho and Livingstone<sup>232,233</sup> 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  $\mu_{\text{eff}}$  was field-independent, excluding ferromagnetic species, and that the analogous  $\text{Fe}^{\text{II}}$  complexes were not obtainable. Room temperature  $\mu_{\text{eff}}$  values were 2.3 – 5.8 B.M. for their choice of  $\text{R}_1, \text{R}_2$ , for  $\text{R}_1 = p\text{-tolyl}$ ,  $\text{R}_2 = \text{CF}_3$ ,  $\mu_{\text{eff}}$  varied from 2.11 B.M. at 83°K to 5.06 B.M. at 378°K.

Fitzsimmons and co-workers<sup>234</sup> studied the Mossbauer spectra and magnetic moments of the four complexes where  $\text{R}_1$  or  $\text{R}_2 = \text{Ph}$  or  $\text{Me}$ . They found similar magnetic behaviour to that found previously<sup>232,233</sup> 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  $\delta \sim 0.75 \pm 0.15 \text{ mm} \cdot \text{sec}^{-1}$ ,  $\Delta E \approx 0$ , whilst the low-spin species have  $\delta \sim 0.65 \pm 0.05 \text{ mm} \cdot \text{sec}^{-1}$ , and  $\Delta E$  values up to  $1.9 \text{ mm} \cdot \text{sec}^{-1}$ . The individual spin-isomers were also observed in the EPR spectra of the complexes<sup>199</sup>, 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  $g_{\text{eff}} \approx 4.3$  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  $^{57}\text{Fe}$  excited state.

#### (g) Other complexes

Berzelius<sup>235</sup> reported the dark brown  $\text{Fe}_2(\text{CS}_3)_3$  as the product of reaction between  $\text{FeCl}_3$  and  $\text{Na}_2\text{CS}_3$ , but more recent work would be welcomed on this and  $\text{Fe}(\text{SEt})_3$ , the amorphous red product of the analogous reaction with  $\text{NaSEt}$ <sup>236</sup>. 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  $2\text{FeCl}_3 \cdot \text{MeSe}(\text{CH}_2)_3 \cdot \text{SeMe}$  whose reported<sup>237</sup> magnetic moment is 5.34 B.M. Two possible structures are (i) a polymer with antiferromagnetic interaction, or (ii) a species of the type  $[\text{FeCl}_2(\text{MeSe}(\text{CH}_2)_3\text{SeMe})_2]^+ (\text{FeCl}_4)^-$  which would require  $\mu_{\text{eff}}$  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

#### (1) Monodentate

$\text{FeCl}_3 \cdot \text{PPh}_3$  and  $\text{FeCl}_3 \cdot \text{AsPh}_3$  were prepared<sup>238</sup> by refluxing  $\text{Fe}_3(\text{CO})_{12}$  in  $\text{CHCl}_3$  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  $\nu(\text{Fe}-\text{P})$  at  $525 \text{ cm}^{-1}$  and  $\nu(\text{Fe}-\text{Cl})$  at  $370$  and  $320 \text{ cm}^{-1}$ . A number of amine complexes of reportedly similar stoichiometry were shown to be iron(II) complexes by Birchall<sup>239</sup>, who found the Mossbauer spectra of the phosphine and arsine complexes quite consistent with a pseudo-tetrahedral structure. For  $\text{FeCl}_3 \cdot \text{PPh}_3$  at  $77^\circ\text{K}$ ,  $\delta = 0.54 \text{ mm} \cdot \text{sec}^{-1}$  and  $\Delta E = 0.21 \text{ mm} \cdot \text{sec}^{-1}$ , whilst  $\text{FeCl}_3 \cdot \text{AsPh}_3$  gave  $\delta = 0.57 \text{ mm} \cdot \text{sec}^{-1}$ ,  $\Delta E = 0.23 \text{ mm} \cdot \text{sec}^{-1}$ .

