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1. IRON

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CONTENTS

INTRODUCTION

This review follows broadly the same format as that covering 1979 which was published in Vol. 35 of this journal. The literature coverage continues from where that for 1979 ceased. Thus work cited in Chemical Abstracts Vol. 91 (Nos. 21-26), Vol. 92 and Vol. 93 (Nos. 1-18) is reviewed. However, papers published in J. Am. Chem. Soc., Inorg. Chem., J. Chem. Soc., Dalton Trans., J. Chem. Soc., Chem. Commun., and J. Organomet. Chem., have been covered up to the end of 1980.

The division of the review reflects current interest in iron chemistry. Thus there remains a considerable interest in carbonyl and related low valent complexes and the interest in the biological rôle of iron continues to grow. The number

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of publications concerning classical coordination and inorganic chemistry of iron appears to be decreasing although, amongst those published, there remains some interesting new findings. Of particular interest are a small number of very detailed studies of spin equilibria in iron complexes, and these are gathered together in Section 1.8.

1.1 CARBONYL, THIOCARBONYL, ISONITRILE AND RELATED COMPLEXES

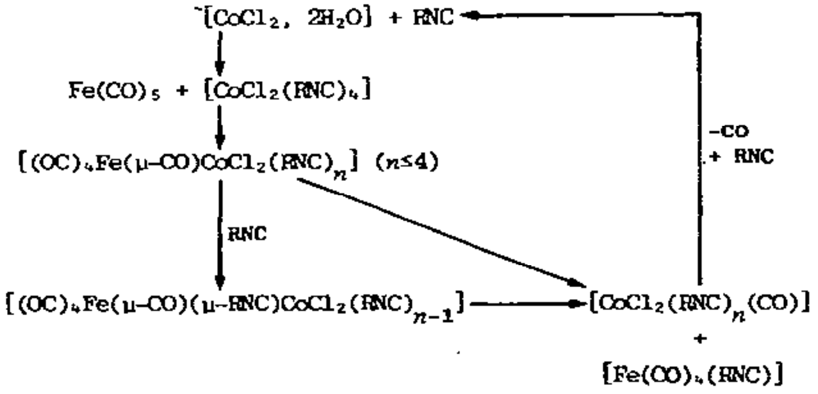
Undoubtedly the most novel publications in this area are those concerning the isonitrile analogues of pentacarbonyliron(0), $[Fe(CNR)_5]$. Stone and coworkers have presented full details of such complexes, prepared by reduction of $FeBr_2$ in the presence of excess RNC (R = CMe_3, $CHMe_2$, Et or $2,6\text{-}Me_2C_6H_3$). A structural study has shown the geometry of $[Fe(CNCMe_3)_5]$ to deviate from an idealised trigonal bipyramid, and that the equatorial ligands are non-linear ($C\hat{N}C = 135^\circ$). Reaction with PPh_3 yields $[Fe(CNR)_4(PPh_3)]$, and isonitrile metathesis has also been effected (equation 1). $[Fe(CNCMe_3)_5]$ can also be

$$[Fe(CNEt)_5] + 2RNC \longrightarrow [Fe(CNEt)_3(CNR)_2] + 2EtNC \qquad (1)$$

$$(R = 2,6\text{-}Me_2C_6H_3)$$

protonated by $H[BF_4]$ or the metal hydrides $[MnH(CO)_5]$ and $[OsH_2(CO)_4]$ [1].

Reaction of $[Fe(CO)_5]$ with xylylisonitrile (XyNC) in the presence of catalytic amounts of transition metal salts yields $[Fe(CO)_4(CNXy)]$ in greater than 90% yield at 45 °C whereas, in the absence of such catalysts, the yield is less than 5%. In benzene under reflux, $[Fe(CO)_3(CNXy)_2]$, $[Fe(CO)_2(CNXy)_3]$, $[Fe(CO)(CNXy)_4]$ and $[Fe(CNXy)_5]$ are obtained. The mechanistic sequence shown in Scheme I is advanced for the reaction catalysed by $CoCl_2.2H_2O$ [2].



SCHEME I: The proposed mechanism for the formation of $[Fe(CO)_4(RNC)]$.

The first stable thiocarbonyl derivation of $[\mathrm{Fe(CO)_5}]$ has been prepared by treating $[\mathrm{Fe(CO)_2\{P(OPh)_3\}_2(CS_2)}]$ with $\mathrm{PBu_3}$. In $\mathrm{CHCl_3}$ or $\mathrm{C_6H_6}$, replacement of coordinated phosphite by the phosphine occurs, but in $\mathrm{CCl_4}$, the phosphine does play some rôle in desulphurisation giving low yields of $[\mathrm{Fe(CO)_2\{P(OPh)_3\}_2(CS)}]$. This complex adopts the expected trigonal-bipyramidal structure with phosphite ligands in the axial sites [3].

$[\mathrm{FeBr(CO)_2(cp)}]$ also reacts with a wide range of isonitriles to form $[\mathrm{FeBr(CNR)_2(cp)}]$ and, in the presence of excess isonitrile, $[\mathrm{Fe(CNR)_3(cp)}]$. When $[\mathrm{Fe(CO)_2(thf)(cp)}]^+$ is employed, $[\mathrm{Fe(CO)}_{3-n}\mathrm{(CNR)}_n\mathrm{(cp)}]^+$ (n = 1 or 2) are formed. $[\mathrm{FeBr(CNR)_2(cp)}]$ undergoes a one electron oxidation reaction, the product isolated being $[\mathrm{Fe(CNR)_3(cp)}]^+$, although as many as six intermediates could be seen by NMR spectroscopy, among which may be $[\mathrm{Fe(CNR)_2(Me_2CO)(cp)}]^+$ and $[\mathrm{(cp)(RNC)_2Fe(\mu\text{-}Br)Fe(CNR)_2(cp)}]^+$. In ethanenitrile, $[\mathrm{Fe(CNR)_2(MeCN)(cp)}]^+$ is formed [4]. Photolysis of $[\mathrm{Fe(CO)(CNMe)_2(cp)}]^+$ in the presence of an excess of the ligands L leads to $[\mathrm{Fe(CNMe)_2L(cp)}]^+$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{SbPh_3}$, py, MeCN or $\mathrm{C_2H_4}$). Similar reactions of $[\mathrm{Fe(CO)_2(NCMe)(cp)}]^+$ led to sequential displacement of both CO ligands in all cases except ethene. There was no evidence for replacement of the isonitrile ligand, and no evidence for thermally induced substitution in either cation. In the absence of light the sequence shown in equation 2 is observed (L = MeCN or py) [5].

$$[\mathrm{Fe(CNMe)L_2(cp)}]^+ \longrightarrow [\mathrm{Fe(CNMe)_2L(cp)}]^+ \longrightarrow [\mathrm{Fe(CNMe)_3(cp)}]^+ \qquad (2)$$

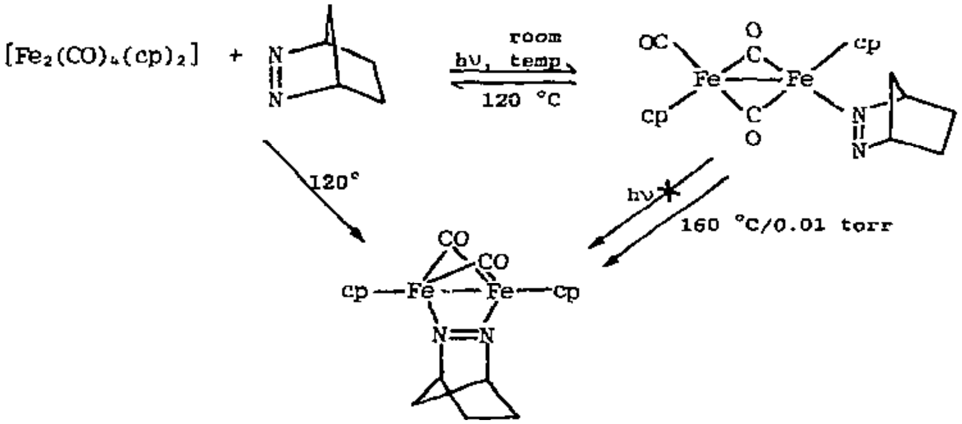
An X-ray crystallographic study of $[\mathrm{Fe_2(CO)_4(\eta^5\text{-}C_5Me_5)_2}]$ has confirmed the expected similarity to the cp analogue {r(Fe–Fe) = 256.0 pm}, the main difference being that, unlike the cp compound, there are no significant variations in the C–C bond lengths of the $\mathrm{C_5Me_5}$ rings. This may have a bearing on the different catalytic properties exhibited by the two complexes [6]. The structure of $[\mathrm{(cp)(OC)Fe(\mu\text{-}CO)(\mu\text{-}CS)Fe(CO)(cp)}]$ has also been reported. The bridging thiocarbonyl group has an elongated C–S bond of 160 pm. The Fe–Fe distance of 250.5 pm is to be compared with 253.1 and 248.2 pm for the $(\mu\text{-CO})_2$ and $(\mu\text{-CS})_2$ analogues respectively. The cp ligands are mutually *cis* [7]. A UVPES study of the electronic structure of $[\mathrm{Fe_2(CO)_4(cp)_2}]$, supported by *ab initio* MO calculations, has been published [8].

$[\mathrm{Fe_2(CO)_3(CNR)(cp)_2}]$ (R = Me, Et, $\mathrm{CHMe_2}$, $\mathrm{CMe_3}$ or Ph) have been shown to exist as isomeric mixtures in solution containing both terminal and bridging RNC forms and to be fluxional. The bridge-terminal exchange process follows the Adams-Cotton mechanism involving synchronous opening and closing of bridges. Protonation and alkylation of the complexes lead to $[\mathrm{Fe_2(CO)_3(CNRR')(cp)_2}]^+$ (R' = H, Me or $\mathrm{CHMe_2}$) [9].

Evidence has been presented for two different primary photoproducts from the photolysis of $[Fe_2(CO)_4(cp)_2]$. These arise by CO loss to give $[Fe_2(CO)_3(cp)_2]$ (quantum yield ~0.05) and by dimer homolysis to yield $[Fe(CO)_2(cp)]$ (quantum yield ~0.23). Both intermediates react with CCl_4 to give $[FeCl(CO)_2(cp)]$ and the former reacts with PPh_3 *via* a second intermediate to form $[Fe_2(CO)_3(PPh_3)(cp)_2]$. The second intermediate is thought to be an isomeric form of the phosphine-containing product which is believed to contain a $(\mu_2\text{-}CO)_2$ unit but no Fe–Fe bond [10].

$[Fe_2(CO)_4(cp)_2]$ also reacts with SbF_3 to yield either $[\{Fe(CO)_2(cp)\}_3SbF]^+$ or $[\{Fe(CO)_2(cp)\}_3SbOSb\{Fe(CO)_2(cp)\}_3]^{2+}$, which were isolated as $[SbF_4]^-$, $[Sb_2F_7]^-$ or $[Sb_5F_{17}]^-$ salts. The latter cation reacts with iodine to form $[\{Fe(CO)_2(cp)\}_3SbI][I_3]$, whereas with AsF_3 $[\{Fe(CO)_2(cp)\}_2AsF_2][AsF_6]$ is formed, which on treatment with water and alcohols gives the cations $[\{Fe(CO)_2(cp)\}_2As(OH)_2]^+$, $[\{Fe(CO)_2(cp)\}_2As(OMe)_2]^+$ and $[\{Fe(CO)_2(cp)\}_2AsF(OEt)]^+$. $[Fe_2(CO)_4(cp)_2]$ also reacts with R_2AsX to give $[\{Fe(CO)_2(cp)\}_2AsR_2]^+$, and with $RAsX_2$ to give $[\{Fe(CO)_2(cp)\}_2As(R)X]^+$ [11].