On the other hand, Naldini<sup>240</sup> examined the reactions of triphenylphosphine and triphenylarsine with a number of ferric salts. Etheral solutions of  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{As}$  reacted with anhydrous  $\text{FeCl}_3$  to give very dark red crystals of  $\text{Fe}(\text{Ph}_3\text{R})_2\text{Cl}_3$  ( $\text{R} = \text{P}, \text{As}$ ), which gave non-conducting MeCN solutions. A similar reaction occurred with  $\text{Fe}(\text{NCS})_3$  to give the red  $\text{Fe}(\text{Ph}_3\text{P})_2(\text{NCS})_3$ , ethanolic ferric nitrate on treatment with the ligands in ether gave the yellow  $\text{Fe}(\text{Ph}_3\text{R})_2(\text{NO}_3)_3$ . These were non-electrolytes in nitrobenzene. All of

these complexes were high-spin, with  $\mu_{\text{eff}}$  values of 5.75 – 6.14 B.M. at room temperature Nyholm<sup>241</sup> reported complexes of various tertiary arsines of two types,  $\text{FeCl}_3(\text{R}'\text{R}_2''\text{As})_2$  and  $(\text{FeCl}_3)_2(\text{R}'\text{R}_2''\text{As})_3$ . When  $\text{R}' = \text{Me}$ ,  $\text{R}'' = \text{Ph}$ , both types of complex were isolated, when  $\text{R}' = o\text{-tolyl}$ ,  $\text{R}'' = \text{Me}$ , only the former were obtained, and when  $\text{R}'$  and  $\text{R}'' = p\text{-tolyl}$  or  $\text{Me}$ , only the latter were isolated. The colour of the complexes varied from yellow to brown. Isslieb and Brack<sup>242</sup> isolated the yellow  $\text{FeCl}_3 \cdot \text{P}(\text{C}_6\text{H}_{11})_3$  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  $\text{FeCl}_3$  in ethanol or benzene with diars affords the crimson  $\text{FeCl}_3 \cdot \text{diars}$  which is in fact<sup>243</sup>

$[\text{FeCl}_2(\text{diars})_2]^- (\text{FeCl}_4)^+$ , having  $\mu_{\text{eff}} = 4.55$  B.M. per Fe atom. Treatment of an acetone solution of the complex with  $\text{HClO}_4$  affords the red  $[\text{Fe}(\text{diars})_2\text{Cl}_2]^+ \text{ClO}_4^-$ , with  $\mu_{\text{eff}} = 2.34$  B.M.<sup>243, 244</sup> the  $\text{FeCl}_4^-$  ion is of course high-spin.

Addition of diars to excess anhydrous  $\text{FeBr}_3$  in benzene affords the chocolate-brown  $\text{FeBr}_3 \cdot \text{diars}$  ( $\mu_{\text{eff}} = 4.57$  B.M. per Fe), being  $[\text{Fe}(\text{diars})_2\text{Br}_2]^+ (\text{FeBr}_4)^-$ . On careful hydrolysis, the green  $[\text{Fe}(\text{diars})_2\text{Br}_2]^+ \text{Br}^-$  is formed (this can also be prepared from a 1:1 ratio of reactants in ethanol). Far-IR assignments are  $\nu(\text{Fe}-\text{Cl})$  at  $376 \text{ cm}^{-1}$  in  $[\text{Fe}(\text{diars})_2\text{Cl}_2]^+ \text{BF}_4^-$ ,  $\nu(\text{Fe}-\text{Br})$  at  $292 \text{ cm}^{-1}$  in  $[\text{Fe}(\text{diars})_2\text{Br}_2]^+ \text{BF}_4^-$ , and 273 and  $306 \text{ cm}^{-1}$  in  $[\text{Fe}(\text{diars})_2\text{Br}_2]^+ \text{Br}^-$  (refs. 245, 246).