The cations $[Fe(CO)_2L(cp)]^+$ (L = aldehyde, ketone, ester or amide) have been prepared by the reaction of $[Fe_2(CO)_4(cp)_2]$ or $[FeBr(CO)_2(cp)]$ with $Ag[PF_6]$ in the presence of L, or by ligand exchange with $[Fe(CO)_2(cp)(\text{isobutylene})]^+$. In all cases coordination to the metal is by σ donation from the ketonic carbonyl, rather than by π coordination of this group [12]. With 2,3-diazanorbornene, $[Fe_2(CO)_4(cp)_2]$ undergoes the reactions shown in Scheme II [13].



SCHEME II: Reaction of $[Fe_2(CO)_4(cp)_2]$ with 2,3-diazanorbornene.

Interest in the generation of metal carbonyl radical cations and anions continues to grow. A CV study of $[Fe(CO)_3L_2]$ (L = PPh_3, $AsPh_3$, $PMePh_2$, $P(NMe_2)_3$, or $P(OPh)_3$; L_2 = $Ph_2P(CH_2)_nPPh_2$ (*n* = 1 or 2)) shows the complexes to undergo one-electron oxidation. The radical cations may also be generated chemically by use of either Ag^+ or $[(Br\text{-}4\text{-}C_6H_4)_3N]^+$, and react with halogens, X_2, to give

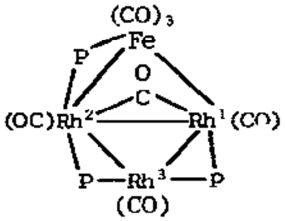
$[FeX(CO)_3L_2]^+$, whereas with halide ions, X^-, $[Fe(CO)_3L_2]$ and $[FeX_2(CO)_{4-n}L_n]$ are formed. The radical cation, $[Fe(CO)_3(PPh_3)_2]^{+\cdot}$ also undergoes some novel radical-radical reactions and redox reactions with paramagnetic and diamagnetic ligands. With NO, there is quantitative formation of $[Fe(CO)_2(NO)(PPh_3)_2]^+$, whereas with NO_2 *mer,trans*-$[Fe(NO_2)(CO)_3(PPh_3)_2]^+$ is produced. On heating the latter, CO_2 is evolved and the nitrosyl cation formed. Reaction with $Me_2NC(S)SSC(S)NMe_2$ (a source of $Me_2NCS_2\cdot$ radicals) gives $[Fe(CO)_2(PPh_3)_2(S_2CNMe_2)]^+$, whereas with $[Me_2NCS_2]^-$, a mixture of this cation and $[Fe(CO)_3(PPh_3)_2]$ is obtained [14].

Polarographic reduction of $[Fe(CO)_{3-n}L_n(cp)]^+$ (L = PPh_3, n = 1 or 2; L = MeNC, n = 1, 2 or 3) shows increasingly anodic one-electron reduction waves as CO is successively replaced by L: this effect is greater for MeNC than PPh_3. The 19-electron reduced species lose a molecule of the ligand L, dimerise or decompose [15]. An EPR study has been made of $[Fe_3(CO)_{12-n}L_n]$ (L = CO, $P(OR)_3$, or PR_3), $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ which have been reduced either chemically or electrochemically, or photolysed; the corresponding radical anions were characterised at low temperatures. However, iron-containing radical anions readily undergo what are believed to be disproportionation reactions to yield iron(II), iron(-I) and iron(-II) species *via* the dianions $[Fe_3(CO)_{12-n}L_n]^{2-}$. Solutions of $[Fe_2(CO)_9]$ in thf, on reduction, give the same EPR spectrum as that from $[Fe_3(CO)_{12}]$, and this arises from $[Fe_3(CO)_{12}]^{\dot{-}}$, which can be produced in thf solutions of both $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$, even in the absence of added reducing agents [16]. The photo-dissociation spectrum accompanying conversion of $[Fe(CO)_3]^{\dot{-}}$ to $[Fe(CO)_2]^{\dot{-}}$ has been reported [17].

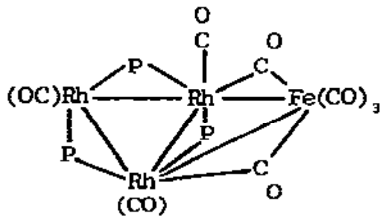
A structural study of $[Fe(CO)_4(PPh_3)]$ shows the phosphine ligand to occupy an axial site in the distorted trigonal bipyramidal coordination sphere [18]. Photolysis of *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$ (Ar = Ph or 2- or 4-MeC_6H_4) leads to loss of CO and the formation of red products which cannot be isolated, but which react with donor ligands, L, to form $[Fe(CO)_2\{P(OAr)_3\}_2L]$ (L = CO, PR_3, $P(OR)_3$, CNR, CS_2, SO_2, tcne or R_2C_2) and with addends, XY, to yield $[Fe(CO)_2\{P(OAr)_3\}_2(X)Y]$ (XY = H_2, D_2, HCl or $SnCl_4$). With CCl_4, red intermediates are formed which subsequently yield $[Fe(CO)_2\{P(OAr)_3\}_2Cl_2]$ and $[Fe(CO)_2\{P(OAr)_3\}Cl]$, the latter containing a metallated ligand. The red intermediates are believed to be the metallated hydrides, $[Fe\{P(OC_6H_3X)(OAr)_2\}\{P(OAr)_3\}(CO)_2H]$ (X = H or Me) [19].

The ligand $PPh_2(CH_2SiMe_3)$ reacts with $[Fe_3(CO)_{12}]$ to give $[Fe(CO)_4\{PPh_2(CH_2SiMe_3)\}]$ and $AsPh_2(CH_2SiMe_3)$ reacts with $[Fe_2(CO)_9]$ to yield $[Fe(CO)_4\{AsPh_2(CH_2SiMe_3)\}]$ [20]. $[Fe(CO)_3(\eta^4\text{-cot})]$ reacts with 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene, PP, to yield $[Fe(CO)_3(PP)]$ [21]. $[Fe(CO)_3(PhPHPPh_2)]$, $[(OC)_4Fe\{P(H)PhP(H)Ph\}Fe(CO)_4]$ and $[Fe(CO)_4\{PPh(PPh)_2\}]$ have also been reported. The last of these shows NMR evidence for coordinative migration of the metal atom from the medial to the terminal phosphorus atom [22].

The secondary phosphine complex, $[Fe(CO)_4(PPh_2H)]$, reacts with $[Rh_2Cl_2(CO)_4]$ to give a number of products, one of which has been characterised by X-ray crystallography as (1). In this compound the Fe atom and Rh^1 and Rh^2 have



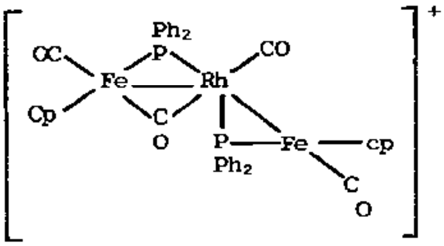
(1; P≡PPh$_2$)



(2; P≡PPh$_2$).

18-electron configurations, while Rh^3 is 16-electron, a difference which is reflected in the various Rh-P bond lengths. In solution, (1) rearranges to (2), which, in turn, reacts with CO to form $[Rh_2(CO)_2(PPh_2)_4]$. In the absence of CO, this last compound is unstable with respect to $[Rh_4(CO)_6(PPh_2)_4]$ [23].

The reactivity of the phosphido complex, $[Fe(CO)_2(PPh_2)(cp)]$, with rhodium and iridium compounds has also been examined. With $RhCl_3.3H_2O$ or $[Rh_2Cl_2(cod)_2]$, the cation (3) is obtained; the iridium analogue has also been prepared. The

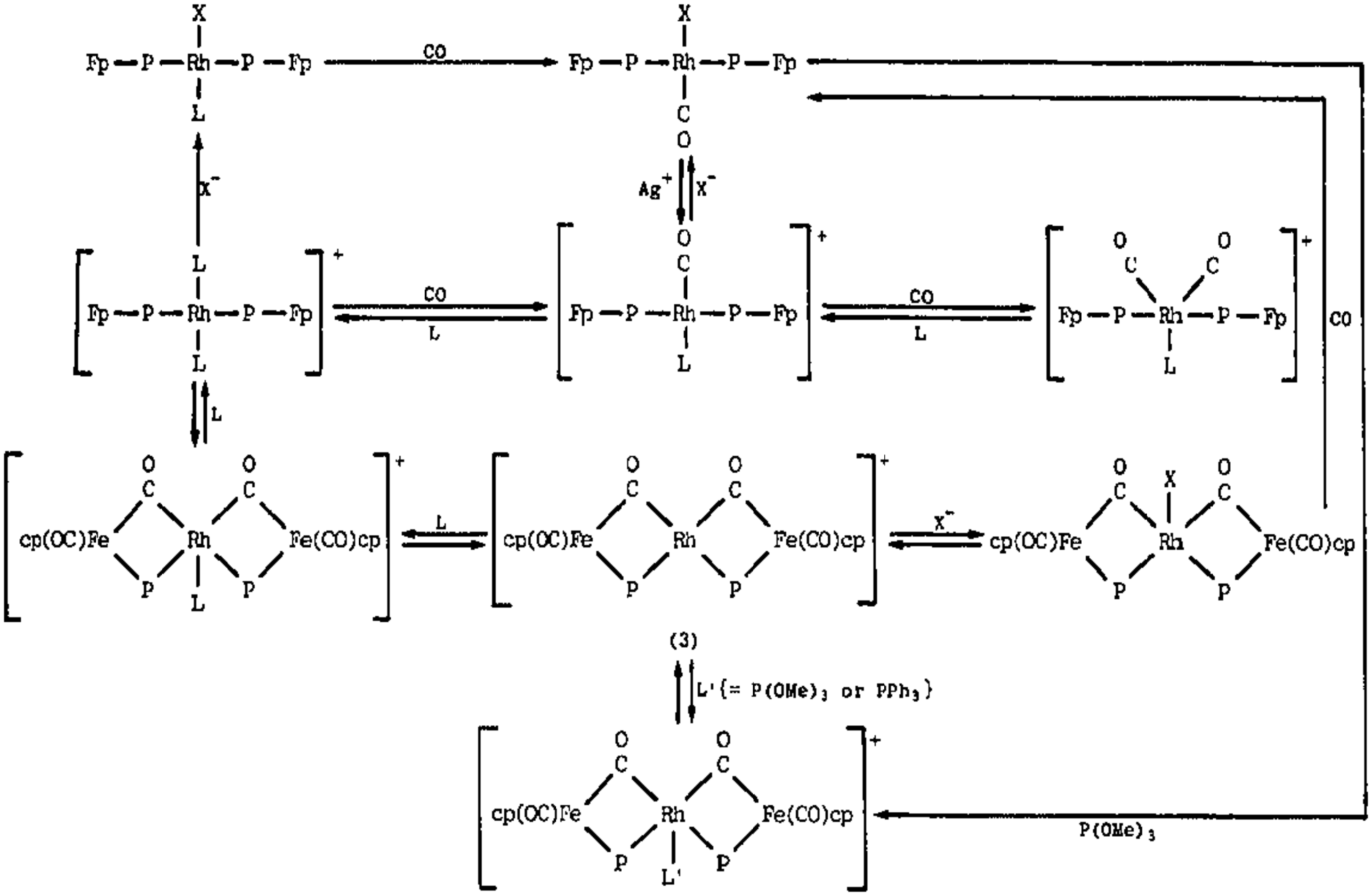


(3)

cation (3) exhibits an extensive chemistry in donor solvents (L = thf, Me_2CO, *etc.*) that arises as a consequence of solvent coordination to rhodium, leading to the formation of species containing no bridging CO ligands. This chemistry is illustrated in Scheme III [24].