The 1,2-bis(dimethylarsino)ethylene (edas) complexes  $\text{Fe}(\text{edas})_3(\text{ClO}_4)_3$  and  $[\text{Fe}(\text{edas})_2\text{Cl}_2]^+ (\text{FeCl}_4)^-$  have been prepared, the former by  $\text{HNO}_3$  oxidation of the  $\text{Fe}^{\text{II}}$  analogue, and the latter by direct reaction of the ligand with anhydrous  $\text{FeCl}_3$  in ethanol.<sup>247</sup>

Methyl-bis(3-propane-dimethylarsine)arsine (TAS,  $\text{MeAs}[(\text{CH}_2)_3\text{AsMe}_2]_2$ ) is a terdentate ligand and the deep green complex  $\text{Fe}(\text{NCS})_3 \cdot \text{TAS}$ , a non-electrolyte having  $\mu_{\text{eff}} = 2.22$  B.M., has been isolated.<sup>248</sup> Reportedly, other ferric halides form analogous complexes. Further investigation is merited here.

The analogous tetradentate ligand TTA ( $= \text{As}[(\text{CH}_2)_3\text{AsMe}_2]_3$ ) reacts with anhydrous  $\text{FeCl}_3$  in ethanol to form  $[\text{Fe}(\text{TTA})\text{Cl}_2]^+ (\text{FeCl}_4)^-$   $\mu_{\text{eff}}$  per Fe = 4.45 B.M., so that  $\mu_{\text{eff}}$  for  $[\text{Fe}(\text{TTA})\text{Cl}_2]^+$  is ca. 2.2 B.M. The chlorines are thought<sup>249</sup> 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

$\text{K}_3\text{Fe}(\text{CN})_6$  is well known, as are pentacyano species of the type  $[\text{Fe}(\text{CN})_5\text{X}]^{2-}$ , where  $\text{X} = \text{F}, \text{H}_2\text{O}, \text{NO}_2$ ; these are all  $S = 1/2$  systems.

The blue solids formed from reaction of  $\text{Fe}^{\text{III}}$  with  $\text{Fe}(\text{CN})_6^{4-}$  or  $\text{Fe}^{\text{II}}$  with  $\text{Fe}(\text{CN})_6^{3-}$  are also familiar, and appear to be based upon a cubic array of iron atoms with  $\text{CN}^-$  ions

along cube edges between them<sup>250</sup> Mössbauer spectra show that these complexes contain discrete ferrous and ferric ions, measurements on  $\text{Fe}(\text{CN})_6^{3-}$  have been made by a number of workers<sup>158, 251</sup>. Magnetic measurements over a temperature range<sup>146</sup> on  $\text{K}_3\text{Fe}(\text{CN})_6$  have been interpreted in terms of an orbital reduction factor  $k \approx 0.8$  and an axial field  $\Delta = 400 \text{ cm}^{-1}$  EPR results<sup>21</sup> give  $k = 0.87$ ,  $\Delta = 220 \text{ cm}^{-1}$ , the  $g$  values being  $g_x = 2.35$ ,  $g_y = 2.10$ ,  $g_z = 0.915$ .

For  $\text{K}_3\text{Fe}(\text{CN})_6$ , reportedly having a monoclinic unit cell ( $C_{2h}^5 - P2_1/c$ ),  $\nu_{\text{as}}(\text{Fe}-\text{CN})$  has been assigned<sup>252</sup> to an IR band near  $520 \text{ cm}^{-1}$ , and  $\delta(\text{Fe}-\text{CN})$  near  $400 \text{ cm}^{-1}$  Raman studies in solution<sup>253</sup> give results rather similar, although  $\nu(\text{Fe}-\text{CN})$  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  $\pi$ -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,  $[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2]^+$ , which contains one unpaired electron and may be formally regarded as a ferric complex. It seems that  $[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2] \text{I}_3$  contains a planar ferricinium ion<sup>254</sup>, although the X-ray study was complicated by disorder.

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

Some carborane systems have been synthesised<sup>256, 256</sup> such as  $[\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$  and  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})]$ . Crystallographic study<sup>257</sup> of the latter complex showed that both the 'carbollide' and cyclopentadienyl ligands were  $\pi$ -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<sup>258</sup> examined the EPR of a number of iron(III)-carborane systems at  $85^\circ\text{K}$ , 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  $(a_{1g}^1)^2(e_{2g}^+)^3$ .