The related arsido complex, $[Fe(CO)_2(AsMe_2)(cp)]$ can be prepared from Me_2AsCl and $Na[Fe(CO)_2(cp)]$. The reaction also yields $[\{Fe(CO)_2(cp)\}_2AsMe_2]Cl$ (*cf.* [11]), but the former can be obtained in quantitative yield from treatment of $Na[Fe(CO)_2(cp)]$ with $[Mo(CO)_3(AsMe_2)(cp)]$ [25].

$[Fe(CO)_5]$ reacts with primary and secondary aliphatic amines to form both 1:1 and 1:2 adducts. It is suggested that the amine must be at high enough

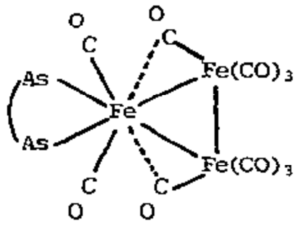


SCHEME III: Some reactions of (3) ($P = PPh_2$, $L' = P(OMe)_3$ or PPh_3, $Fp = \{Fe(CO)_2(cp)\}$, L = thf or Me_2CO).

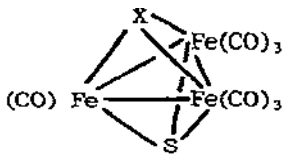
concentration to undergo self association by hydrogen bonding before adduct formation occurs and that the adducts have ion-pair and ion cluster structures [26]. With methyl-substituted imidazoles, imid, $[Fe(CO)_5]$ forms $[Fe(imid)_6][Fe_2(CO)_8]$, $[Fe(imid)_6][Fe(CO)_4]_2$, $[Fe(imid)_4][Fe(CO)_4]$ and $[Fe(imid)_2(CO)_2]$. The crystal structures of the first two compounds have been determined [27].

Matrix isolation UV photolysis of $[Fe(CO)_4L]$ (L = Me_3N or py) gives $[Fe(CO)_3L]$, which has a structure of C_{3v} symmetry. This isomerises to a structure of C_s symmetry after IR photolysis [28]. The heterodimetallic diazine complexes $[\{(OC)_5M\}Z\{Fe(CO)_4\}]$ (M = Cr or W; Z = pentamethylenediazine) are prepared by treating $[Fe(CO)_4(thf)]$ or $[Fe_2(CO)_9]$ with $[M(CO)_5Z]$ [29].

With 1,2-$C_6H_4(AsMe_2)_2$, $[Fe_2(CO)_9]$ forms (4) which exhibits a very asymmetric structure. The presence of semi-bridging CO ligands arises presumably as the unique Fe has an excess of negative charge because the arsenic atoms cannot back bond as efficiently as CO. The semi-bridging CO ligands can accept this excess charge [30].

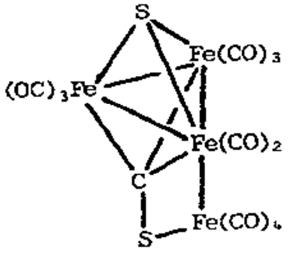


(4)



(5; X = CO)
(6; X = SO)

When $[Fe_3(CO)_{12}]$ is treated with methanolic NaOH, followed by acidification in the presence of $Na_2[SO_3]$, (5) is formed. Similar treatment of $[Fe(CO)_5]$ gives a precipitate of $[Fe_3(CO)_9S_2]$, but if precipitation is induced with PhMe, (6) is isolated which contains the first example of a cluster bound [SO] group [31]. Reaction of $[Fe_3(CO)_{12}]$ with CS_2 at 80 °C under a CO/Ar atmosphere gives (7) which may be considered as a butterfly arrangement of the Fe_4 unit with a broken edge [32]. Variable temperature NMR of $[Fe_3(CO)_9(X)_2]$ (X = S, Se, Te or NMe) show two distinguishable steps in the CO exchange process. In the first the CO ligands on the apical iron atom attain equivalence and then those on the basal iron atoms become equivalent. Substitution of these complexes with Group VB donor ligands is easier at the basal iron atoms and the products, $[Fe_3(CO)_8L(X_2)]$, are formed *via* the adducts $[Fe_3(CO)_9L(X)_2]$, which are thought to have the structure (8). A kinetic study of substitution of $[Fe_2(CO)_6(\mu\text{-}S)_2]$



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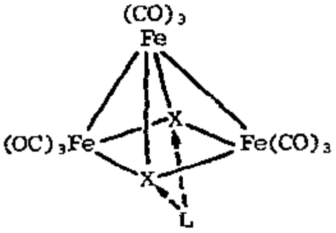
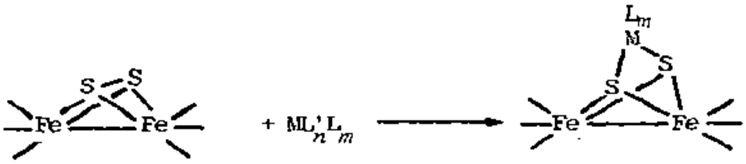


(8)

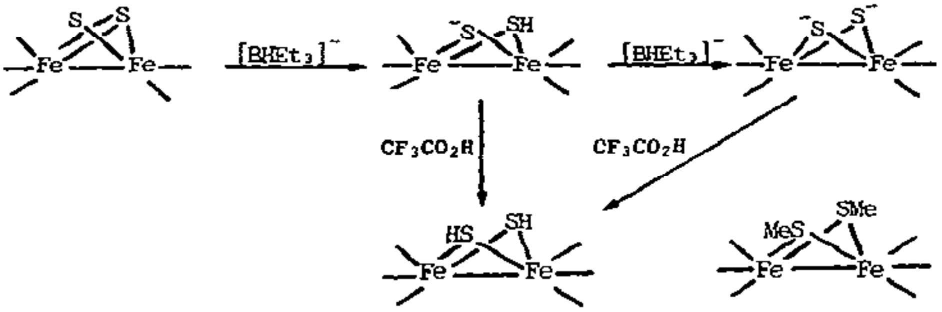
also suggests the formation of an intermediate, $[Fe_2(CO)_6L(\mu\text{-}S)_2]$, which can lose CO or react further with L [33].

The structure of $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ has been reported and the Fe-Fe, Se-Se and Fe-Se bond lengths of 257.5, 229.3 and 236.4 pm, respectively, compare with analogous values of 255.2, 200.7 and 223 pm for the $(\mu\text{-}S_2)$-compound. These differences are all well within the change in covalent radius on moving from S to Se [34]. The reactivity of $[Fe_2(CO)_6(\mu\text{-}X_2)]$ (X = S, Se or Te) has been studied and reactions occur mainly at the X-X bond, thereby mimicking organic disulphides. Thus reaction with other metal complexes follows equation (3),



(3)

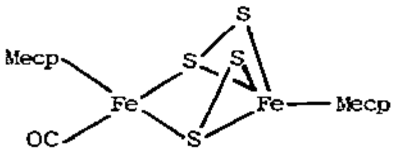
where ML_m = Ni(dppe), $Pd(PPh_3)_2$, $Pt(PPh_3)_2$ or $Co(SnMe_2)(cp)$. Identical products can be obtained by reaction of ML_mCl_2 with $[Fe_2(CO)_6(\mu\text{-}S_2)]^{2-}$. An improved synthesis of this anion has been reported as part of the sequence of reactions outlined in Scheme IV [35].



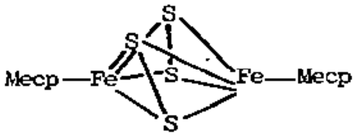
SCHEME IV: Some reactions of $[Fe_2(CO)_6(\mu\text{-}S_2)]$.

Reaction of $[Fe_3(CO)_9S_2]$ with $1\text{-}C_{12}H_{25}SH$ gives a 25% yield of a mixture of *syn*- and *anti*-$[Fe_2(CO)_6(\mu\text{-}SR)_2]$ and a small amount of $[Fe_2(CO)_6(\mu\text{-}S)_2]$ [36]. $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$ has been obtained by treatment of $[Fe_2(CO)_9]$ with PhNHNSO, a finding in contrast to that employing PhN=S=O which gives a low yield of $[Fe_2(CO)_6(PhNS)]$ [37].

Photoreaction of $[Fe_2(CO)_4(\eta^5\text{-}C_5H_4Me)_2]$ with S_8 gives the binuclear complexes, $[(\eta^5\text{-}C_5H_4Me)_2Fe_2(\mu\text{-}S_2)_2]$, (9) and (10) [38]. The clusters (11) and (12) are chiral in solution and thus must have rigid Fe–S frameworks. As an earlier study demonstrated similar behaviour for $[MoFeCo(CO)_8S(cp)]$, it is likely that this is a common feature of sulphur-bridge clusters [39].



(9)



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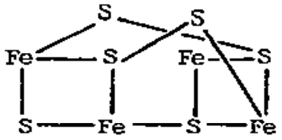
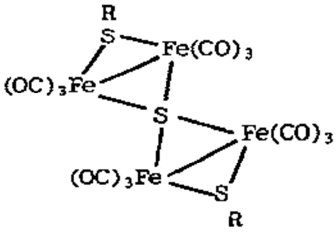


(11; cp groups omitted for clarity)

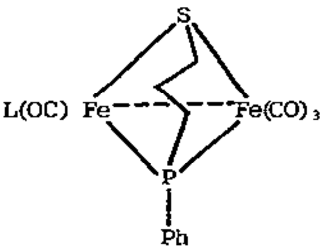


(12)

^{13}C NMR studies on $[Fe_2(CO)_6(\mu\text{-}SR)_2]$, $[Fe_2(CO)_5(PBu_3)(\mu\text{-}SR)_2]$ (R = Me or Ph) and $[Fe_2(CO)_6(\mu\text{-}X)_2]$ (X = S or Se) have shown that the solid state structures are maintained in solution. $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$ is present in two isomeric forms, the *anti* form predominating: these isomers could not be separated [40].

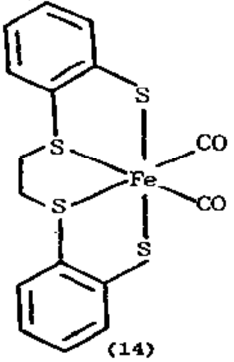
In order to ascertain the influence of the bridging groups on the basicity of the metal-metal bond, protonation of $[Fe_2(CO)_4L_2(\mu\text{-}A)(\mu\text{-}A')]$ ($L = PPh_nMe_{3-n}$; A = A' = SPh, PPh_2 or PMe_2; A = SPh, A' = PPh_2) has been studied. Replacement of the first SPh group by PPh_2 markedly increases the basicity, but introduction of the second $\mathrm{PPh_2}$ unit has no additional effect [41]. The structure of $[\mathrm{Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}PPh_2)}]$ has been determined and the Fe–Fe bond length of 261.9 pm is slightly shorter than that of the diphosphido analogue [42].