Recent EPR studies on highly purified samples of  $[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2]^+$  salts gave similar spectra at  $77^\circ\text{K}$ , implying a similar ground-state configuration. These workers ascribe the previous non-observation of spectra at  $77^\circ\text{K}$  to the extensive line-broadening effect of small quantities of impurity<sup>259</sup>. Prins<sup>260</sup> has also investigated the EPR spectra of some ferricinium systems. His spectrum from  $[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2]^+ \text{I}_3^-$  is not as well resolved as those of Horsfield and Wasserman<sup>259</sup>, 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  $a_{1g}^2 \leq e_{2g}^3 < *e_{1g}$ . The calculated separation between the  $|M_J| = 5/2$  and  $|M_J| = 3/2$  levels is  $800 \text{ cm}^{-1}$  in the ferricinium ion, this small splitting is undoubtedly responsible for the short relaxation times above  $77^\circ\text{K}$ .

TABLE 6

Values of  $g$  for ferricinium-type systems

| Compound  | $g_{\perp}$ | $g_{\parallel}$ | Medium                                   |
|---|-------------|-----------------|--|
| $\{\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2\}^-$  | 3.94        | 1.532           | Glass (1:1 DMF-CHCl <sub>3</sub> )       |
| $\{\text{Fe}(\text{B}_9\text{H}_9\text{C}_2\text{Me}_2)_2\}^-$                                      | 2.79        | 1.711           | Glass (1:1 DMF-CHCl <sub>3</sub> )       |
| $\{(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})\}$                        | 3.58        | 1.778           | Glass (1:1 DMF-CHCl <sub>3</sub> )       |
| $\{\text{Fe}(\text{B}_9\text{H}_9\text{C}_2\text{HPh})_2\}^-$                                       | 3.57        | 1.799           | Glass (1:1 DMF-CHCl <sub>3</sub> )       |
| $\{\text{Fe}(\text{B}_9\text{H}_9\text{C}_2\text{HPh})_2\}^-$                                       | 3.70        | 1.725           | Powder                                   |
| $\{\text{Fe}(\pi\text{-C}_5\text{H}_5)_2\}^+$   | 3.28        | 1.87            | Single crystal                           |
| (trichloroacetate) <sup>-</sup>   | 3.26        | 1.86            | Powder                                   |
|   | 3.35        | 1.85            | Glass (CH <sub>2</sub> Cl <sub>2</sub> ) |
| $\{\text{Fe}(\pi\text{-C}_5\text{H}_5)_2\}^+(\text{picrate})^-$                                     | 3.15        | 1.82            | Powder                                   |
| $\{\text{Fe}(\pi\text{-C}_5\text{H}_5)_2\}^+\text{Cl}^-$  | 3.20        | 1.90            | Glass (H <sub>2</sub> O)                 |
| $\text{Fe}(\pi\text{-C}_5\text{H}_5)_2\text{I}_3^-$   | 4.35        | 1.26            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\cdot\text{CH}_3)^+$                   | 4.17        | 1.47            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\cdot\text{C}_6\text{H}_5)^+$          | 3.98        | 1.58            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_4\cdot\text{CH}_3)_2^+$   | 3.83        | 1.67            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_4\cdot\text{C}_6\text{H}_9)_2^+$                                  | 3.88        | 1.68            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\cdot\text{C}_6\text{H}_5\text{CO})^+$ | 3.69        | 1.73            | Glass (DMF)                              |
| $\text{Fe}(\pi\text{-C}_5\text{H}_4\cdot\text{C}_6\text{H}_5)_2^+$                                  | 3.63        | 1.74            | Glass (H <sub>2</sub> SO <sub>4</sub> )  |
| $\text{Fe}(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\cdot\text{CH}_3\text{CO})^+$          | 3.62        | 1.76            | Glass (DMF)                              |

There is obviously much scope here for work on complexes containing  $\sigma$ -bonded carbon. An obvious reaction which could be tried is that of a benzyl Grignard with ferric chloride, in the hope of obtaining  $\text{Fe}(\text{CH}_2\text{Ph})_3$  or a related compound.