Two-electron reduction of $[\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)_2}]$ yields the analogous dianion which contains no metal-metal bond; cleavage of this bond leads to a complete flattening of the $\mathrm{Fe_2P_2}$ ring [43]. $[\mathrm{Fe_2(CO)_9}]$ reacts with $\overline{\mathrm{P(S)(Ph)CH_2CH_2CH_2S}}$ to yield the complexes (13) [44].

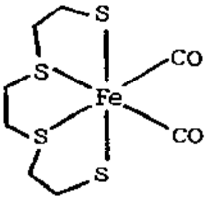


(13; L = CO or $\overline{\mathrm{P(S)(Ph)CH_2CH_2CH_2S}}$)

cis-$[\mathrm{Fe(CO)_2(C_6H_4S_2)_2}]^{2-}$ and *cis*-$[\mathrm{Fe(CO)_2(MeSC_6H_4S)_2}]$ react with $\mathrm{PMe_3}$ to form $[\mathrm{Fe(CO)_2(PMe_3)_2(C_6H_4S_2)_2}]^{2-}$ and $[\mathrm{Fe(CO)_2(PMe_3)(MeSC_6H_4S)_2}]$ respectively. A similar reaction of $[\mathrm{Fe(MeSC_6H_4S)_2}]$ yields $[\mathrm{Fe(PMe_3)(MeSC_6H_4S)_2}]$. $[\mathrm{Fe(CO)_2(C_6H_4S_2)_2}]^{2-}$ also reacts with 1,2-$\mathrm{C_2H_4Br_2}$ to give (14) and similar treatment of $[\mathrm{Fe(CO)_2(S_2C_2H_4)}]^{2-}$ yields (15) [45].



(14)



(15)

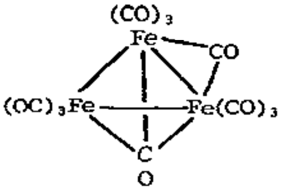
Reaction of $[\mathrm{Fe_2(CO)_9}]$ with MeC(NHR)S (R = H or Ph) gives $[\mathrm{Fe(CO)_4\{SC(NHR)Me\}}]$. In a related reaction, $[\mathrm{Fe(CO)_2(cp)(CONHMe)}]$ reacts with CSX (X = O, S) to yield $[\mathrm{Fe(CO)_2(cp)\{SC(X)NHMe\}}]$ and $[\mathrm{Fe(CO)(S_2CNHMe)(cp)}]$ [46].

Force constant calculations for the Fe–Fe, Fe–S and S═O bonds of $[\mathrm{(OC)_4Fe\{\mu\text{-}SO_2\}Fe(CO)_4}]$ are compatible with strong electron donation from the $\mathrm{SO_2}$ ligand [47]. Reaction of $[\mathrm{Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SMe)_2}]$ with $\mathrm{SO_2}$ yields leads to $[\mathrm{Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SMe)_2(\mu\text{-}SO_2)}]$, in which the $\mathrm{SO_2}$ molecule replaces the Fe–Fe bond. Interestingly, the Fe–SO_2 distance is 222.6 pm compared to 235.6 pm for the Fe–SMe bond length [48]. $[Fe(CO)_2\{P(OR)_3\}_2(SO_2)]$ (R = Ph or 2-C_6H_4Me) both exist as a mixture of isomers in solution. In the solid state both exhibit planar geometry of the SO_2 group and trigonal bipyramidal coordination of the metal; however, in one case (R = Ph), the equatorial ligands are $[(SO_2)(CO)_2]$ while in the other they are $[(SO_2)\{P(OR)_3\}_2]$ [49]. $[Fe(CO)_2(SO_2)(cp)]^+$ reacts with $ROSO_2F$ to form $[Fe(CO)_2\{S(O)_2OR\}(cp)]$ (R = Me, Et, Pr or $CHMe_2$) which is also formed from $[Fe(CO)_2(H_2O)(cp)]^+$ and $NaS(O)_2OR$ [50].

[Fe(*N*CS)$(CO)_2$(cp)] interconverts with the *S*CN isomer both in the solid and in solution. It has been previously suggested that this involves a bridged Fe–*N*CS.....Fe intermediate. However, determination of the crystal structure of this molecule shows the shortest Fe.....S distance to be 425 pm and this is clearly inconsistent with the operation of such a mechanism in the solid state [51]. $[Fe(CN)(CO)_2(cp)]$ reacts with both Me_3NBH_2I and B_2H_6 to yield $[Fe(CO)_2(CNBH_2.NMe_2)(cp)]I$ and $[Fe(CO)_2(CNBH_3)(cp)]$, respectively [52].

In diethyl ether (dielectric constant, 4.3), $Na[Fe(CO)_4(CN)]$ exists predominantly as contact ion pairs with the sodium atom showing a preference for the cyanide site. These are converted to solvent-separated ion pairs on addition of 15-crown 5, or by dissolution in thf (dielectric constant, 7.4) [53]. Treatment of $[Fe(CO)_5]$ with $Li_2[Ph_2CO]$ gives $[Fe(CO)_4]^{2-}$ [54].

An X-ray diffraction study of the $[Fe_3(CO)_{11}]^{2-}$ anion as its $[NEt_4]^+$ salt, shows it to adopt the structure shown in (16). The anion shows only one ^{13}C



(16)

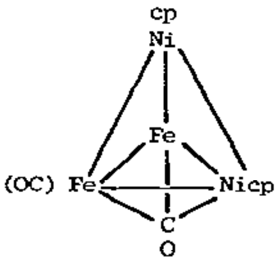
resonance in its NMR spectrum and this has led the authors to suggest a new possible mechanism for carbonyl interconversion involving a synchronous movement of a terminal axial CO, and both bridging CO ligands, over both triangular faces [55].

Photolysis of $[Fe(CO)_5]$ and $[Os_3H_2(CO)_{10}]$ gives $[FeOs_3(CO)_{13}H_2]$ in 95% yield, but reaction of $[Fe_3(CO)_{12}]$ with $[V(CO)_6]$ under similar conditions yields only $[Fe_3(CO)_{11}H]^-$ [56]. Interaction of $[Fe_3(CO)_{12}]$ and $[Fe(CO)_5]$ with surface alumina and silica yields the supported hydrido complex M-$HFe_3(CO)_{11}$ (M = $Al(O-)_x$ or $Mg(O-)_y$) [57]. The pK_a values (in parenthesis) have been reported for the following hydrides: $[Ru_4(CO)_{12}H_4]$ (11.7); $[FeRu_3(CO)_{12}H_4]$ (13.4), $[Ru(CO)_{13}H_2]$

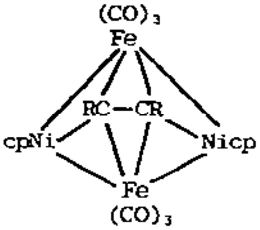
(14.7), $[FeRu_3(CO)_{13}H_2]$ (14.3); $[Os_4(CO)_{12}H_4]$ (12.0), $[FeH_2(CO)_4]$ (12.4) and $[OsH_2(CO)_4]$ (12.8) [58].

Photolysis of $SiCl_3H$ and $[Fe(CO)_5]$ gives *cis*-$[Fe(CO)_4(SiCl_3)_2]$, whereas reaction with $[Fe_2(CO)_9]$ in the presence of Et_3N is reported to yield $[Si\{Fe(CO)_4\}_4]$. Treatment of $[Fe_2(CO)_9]$ with $Si_2Me_4H_2$ produces $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}Si_2Me_4)Fe(CO)_3]$ [59]. Reaction of $[Fe(CO)_2(cp)]^-$ with *cyclo*-$Si_5Me_9(SiMe_2Cl)$ and *cyclo*-$Si_5Me_8Cl(SiMe_2Cl)$ yields [*cyclo*-$Si_5Me_9(SiMe_2\{Fe(CO)_2(cp)\})$] and [*cyclo*-$Si_5Me_8\{Fe(CO)_2(cp)\}(SiMe_2\{Fe(CO)_2(cp)\})$] respectively [60]. A similar reaction involving PbR_3Cl gives $[PbR_3\{Fe(CO)_2(cp)\}]$ (R = Me or Et) [61]. When $[Br_2Sn\{Fe(CO)_2(cp)\}]$ is treated with $[Co_2(CO)_8]$, $[BrSn\{Co(CO)_4\}\{Fe(CO)_2(cp)\}]$ is formed [62].

$[Ni(cp)_2]$ reacts with various iron carbonyl compounds to yield (17), (18)



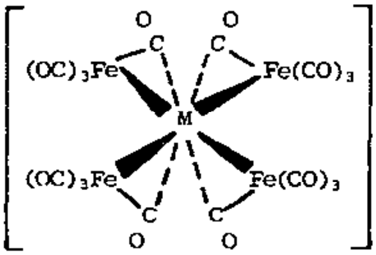
(17)



(18)

and $[(cp)_2NiFe(CO)_3]$ [63].

Reaction of $[Fe_3(CO)_{11}]^{2-}$ with palladium(II) and platinum(II) salts gives $[Fe_4M(CO)_{16}]^{2-}$ (19; M = Pd or Pt). If a large amount of platinum(II) salt is

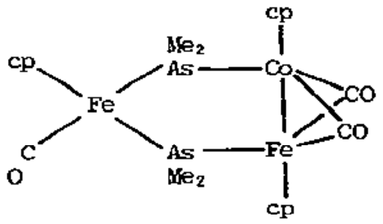


(19)

employed, $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_4Pt_6(CO)_{22}]^{2-}$ are obtained. Using $[Fe_4(CO)_{13}]^{2-}$, a complex mixture of products is obtained, from which both $[Fe_6Pd_6(CO)_{24}]^{4-}$ and $[Fe_6Pd_6(CO)_{24}H]^{3-}$ have been isolated. The latter has a trigonal prismatic array of Pd atoms with the six lateral surfaces capped by six iron atoms. Of the twenty-four CO ligands, twelve are terminal (two per Fe), six are doubly bridging Fe-Pd edges and six are triply bridging $\{FePd_2\}$ faces. The hydrogen atom was not located [64].

Treatment of $[FeBr(CO)_3(\eta^3\text{-}C_3H_4R)]$ (R = H or 1-Ph) with zinc dust followed by $[AuCl(PPh_3)]$ yields $[Fe(CO)_3\{Au(PPh_3)\}(\eta^3\text{-}C_3H_4R)]$. The allyl-containing complex exhibits pentagonal bipyramidal, C_5, coordination with the $Au(PPh_3)$ ligand located on an edge between two CO ligands. The Au-Fe-CO angles are thus very acute (71°) [65]. When the monomer, $[(NH_3)_3ZnFe(CO)_4]$ is heated in the solid state, ammonia is lost and $[\{ZnFe(CO)_4\}_4]$ is formed. This, in turn, takes up bipy to yield the complex $[(bipy)Zn\{\mu\text{-}Fe(CO)_4\}_2Zn(bipy)]$, the structure of which has been determined [66]. $[L_2GaFe(CO)_4]$ ($L_2 = (py)_2$, bipy or tmen) and $[(thf)EtGaFe(CO)_4]_2$ have also been reported [67].

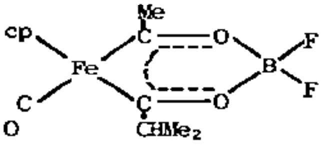
Vahrenkamp and coworkers have continued their detailed studies of $-E_2R$ bridged polymetallic compounds and have reported that $[Ru_3(CO)_{12}]$ reacts with $[\{Fe(CO)_2(cp)\}(AsMe_2)]$ to yield $[Ru_3(CO)_{12-n}(AsMe_2\{Fe(CO)_2(cp)\})_n]$ (n = 1, 2 or 3). $[\{Fe(CO)_2(cp)\}(AsMe_2)]$ also reacts with $[Co(CO)_2(cp)]$ in a 1:1 ratio to give $[\{Fe(CO)_2(cp)\}(Me_2As)Co(CO)(cp)]$; however, when a 2:1 ratio of these reagents is used, (20) is formed. $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4]$ reacts with Me_2ENMe_2 (E = P or As) to form the open chain compounds $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4(EMe_2NMe_2)]$, and similar reaction with Me_2AsCl gives the salt $[(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4][(OC)_4Fe(\mu\text{-}AsMe_2)MnCl(CO)_4]$. Nucleophilic cleavage of the metal-metal bonds of $[(OC)_4Fe(\mu\text{-}EMe_2)M]$ {M = $Co(CO)_3$, $Fe(CO)_2(NO)$, $Mn(CO)_4$, $Mo(CO)_2(cp)$, or $W(CO)_2(cp)$; E = As or P} can also be achieved with $[M'(AsMe_2)]$ {M' = $Fe(CO)_3(cp)$ or $M(CO)_3(cp)$ (M = Cr, Mo or W)}, yielding $[(OC)_4Fe(\mu\text{-}EMe_2)M(\mu\text{-}AsMe_2)M']$ [68].



(20)

The anions $[Fe(CO)_4(CONR_2)]^-$ (R_2N = piperidino or pyrrolidino; R = Me) reacts with $NiBr_2$ to give the square planar nickel complex, $[\{(OC)_4FeCONR_2\}_2Ni]$ [69]. Similarly, reaction of $[(cp)Fe(CO)(CMeO)(OCHMe_2O)H]$ with BF_3 yields (21) in which the chelate ring is boat-shaped rather than planar [70].

The unusual compound (22) is obtained in low yield from the reaction of $[Fe_3(CO)_{12}]$ and $EtNO_2$. A structural study has confirmed that the EtNO fragment acts as a six-electron donor in bridging all four iron atoms [71]. The structure



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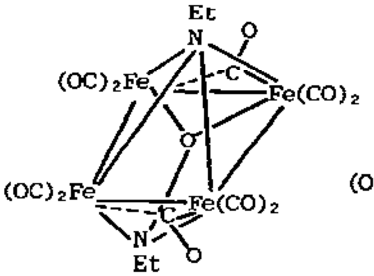

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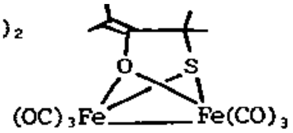


(23)

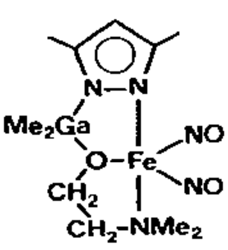
of (23), obtained from $[Fe_2(CO)_9]$ and tetramethyl-3-thietanone has also been reported [72].

Finally, in this section, the stoicheiometry of the products of "total" decomposition of $[Fe_3(CO)_{12}]$ in dmf and dmso have been determined. They are $[Fe_2O_3(H_2O)_5(dmf)]$ and $[Fe_2O_3(H_2O)_3(dmso)(CO)]$ and both contain Fe–O–Fe linkages [73].

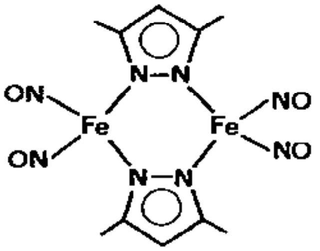
1.2 NITROSYL COMPLEXES

Photolysis of $[Fe(CO)_5]$ in non-polar solvents containing NO gives rise to an EPR spectrum assigned to the free radical complex, $[Fe(CO)(NO)_3]\cdot$. There was no evidence for the formation of $[Fe(CO)_3(NO)]\cdot$ [74]. Electrochemical reduction of $[Hg\{Fe(CO)_3(NO)\}_2]$ gives Hg and $[Fe(CO)_3(NO)]^-$; however, electrochemical oxidation yields Hg^{2+} and $[Fe(CO)_3(NO)]\cdot$. Electroreduction of $[(BuNC)_2Pt\{Fe(CO)_3NO\}_2]$ yields $[Fe(CO)_3NO]$ and $[(BuNC)_2Pt\{Fe(CO)_3NO\}]\cdot$ [75].

The formally 19-electron complex, (24), has been prepared by treatment of $[Fe(NO)_2I]$ with the sodium salt of the pyrazolylgallate. An X-ray structural determination confirmed the structure and showed the presence of two bent FeNO



(24)



(25)

units (Fe$\hat{\mathrm{N}}$O ~160°) [76]. Similar treatment of $[\mathrm{Fe(NO)_2I}]$ with $\mathrm{Na[C_5H_7N_2]}$ yields the paramagnetic 17-electron dimer, (25). The iron atoms have distorted tetrahedral geometry, the $[\mathrm{Fe(N{-}N)_2Fe}]$ ring having a boat conformation. Thus the NO groups can be viewed as *pseudo*-axial and *pseudo*-equatorial; the former has FeNO ~170°, while that of the latter is *ca.* 160° [77].

Protonation of $[\mathrm{Fe(CO)_3(NO)}]^-$ or $[\mathrm{Fe(CO)_2(NO)(PPh_3)}]^-$ with trifluoroethanoic acid, in the presence of excess $\mathrm{PPh_3}$, gives $[\mathrm{FeH(CO)(NO)(PPh_3)_2}]$ which, on reduction with sodium amalgam, gives $[\mathrm{Fe(CO)(NO)(PPh_3)_2}]^-$. Treatment of $[\mathrm{Fe(CO)_2(NO)(PPh_3)}]^-$ with $\mathrm{H[BF_4]}$ in the presence of excess $\mathrm{PPh_3}$ and CO yields the cation $[\mathrm{Fe(CO)_2(NO)(PPh_3)_2}]^+$ [78]. Treatment of $[\mathrm{Fe(CO)_3(NO)}]^-$ with $[\mathrm{RC_6H_4N_2}]^+$ at −78 °C leads to $[\mathrm{Fe(CO)_2(NO)(N_2C_6H_4R)}]$, which could not be isolated, but on treatment with $\mathrm{PPh_3}$ gave the isolable $[\mathrm{Fe(CO)_2(NO)(N_2C_6H_4R)(PPh_3)}]$ (R = 4-Me, 4-MeCONH, H, 4-F, 4-$\mathrm{CF_3}$, 4-$\mathrm{CH_3CO}$, 4-$\mathrm{NO_2}$ or 3-F). Mössbauer data suggest the $[\mathrm{ArN_2}]^+$ ligand is a stronger σ-donor and a weaker π-acceptor than $[\mathrm{NO}]^+$ [79].

$[\mathrm{Fe_2(NO)_4(\mu{-}NH_2)_2}]$ is obtained by treatment of $[\mathrm{Fe(NO)_3Cl}]$ with $\mathrm{Na[AlH_2(OCH_2CH_2OMe)_2]}$ and it is likely that this compound is that reported in 1960 as $[\mathrm{Fe_2(NO)_4(NH)_2}]$ from the reaction of $[\mathrm{Fe_2(CO)_6(NH_2)_2}]$ and NO [80]. The related dimer $[\mathrm{Fe(NO)_2(\mu{-}NPh_2)}]_2$ is obtained from $[\mathrm{Fe(NPh_2)_2(dioxan)_2}]$ and NO at −35 °C. An XPES study suggests the iron atoms in such complexes are in the formal oxidation state of III [81].

Ab initio MO calculations have been reported for the $[\mathrm{Fe(NO)}]^n$ (n = 6, 7 or 8) systems, and the following important points have arisen. The important energetic contribution to the linear geometry observed for $[\mathrm{Fe(NO)}]^6$ arises from interaction of filled 5σ and 1π orbitals of NO with the metal, as well as from the interaction of the NO 2π orbital. The potential energy curve for $[\mathrm{Fe(NO)}]^7$ is virtually flat, in agreement with the observation of a wide variety of experimental geometries and the poor definition of the oxygen position in structural studies on many complexes containing this unit. The ground state of $[\mathrm{Fe(NO)}]^7$ is predicted to be linear ($^2A_1$) with considerable unpaired electron density in the d_{z^2} orbital. $[\mathrm{Fe(NO)}]^8$ shows the expected bent geometry and the tendency for bending in the plane of the better π-acceptor was confirmed [82]. An XPES study of $[\mathrm{Fe(NO)X(diars)}]^+$ and $[\mathrm{Fe(NO)(diars)}]^{2+}$ has been reported [83].

Reaction of $[\mathrm{Fe(NO_3)_3}]$ and $[\mathrm{Fe\{S_2CN(CHMe_2)_2\}_3}]$ yields $[\mathrm{Fe(NO)\{S_2CN(CHMe_2)_2\}_2}]$ and the structure of this molecule has been determined by X-ray methods. In all previous crystallographic studies on $[\mathrm{Fe(NO)(dtc)_2}]$ complexes, distinction between linear and bent Fe$\hat{\mathrm{N}}$O geometry has been prevented by problems of disorder. In this case, the assignment of an Fe$\hat{\mathrm{N}}$O bond angle of 179°, perpendicular to the S_4 plane is unambiguous [84]. $[\mathrm{Fe(NO)(sal_2phen)}]$ is prepared by reaction of $[\mathrm{Fe(sal_2phen)}]$ with NO and shows magnetically distinct $S = 3/2$ and $S = 1/2$ states, at high and low temperature respectively. A recent study of the analogous $[\mathrm{Fe(NO)(sal_2en)}]$ complex shows similar magnetic behaviour, the Fe$\hat{\mathrm{N}}$O angle changing from 147° ($S = \frac{3}{2}$) to 127 ($S = \frac{1}{2}$). The change in ν(NO) observed for [Fe(NO)(sal$_2$phen)] from 1724 cm^{-1} ($S = \frac{3}{2}$ to 1643 cm^{-1} ($S = \frac{1}{2}$) suggests a similar $\mathrm{Fe\hat{N}O}$ variation. [Fe(NO){5,5'-(NO$_2$)$_2$sal$_2$en}] has been prepared and the previously observed temperature dependant spin equilibrium has been confirmed, although the magnetic moment values of both forms are higher than previously reported [85].

Treatment of [Fe(py)$_2$Cl$_2$] with NO and maleonitriledithiolate, bipy or phen (L) yields [Fe(NO)L$_2$] [86]. Similar complexes containing amidinothiourea ligands have also been reported [87].

When [FeL']$_2$ (H$_2$L' = HS(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe(CH$_2$)$_2$SH) is treated with [NO][PF$_6$], the product can be obtained in two crystalline forms. One is [Fe(L')(NO)$_2$], the other is a mixture of this compound and [Fe(L'H)(NO)$_2$]. The latter can be obtained in pure form by reaction of [Fe(NO)$_2$Br$_2$] with L'H$_2$, and has a square pyramidal coordination geometry with $\{S_2(N\mathrm{O})N(\mathrm{HL'})\}$ ligating atoms in the basal plane and a bent NO group at the apex; the former has a *pseudo*tetrahedral geometry, $\{\mathrm{Fe}(N\mathrm{O})_2S_2\}$, with both NO ligands linear and one of the uncoordinated nitrogen atoms of L' protonated and hydrogen bonded to the other. Both complexes are paramagnetic, 17-electron species [88].