## 1. CONCLUSION

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

Ferric iron readily complexes with oxygen donor ligands and with halides (except  $\text{I}^-$ , because of the redox reaction  $\text{Fe}^{3+} + \text{I}^- \rightarrow \text{Fe}^{2+} + \frac{1}{2} \text{I}_2$ ). 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<sup>19</sup> 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  $\zeta$  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

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## APPENDIX

## Crystallographic data for iron(III) complexes

|   | $d(\text{Fe-X})$<br>(Å)                                   | Space group        | $1/\langle$ | Chromophore                              | Ref     |
|---|---|--------------------|-------------|--|---------|
| $\beta\text{-FeF}_3 \cdot 3\text{H}_2\text{O}$  | 1.94(O), 1.94(I)  | $P4/n$             | 2           | $1_4\text{O}_2$                          | 38      |
| $[\text{Fe}(\text{OH})_2\text{Cl}_2] \cdot \text{Cl}^- \cdot 2\text{H}_2\text{O}$     | 2.07(O), 2.30(Cl)   | $C2/m$             | 2           | $\text{O}_4\text{Cl}_2$                  | 25      |
| $[\text{Fe}(\text{OH})_2\text{Cl}_2] \cdot \text{SbCl}_6^- \cdot 4\text{H}_2\text{O}$ | 2.08(O), 2.36(Cl)   | $P4/mmm$           | 2           | $\text{O}_4\text{Cl}_2$                  | 34      |
| $(\text{NH}_4)_2 [\text{FeCl}_5(\text{OH}_2)]$  | 2.08(O), 2.35-2.41(Cl)                                    | $Pmma$             | 4           | $\text{OCl}_5$                           | 35      |
| $[\text{Fe}(\text{Me}_2\text{SO})_4\text{Cl}_2] \cdot \text{FeCl}_4^-$                | 2.07(O), 2.37(Cl)<br>2.162(I), 2.164(I)                   | $I4_1/a$           | 4           | $\text{O}_4\text{Cl}_2$<br>$\text{Cl}_4$ | 50, 162 |
| $(\text{Ph}_4\text{As})^+ \text{FeCl}_4^-$  | 2.19(Cl)  | $I\bar{4}$         | 2           | $\text{Cl}_4$                            | 161     |
| $\text{Na}^+ \text{FeCl}_4^-$   | 2.180-2.218(Cl)   | $P2_12_12_1$       | 4           | $\text{Cl}_4$                            | 163     |
| $[\text{FeCl}_4] \cdot \text{FeCl}_4$   | 2.182-2.187(Cl)   | $Pbcm$ or $Pbc2_1$ | 4           | $\text{Cl}_4$                            | 164     |
| $[\text{Fe}(\text{acac})_3]$  | 1.986-2.004(O)  | $Pbcn$             | 8           | $\text{O}_6$                             | 81      |
| $[\text{Fe}(\text{acac})_2\text{Cl}]$   | 1.95(O), 2.213(Cl)  | $P2_1/n$           | 4           | $\text{O}_4\text{Cl}$                    | 88      |
| $\text{K}_3[\text{Fe}(\text{oxalate})_3] \cdot 3\text{H}_2\text{O}$                   | 2.01-2.06(O)  | $P2_1/c$           | 4           | $\text{O}_6$                             | 113     |
| $[\text{Fe}(\text{tropolonate})_3]$   | 2.008(O)  | $R\bar{3}c$        | 6           | $\text{O}_6$                             | 82      |
| $[\text{Fe}(\text{DTA})\text{OH}_2]$  | 1.93-2.03(O), 2.07(OH <sub>2</sub> )<br>2.19-2.25(N)      | $P2_1/c$           | 4           | $\text{N}_2\text{O}_4$                   | 120     |
| $\text{Rb}[\text{Fe}(\text{LDTA})\text{OH}_2] \cdot \text{H}_2\text{O}$               | 1.974-2.085(O), 2.106(OH <sub>2</sub> )<br>2.312-2.322(N) | $P2/a$             | 4           | $\text{N}_2\text{O}_5$                   | 119     |
| $\text{La}[\text{Fe}(\text{LDTA})\text{OH}_2] \cdot \text{H}_2\text{O}$               | 1.938-2.128(O), 2.107(OH <sub>2</sub> )<br>2.304-2.346(N) | $Pbcn$             | 8           | $\text{N}_2\text{O}_5$                   | 119     |
| $\text{Ca}[\text{Fe}(\text{DCTA})\text{OH}_2] \cdot 8\text{H}_2\text{O}$              | 2.017-2.092(O), 2.09(OH <sub>2</sub> )<br>2.29(N)         | $C2/c$             | 4           | $\text{N}_2\text{O}_5$                   | 125     |
| $[\text{Fe}(\text{salen})\text{Cl}] \cdot (\text{CH}_3\text{NO}_2)_x^a$               | 1.879-1.885(O), 2.238(Cl)<br>2.064-2.099(N)               | $Pm2_1/a$          | 2           | $\text{O}_2\text{N}_2\text{Cl}$          | 100     |
| $[\text{Fe}(\text{NSiMe}_3)_2]_3\text{I}$   | 1.918(N)  | $P3/c$             | 2           | $\text{N}_3$                             | 142     |