A molecular orbital and reactivity study of $[\mathrm{M(CN)_5(NO)}]^{n-}$ (M = Fe, $n = 2$; M = Mn or V, $n = 3$) has been reported. The HOMO is an orbital of π symmetry localised mainly on the ligands and the LUMO is a degenerate π^* (M–N–O) orbital localised mainly on the nitrogen atom. Analysis of the LUMO as a function of the ligand electronegativity, the number of electrons in the complex, and the nature of the metal shows that nucleophilic attack at N or reduction at N is favoured for metals at the right-hand side of the transition series and with a high formal charge on the metal. For $[\mathrm{M(NO)}]^{n}$ (n = 4, 5 or 6), the site of nucleophilic attack is independant of the number of electrons or the nature of the ligands. The energy of the LUMO decreases with the number of electrons, with increasing electronegativity of the ligands and on going from right to left across the periodic table making nucleophilic attack at any site more facile [81].

The mechanism of the reaction of $[\mathrm{Fe(CN)_5(NO)}]^{2-}$ with NH$_3$ has been studied, and at low ammonia concentrations the initial attack is by [OH]$^-$ to give an intermediate which subsequently yields $[\mathrm{Fe(CN)_5(NH_3)}]^{3-}$. At high ammonia concentration, there is probably direct attack by NH$_3$ on the NO ligand [90].

The structures of Tl$_2$[Fe(CN)$_5$(NO)] and Ca[Fe(CN)$_5$(NO)].4H$_2$O have been reported. Both, in common with all other examples of this anion so far examined, exhibit very distorted octahedral coordination of the iron atom, this being displaced from the (CN)$_4$ plane towards the NO ligand. The latter contains seven-coordinate $\{\mathrm{Ca}O_3N_4\}$ centres [91].

1.3 HALIDES, OXOHALIDES AND HALIDE COMPLEXES

Infrared spectra of the crystalline material obtained by treating freshly precipitated $Fe(OH)_3$ with HF is consistent with the presence of $H_3[FeF_6]$ [92]. The electronic structure of FeF_2 and FeF_3 have been studied by X-ray emission spectroscopy and XPES [93]. Thermolysis of $Fe_2F_5.nH_2O$ (n = 7 or 2) shows dehydration of the heptahydrate to the dihydrate followed by conversion to the hemi-hydrate. However, the processes are much more complex than previously thought as there is loss of HF as well as H_2O [94].

The vapour phase structure of $[Fe_2Cl_6]$ consists of iron atoms in distorted tetrahedral environments, thus giving rise to a puckered $\{Fe_2Cl_2\}$ ring. Pertinent distances and angles are $r(FeCl)_t$ = 212.7 pm, $r(FeCl)_b$ = 232.6 pm, $Cl_t\hat{F}eCl_t = 124°$, $Cl_b\hat{F}eCl_b = 91°$ [95].

X-ray diffraction studies of concentrated aqueous solutions of $FeCl_3.6H_2O$ and $FeCl_3$ shows the former to contain $[Fe(OH_2)_6]^{3+}$ octahedra (Fe–O = 204 pm) and ion-pair $Fe^{3+}.....Cl^-$ interactions (Fe.....Cl = 410 pm), whereas the latter has tetrahedral coordination with bridging chloride (Fe–Cl = 228 pm) [96]. A second X-ray diffraction study of $FeCl_3$ in both aqueous solutions and hydrated melts established $[FeCl(H_2O)_5]^{2+}$ and $[FeCl_3(H_2O)_3]$ as the principal species in neutral or acid solutions, whereas $[FeCl_4]^-$ is formed in the hydrated melt [97].

A structural study of $FeCl_3.2.5H_2O$ shows it to consist of the *cis*-$[FeCl_2(H_2O)_4]^+$ cation {r(Fe–Cl) = 223.6, 225.1 pm}, the $[FeCl_4]^-$ anion {r(Fe–Cl) = 216.9–222.0 pm} and a molecule of water of crystallisation [98]. The structures of $[3\text{-CNpyH}][FeCl_4].3\text{-CNpy}$ [99] and $Cs_2[FeCl_5(H_2O)]$ [100] have also been reported.

Reaction of anhydrous $FeCl_2$ with $[dmenH_2]Cl_2$ in methanol yields $[dmenH_2][FeCl_5(MeOH)]$, which on holding under vacuum for 3 h gives $[dmenH_2][FeCl_5]$ [101]. When metallic iron is treated with dmso and CCl_4 at above 100 °C, a mixture of *cis*- and *trans*-$[FeCl_2(dmso)_4]Cl$, *trans*-$[FeCl_2(dmso)_4][FeCl_4]$ and *cis*-$[FeCl_2(dmso)_4]_2[FeCl_4]$ are formed. At lower temperatures, only *trans*-$[FeCl_2(dmso)_4][FeCl_4]$ and *trans*-$[FeCl_2(dmso)_4]Cl$ are obtained. Use of dmf gives *cis*-$[FeCl_2(dmf)_4][FeCl_4]$, while with MeCN, $[Fe(MeCN)_6][FeCl_4]_2$ is produced [102].

Three publications have reflected the growing interest in layer compounds based on FeOCl. When FeOCl is treated with sodium methoxide FeO(OMe) is formed and this has an interplanar spacing of *ca.* 100 pm, approximately 20 pm larger than that of FeOCl [103]. The compound, $Fe_2O_2(OCH_2CH_2O)$ is obtained by heating $FeOCl(4\text{-}NH_2py)_{\frac{1}{4}}$ with ethylene glycol at 110 °C for 6 days. A one-dimensional X-ray density map showed the layer separation was 145 pm when the product was still in ethylene glycol, but that it shrank to 109.8 pm after washing with propanone [104]. $P(OMe)_3$ and PEt_3 (L) can be intercalated into FeOCl in which half of the 'guest' molecular sites in the van der Waals' layer are occupied yielding $FeOClL_{1/6}$. Intercalation causes major expansion of the b axis, of 647 and 396 pm respectively; Mössbauer spectra show the presence of two different iron sites in the lattice, representing those with a guest molecule as a nearest neighbour (one sixth of the total) and those which are more distant from L. Isomer shift and quadruple splitting parameters show the binding energy in the van der Waals' layer to be *ca.* 3 kJ mol^{-1} [105].

1.4 CYANIDES

A neutron diffraction study on Prussian Blue, $Fe_4[Fe(CN)_6]_3.xH_2O$ (x = 14–16) has been published. Six water molecules are coordinated to the iron(III) atoms at empty nitrogen sites, and the additional six to eight water molecules are hydrogen bonded to those which are coordinated. Magnetic properties are consistent with high spin iron(III) [106]. A neutron diffraction study on $CsK[Fe(CN)_6]$ at 4.2 K shows the Fe–C and C–N distances to be 193 and 115 pm respectively, which is not essentially different to the room temperature structure [107]. The structure of the zeolite, $K_2Zn_3[Fe(CN)_6]_2.xH_2O$ shows the $\{FeC_6\}$ octahedra are linked to the $\{ZnN_4\}$ tetrahedra by bridging cyanide groups, thereby constituting a three-dimensional framework with large cavities. Although the potassium ions and water molecules were not well located, this structure allows an understanding of the zeolitic character and ion-exchange properties of hexacyanoferrates(II) [108]. A structural study of $Fe_3[Co(CN)_6]_2.12H_2O$ shows the CN ligands to bridge the Fe and Co ions $\{r(Co–C) = 187.6$ pm; $r(Fe–N) = 215$ pm$\}$, the former also being coordinated to water molecules [109].

The kinetics of the reaction of $[Fe(CN)_6]^{4-}$ with HNO_2 in the presence of acid, giving NO, H_2O and $[Fe(CN)_6]^{3-}$, suggest that the oxidising species is $[NO]^+$, hence equations (4a) and (4b) [110]. A kinetic study has also been made of the

$$H^+ + HNO_2 \overset{\text{slow}}{\rightleftharpoons} [NO]^+ + H_2O \tag{4a}$$

$$[NO]^+ + [HFe(CN)_6]^{3-} \xrightarrow{\text{fast}} [Fe(CN)_6]^{3-} + NO + H^+ \tag{4b}$$

reaction of $[Fe_2(CN)_{10}]^{4-}$ and a HNO_2/HNO_3 mixture; the primary product appears to be a binuclear {Fe(II), Fe(III)} complex with coordinated $[NO]^+$ linked to the Fe(II) ion. Similar reactions of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_4L]^-$ (L = bipy or phen) have also been studied. All form cyano-nitrosyl complexes and these are presumably generated *via* NO_2 [111].

Previous workers have presented evidence for the equilibrium (5) with $K = 1.37\ 0.2 \times 10^{-8}$ *M* at 25 °C, however, Davies and Garafalo have shown that

$$[Fe(CN)_5(H_2O)]^{3-}_{aq} \rightleftharpoons [Fe(CN)_5(OH)]^{4-}_{aq} + H^+_{aq} \tag{5}$$

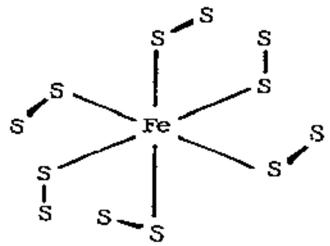
this was not in fact the reaction under study [112]. The mechanism of the reaction of the binuclear dimer of $[Fe(CN)_5(H_2O)]^{3-}$ with the ligands py, PhNO, 3-CNpy or 4-CNpy has also been studied [113]. Association constants for $[Fe(CN)_5(H_2O)]^{2-}$ and imidazole or the imidazolate ion have been determined [114].

The kinetics of the reduction of $[Fe(CN)_6]^{3-}$ with $[S_2O_4]^{2-}$ show that the dithionite ion dissociates into two $[SO_2]^{\dot{-}}$ ions, and these rapidly effect the observed reduction. In the presence of a large excess of dithionite, two parallel reactions are observed, involving reduction by the $[SO_2]^{\dot{-}}$ and $[S_2O_4]^{2-}$ ions [115]. Reduction of $[Fe(CN)_5(4,4'\text{-bipy})]^{2-}$ and $[Fe(CN)_5(py)]^{2-}$ by $[Co^{II}(edta)]^{2-}$ proceeds in two stages. The first corresponds to an inner sphere redox process giving the binuclear complex $[(edta)Co^{III}NCFe^{II}(CN)_4L]^{4-}$; this binuclear complex is metastable and thus decomposes. However, its decomposition represents a "dead end" towards the formation of mononuclear products, and these are formed by an alternative outer sphere reaction of $[Co(edta)]^{2-}$ and $[Fe(CN)_5L]^{2-}$ [116].

1.5 OXIDES, SULPHIDES AND COMPOUNDS OF SIMPLE ANIONS

$Sr_2Fe_2O_5$ has been prepared by CO_2-laser irradiation of iron(II) oxalate and strontium oxide [117]. The heats of formation of $LiFe_5O_3$ and $LiFeO_4$ and the kinetics of the synthesis of $BaFe_{12}O_{19}$ have been reported [113,119]. $Sr_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$ contains high spin iron(IV), which is stable in an elongated D_{4h} site [120]. $Cr_{0.42}Fe_{2.56}O_4$ is obtained by nitrate oxidation of Cr^{3+}, Fe^{2+} and $[SO_4]^{2-}$, and proceeds by formation of an intermediate compound which is a complex of $Cr(OH)_3$, $Fe(OH)_2$ and $[SO_4]^{2-}$ [121]. $(Na_{0.5}M_{1.5})(Fe_{0.5}Te_{1.5})O_7$ (M = Ca or Cd) adopts a Weberite structure [122].

FeS_2, iron pyrite, has been shown to contain low spin iron(II) surrounded by a trigonally distorted $(S_2)_6$ octahedral array of ligands (26). The trigonal twist splits the degeneracy of the t_{2g} levels, and the occupancies of these orbitals are $(a_g)^2(e_g)^{3.2}(e_g)^{0.8}$ [123].



(26)

Reaction of $Fe(OH)_3$ with disulphide ions at pH 9.5 gives $Na_{1.5}FeS_{1.5}(OH)_{1.5}$; however in the presence of excess S^{2-}, $NaFeS_2$ is formed [124]. Single crystals of β-$BaFe_2S_4$ have been prepared by heating BaS and Fe (1:2 ratio) at 800 °C in sulphur vapour (6.7 atm). The compound contains an $\{FeS_2\}_\infty$ framework formed by isolated columns of edge sharing $\{FeS_4\}^-$ tetrahedra, with the barium atoms located between the columns [125]. $TlFeS_2$ (synthetic raguinite) and $TlFeSe_2$ also both contain infinite linear chains of edge sharing $\{FeX_4\}$ tetrahedra [126]. The structure of Cu_2FeGeS_4 (synthetic briarite) has also been reported [127].

$FePSe_3$ reacts with pyridine to give the intercalation compound $FePSe_3py_{1/3}$, the electrical resistivity of which is closely related to the arrangement of pyridine molecules in interlayers [128]. Auger spectroscopy of FeB and Fe_2B indicates no major charge transfer between iron and boron. Localised boron-boron covalent bonding occurs in FeB, but isolated boron atoms are found in Fe_2B [129].

Mössbauer spectroscopy of voltaite, $K_2Fe_5{}^{II}Fe_3{}^{III}Al(SO_4)_{12}.18H_2O$, shows that the iron(II) ions occupy $\{O_4(OH_2)_2\}$ sites and that the iron(III) ions are in $\{O_6\}$ sites [130]. $FeCO_3$ can be prepared by the reaction of solutions of metal salts, hydroxide or oxide with CO_2 at 600–4,500 atm and 100–400 C [131]. When Fe_2O_3 is treated with H_3PO_4 under various conditions, $Fe(H_2PO_4)_3$, $Fe(HP_2O_7)$, $Fe_4(P_2O_7)_3$, $Fe(H_2P_3O_{10})$ and $Fe(PO_3)_3$ are formed [132]. Single crystals of $Fe_2{}^{III}(MoO_4)_3$ can be grown by hydrothermal techniques from $K_2[MoO_4]$–MoO_3–Fe_2O_3; the iron atoms occupy octahedral $\{O_6\}$ sites $\{r(Fe–O) = 199.2$ pm$\}$ and the molybdenum atoms occupy distorted tetrahedral $\{O_4\}$ sites $\{r(Mo–O) = 175.6$ pm$\}$ [133].

1.6 IRON(II)

1.6.1 Complexes with N-donor ligands

$FeBr_2$ reacts with $K(NPh_2)(dioxan)_3$ to yield $[Fe(NPh_2)_2(dioxan)_2]$, whereas the same reaction performed in the presence of the added ligands, L (L_2 = bipy or $(PEt_3)_2$) gives $[Fe(NPh_2)_2L_2]$. When excess $K(NPh_2)(dioxan)_3$ is used, $K_2[Fe(NPh_2)_4L_4]$ is formed [134]. $[Fe(NCSe)_6]^{4-}$, $[Fe(NCSe)_5(H_2O)]^{3-}$ and $[Fe(NCSe)_4]^{2-}$ have been prepared and Mössbauer data indicate participation of the ligand π orbitals in the bonding [135]. $[L_2Fe(NCX)_2.Hg(NCX)_2]$ (L = dmf, dmso, py or PPh_3; X = S or Se) have also been prepared [136].

The reaction of metallic iron with $[WF_6]$, $[MoF_6]$, $[PF_5]$ or $[NO]^+$ in MeCN, or the reaction of FeF_2 with $[PF_5]$ in the same solvent, gives $[Fe(MeCN)_6]^{2+}$. This cation gives $[FeCl_4]^{2-}$ or $[Fe(MeCN)\{P(OMe)_3\}_5]^{2+}$ on treatment with chlorine or $P(OMe)_3$, respectively [137]. Similar reaction of iron with CCl_4–MeCN gives $[Fe(MeCN)_6][FeCl_4]_2$. When iron is treated with excess NSF_3 in liquid SO_2 $[Fe(NSF_3)_4]^{2+}$ is formed [138].

Gillard reports that $[Fe(2,2'\text{-bipyrazine})_3]^{2+}$ is attacked by both $[OH]^-$ and H_2O at the ligand, and that the ligand is cleaved from the complex. Similar behaviour was observed for attack of $[OH]^-$ on the tris{2,2'-bis(5,6-dihydro-4-H-1,3-oxazine)}iron(II) cation [139]. A kinetic study of $[CN]^-$ and $[N_3]^-$ attack on $[Fe(bipym)_3]^{2+}$ in aqueous solution is also reported to be consistent with the mechanism of initial nucleophilic attack on the ligand, as proposed by Gillard [140].

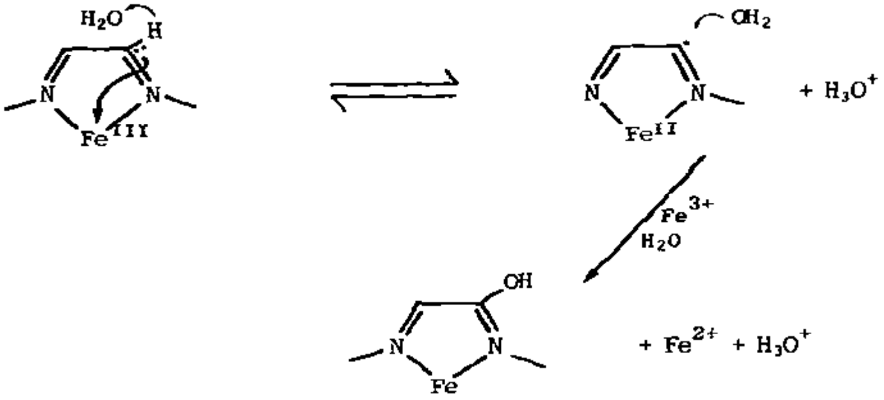
Attack of $[CN]^-$ on Λ-*fac*-$[Fe(3\text{-Mephen})_3]^{2+}$ yields C_2(*trans*)-, C, and C_2(*cis*)-$[Fe(3\text{-Mephen})_2(CN)_2]$ with the Λ enantiomer predominating. The first step of the reaction is reported to be formation of C_2(*trans*)-, C, and C_2(*cis*)-$[Fe(3\text{-Mephen})_2(CN)(H_2O)]^+$; the Δ enantiomers are formed in excess but these undergo configurational inversion to the Λ-compounds which then proceed to form the dicyanides [141].

The isolation of highly optically active (+)-$[Fe(phen)_3]Cl_2$ by a freeze drying method has been reported [142]. The complexes $[Fe(4\text{-X-bipy})_3][ClO_4]_n$ and $[Fe(4,4'\text{-}X_2\text{-bipy})_3][ClO_4]_n$ ($X = NO_2$, $n = 2$; $X = PEt_3$, $n = 5$ or 8) have been prepared [143], and the electrochemical behaviour of $[Fe(LL)_3]^{2+}$ (LL = phen, 3,4,7,8-Me_4phen or 5-NO_2phen) shows that methyl groups facilitate oxidation, whilst the nitro group impedes it [144].

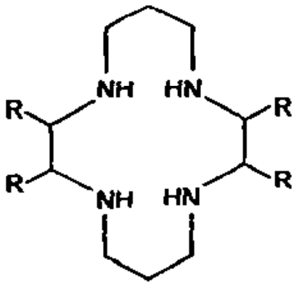
The loss of the red colour of $[Fe(phen)_3]^{2+}$ in dmso in the presence of chloride has been previously ascribed to acid solvolysis; however, Gillard has now suggested that the results were incomplete, naïvely interpreted and are irrelevant to reactions performed in water [145]. Others have studied the similar behaviour of $[Fe(phen)_3]Cl_2$ in 1,2-$C_2H_4Cl_2$, which can also be attributed to formation of $[Fe(phen)_2Cl_2]$, and observed no such change in aqueous solution. The mechanism of the reaction in dichloroethane involves formation of a contact ion pair, followed by displacement of phen by Cl^- ions. With $[Fe(phen)_3][ClO_4]_2$ in this solvent, no colour change is observed, and this is a consequence of the lower donicity of $[ClO_4]^-$ compared to that of Cl^-. In water, the Cl^- is surrounded by a solvent cage that masks its donicity [146].

The room temperature lifetimes, τ, of the excited states formed by 530 nm excitation of $[FeL_3]^{2+}$ in water are as follows: L = terpy, $\tau = 2.54$ ns; L = bipy, $\tau = 0.81$ ns; L = 4,4'-Me_2bipy, $\tau = 0.76$ ns; L = phen, $\tau = 0.8$ ns; L = 4,7-$(SO_3C_6H_4)_2$phen, $\tau = 0.43$ ns. For comparison, the lifetimes of the osmium analogues are in the range 10–100 ns [147].

Electrochemical oxidation of $[FeL_3]^{2+}$ (L = {MeN=CRCR'=NMe}, R,R' = H,H; H,Me; Me,Me; Me,Et; $(CH_2)_4$; $CH_2CHMe(CH_2)_2$; H,Ph; or Me,Ph: L = {C_5H_4NCR''=NR'''}R'',R''' = H,Me; H,Et; Me,Me; Me,Et; Me,Ph; or Me, 3- or 4-$C_6H_4NH_2$) has been reported and previous work from the same laboratory on ligand oxidation of $[Fe(MeN{=}CHCH{=}NMe)_3]^{2+}$ by cerium(IV) has been completed by a kinetic and mechanistic study. The mechanism involves initial oxidation to $[Fe(MeN{=}CHCH{=}NMe)_3]^{3+}$ followed by formation of [Fe(MeN=CHCH=NMe)$_2$(MeN=CHC(OH)=NMe]$^{2+}$, [Fe(Me=NCHCH=NMe)$_2$(MeN=CHCH=NCH OH)]$^{2+}$ and [Fe(MeN=CHCH=NMe)$_3$]$^{2+}$ in the ratio of 6:3:8. The ligand oxidation proceeds as shown in Scheme V [148].



SCHEME V: The mechanism for the oxidation of [Fe(MeN=CHCH=NMe)$_3$]$^{2+}$.