|   |  |   |                          |          |
|---|--|---|--------------------------|----------|
| $[\text{Fe}(\text{B})(\text{NCS})_2]^+(\text{ClO}_4)^-$ <sup>b</sup>                              | 2.23 ± 0.05(N, macro)                        | 4 | $\text{N}_7$             | 159      |
| $\text{Fe}(\text{S}_2\text{CNBu}^n)_2$  | 2.01 ± 0.02(NCS)                             |   |                          |          |
| $\text{FeCl}(\text{S}_2\text{CNEt}_2)_2$  | 2.413–2.426(S)                               | 4 | $\text{S}_6$             | 193      |
| $\text{Fe}(\text{S}_2\text{COEt})_3$  | 2.32(S), 2.27(Cl)                            | 4 | $\text{S}_4\text{Cl}$    | 201      |
| $\text{Fe}(\text{MeCSCHSMO})_3$   | 2.308–2.326(S)                               | 6 | $\text{S}_6$             | 208      |
| $[\text{Fe}(\text{S}_2\text{CSEtO})_2(\text{SEtO})_2]$  | 2.220–2.264(S)                               | 4 | $\text{S}_6$             | 213      |
|   | 2.34(terminal S)                             | 4 | $\text{S}_6^c$           | 206, 207 |
|   | 2.22 (bridging SEt)                          |   |                          |          |
|   | 2.28 (bridging $\text{S}_2\text{CSEtO}$ )    |   |                          |          |
| $[\text{Fe}(\text{S}_2\text{C-p-tol})_2(\text{S}_2\text{C-p-tol})]$                               | 2.19–2.35(S)                                 | 4 | $\text{S}_6$             | 210      |
| $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\pi\text{-B}_9\text{C}_2\text{H}_{11})$                      | 2.07(C, $\text{C}_5\text{H}_5$ )             | 4 | $\text{C}_7\text{B}_3^d$ | 257      |
|   | 2.04(C, $\text{C}_2\text{B}_9\text{H}_{11})$ |   |                          |          |
|   | 2.09(B)                                      |   |                          |          |
| $(\text{Ph}_4\text{As})_2[\text{Fe}(\text{N}_3)_5]$   | 1.963–2.041                                  | 4 | $\text{N}_5$             | 261      |
| $\text{K}_2\text{NaFe}_6$   | 1.910  | 4 | $\text{I}_6$             | 262      |
| $(\text{Bu}^n)_4\text{N}[\text{Fe}(\text{Ph}_3\text{PO})[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2]$ | 2.199–2.239(S)                               | 4 | $\text{S}_4\text{O}$     | 263      |
|   | 1.957(O)                                     |   |                          |          |

<sup>a</sup>  $0 < \lambda < 1$ <sup>b</sup> B = pentadentate macrocycle (see text)<sup>c</sup> Dimer<sup>d</sup> 'Sandwich' compound, coordinated to one  $\text{C}_5$  ring and one  $\text{C}_2\text{B}_3$  'ring'

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