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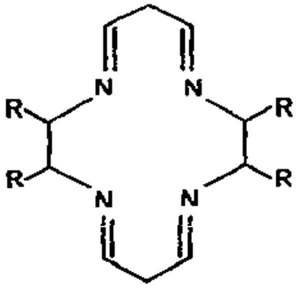
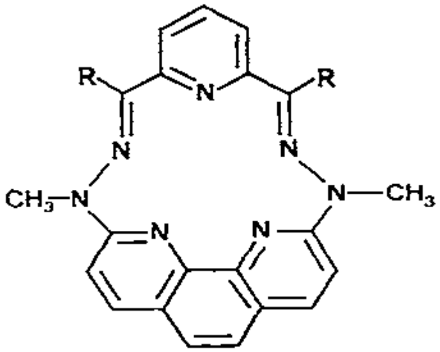


(28)

An X-ray crystallographic study of [Fe(L)(CO)(MeCN)]$^{2+}$ (L = (27; R = Me)) shows the {N_4} core to be almost planar, with the iron atom displaced by 6 pm towards the carbonyl ligand [149]. The related low spin complex, [Fe(L)(MeCN)$_2$][ClO$_4$]$_2$ (L = (27; R = H)) reacts with chloride ion to form high spin [Fe(L)Cl][ClO$_4$] which provides evidence against the argument that a macrocyclic ligand must be unsaturated or substituted for successful preparation of five-coordinate complexes. The same paper also notes that in contrast to the starting material, [FeL'(MeCN)$_2$][ClO$_4$]$_2$ (L' = H$_2$N(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_3$NH$_2$) is high spin and this difference is ascribed to the small constrictive effect of the non-cyclic ligand [150]. The kinetics of replacement of MeCN by imidazole in [FeL(MeCN)$_2$]$^{2+}$ {L = (28; R = Me or Ph)} is consistent with a dissociative mechanism where loss of the first MeCN ligand is rate determining [151].

The pentadentate macrocycles, (29), form the complexes $[FeL'(OH_2)_2]^{2+}$,



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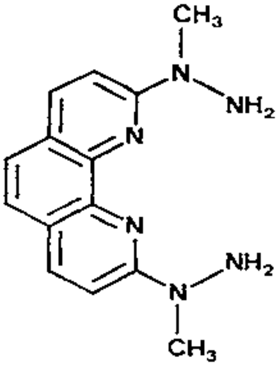

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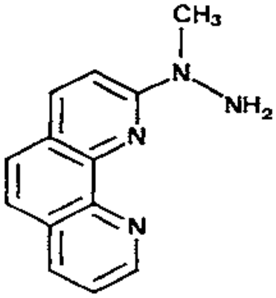
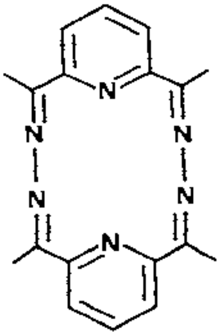


(31)

$[FeL''(OH_2)_2]^{2+}$, $[FeL''(NCS)_2]$ and $[FeL''(OH_2)][PF_6]_2$ {L' = (29, R = H); L'' = (29, R = Me)} and all are high spin. A structural study on the second of these has confirmed pentagonal bipyramidal coordination with the five nitrogen atoms coplanar and the two water molecules in axial sites. Cyclic voltammetry shows one-electron reduction of these complexes produces π-anion radicals [152]. The related acyclic ligands (30) and (31) form the complexes, $[Fe\{(30)\}]X_2.nH_2O$ ($X = Cl$, $n = 1$; $X = NCS$, $n = 2$), $[Fe\{(31)\}_2]Cl_2$ and $[Fe\{(31)\}][BF_4]_2.1.5H_2O$ [153].

In order to obtain information on the electronic effects of the extensive conjugation in macrocyclic ligands, the complex $[Fe\{(32)\}(MeCN)_2]^{2+}$ has been



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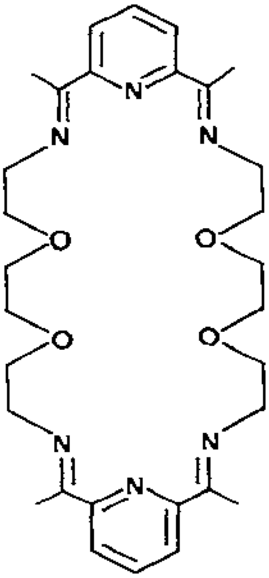

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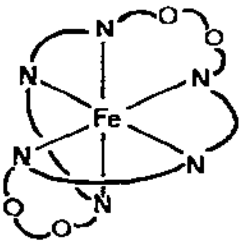


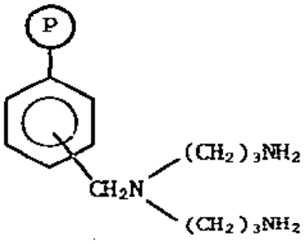
(34)

prepared. This undergoes one-electron oxidation to $[Fe\{(32)\}(MeCN)_2]^{3+}$ and also reduction to firstly $[Fe\{(32)\}(MeCN)]^+$ and then to $[Fe\{(32)\}]$. This neutral complex undergoes oxidative addition with MeI to yield $[Fe\{(32)\}(Me)I]$, which can also be obtained from $[Fe\{(32)\}I_2]$ and MeMgI [154]. The 30-membered macrocycle (33) forms the low spin cation $[Fe\{(33)\}]^{2+}$ when iron(II) salts are treated with $[Pb_2\{(33)\}(SCN)_4]$. The lead complex has all ten donor atoms bonded to the two metal ions, but there is no evidence for such iron analogues and the isolated iron complex is six-coordinate, as shown in (34) [155].

$[Fe(CO)_5]$ reacts with 1,2-$C_6H_4(CN)_2$ in dmf at 110 to 140 °C to give a 70% yield of [Fe(Pc)(CO)(dmf)], which on heating *in vacuo* gives α- and β-[Fe(Pc)] [156]. Other adducts, [Fe(Pc)(CO)L] (L = thf, H_2O, MeOH, Et_2NH or Et_3N) have also been prepared, and the structure of the diamagnetic dmf complex determined {r(Fe–CO) = 172 pm} [157]. The first bis-adduct of [Fe(Pc)], $[Fe(Pc)(dmso)_2]$.2dmso has also been isolated, and both dmso ligands are *S*-bonded [158]. [Fe(Pc)] has been shown to be an effective catalyst for the decomposition of N_2H_4 to NH_3 and N_2; the α-form is several orders of magnitude more effective than the β-form [159]. A re-examination of the reaction of [Fe(Pc)] with O_2 has led to the characterisation of $[\{Fe(Pc)\}_2O]$, rather than $[\{Fe(Pc)\}_2O_2]$ as previously reported [160].

The ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine, (L), forms the five-coordinate complexes, $[Fe(L)X][BPh_4]$ (X = Cl or Br) and the octahedral complex, $[Fe(L)(NCS)_2]$ [161]. The related ligands, 1,1'-methylene-bis(3,5-dimethyl-pyrazole)(L'), tris(1-pyrazolyl)methane(L'') and bis(3,5-dimethyl-pyrazolyl)methane(L''') form the *pseudo*tetrahedral complexes $[Fe(L')X_2]$ (X = Cl or Br) and $[Fe(L''')][ClO_4]_2$, the *pseudo*octahedral complexes $[Fe(L')_2X_2]$ (X = I or NCS) and $[Fe(L'')Br_2]$, the trigonal bipyramidal complexes, $[Fe(L')_2X][BPh_4]$ (X = Cl, Br or I) and the polymeric complex, $\{Fe(L'')(NCS)_2\}_n$ [162,163]. A structural study of $[Fe\{HB(R_3)\}_2]$ (R = pyrazolyl or 3,5-dimethylpyrazolyl) has shown the Fe–N distances to be 197.3 or 217.2 pm respectively. The former complex is low spin and the latter high spin; this bond length difference is one of the largest so far reported between closely related complexes varying in spin state [164].

The polymer supported triamine (35) has been prepared and used to make Schiff



(35)

base ligands. The iron(II) complex formed under anaerobic conditions, undergoes irreversible oxidation upon exposure to oxygen to give an Fe–O–Fe containing species; this was presumed to occur because the Fe atoms are insufficiently separated on the surface [165].

Reaction of $[FeClL_2(cp)]$ (L = PPh_3, $P(OMe)_3$, $P(OPh)_3$ or CO) with silver triazenides yields $[FeL(RN_3R')(cp)]$ (R,R' = 4-MeC_6H_4 or 4-ClC_6H_4), a reaction which proceeds *via* initial formation of an Fe–Ag bond. These compounds undergo one-electron electrochemical oxidation, but chemical oxidation with $[NO]^+$ gives $[Fe(CO)(NO)(RN_3R')(cp)]^+$ [166].

$FeCl_2.2H_2O$ reacts with $Na[BH_3(CN)]$ and $P(OR)_3$ (R = Me or Et) to give $[Fe\{BH_3(CN)\}_2\{P(OR)_3\}_4]$, which can also be obtained electrochemically by anodic dissolution from an iron electrode into an ethanenitrile solution of $[BH_3(CN)]^-$ and $P(OR)_3$. The chemical route gives only the *trans* product in methanol, but in ethanenitrile a *cis*, *trans* (30:70) mixture is obtained: the electrochemical method gives a *cis*, *trans* (65:35) mixture with $P(OEt)_3$. The reasons for these differences are not clear. In the absence of phosphite, the electrochemical method yields $[Fe\{BH_3(CN)\}_2(MeCN)_4]$ [167].

Other studies on complexes of N-donor ligands are detailed in Table 1.

1.6.2 Complexes with O-donor and S-donor ligands

Dissolution of iron in SO_2–dmso gives $[Fe(dmso)_6][S_2O_7]$. The presence of the $[SO_2]^{\dot{-}}$ radical anion and $Fe^{2+}/[SO_2]^{\dot{-}}$ ion pairs in the solution was demonstrated [168]. The octahedral complexes, $[Fe(dioxan)_6][InCl_4]_2$ [169a] and $[Fe(caprolactam)_6][BF_4]_2$ [169b] have been prepared, and the crystal structure of $[Fe(urea)_6][ClO_4]_2$ has been determined [170].

The aryloxy and alkoxy complexes $[Fe(OC_6H_4X)_2L_n]$ and $[Fe(OR)_2L_n]$ (L = bipy; X = NO_2, CN, Cl, Ph, H or Me; R = Me, Et, $CHMe_2$ or $PhCH_2$) have been prepared, and are active as catalysts for transesterification and for the dimerisation of benzaldehyde [171].

Quinoline *N*-oxide (quinNO) and pyridine-N-oxide (pyNO) form the complexes, $[Fe(quinNO)_2][FeBr_4]$ and $[Fe(oxalate)L_n]$ (L = quinNO or pyNO; n = 2 or 4) [172]. The polymeric compounds $\{FeL'_xX\}_n$ (L' = $(CH_2{=}CHCH_2O)_3PO$; X = ClO_4, BF_4, Cl, Br, I, NCS or NO_3; x = 2–4) were prepared by reaction of poly(triallylphosphate) with the respective metal salts [173].

Complexes containing acacH and $MeC(O)CH_2CO_2Et$ ligands in their keto forms have been prepared by a chloride-ion transfer reaction, which involves treating iron(II) chloride with $InCl_3$ and anhydrous acacH or $MeC(O)CH_2CO_2Et$ (1:2:3.05 ratio) in nitromethane. The products $[Fe(acacH)_3][InCl_4]_2$ and $[Fe(MeC(O)CH_2CO_2Et)_3][InCl_4]_2$ both contain octahedral cations [174]. Other complexes containing *O*-donor ligands are listed in Table 1.

TABLE 1

Miscellaneous Studies on some Iron(II) Complexes

Compound	Comments	Ref.
$[Fe(LH)_2].2H_2O$, $[FeCl(LH)].2H_2O$ (LH_2 = 5-(pyridin-2-yl)-tetrazole)	preparations described	a
$[Fe(CN)_4\{(1R,2R)\text{-}1,2\text{-cyclopentanediamine}\}]^-$	preparation and CD spectrum	b
$\{Fe(O_2CCH_2OC_6H_4X\text{-}4)_2\}_n$ (X = NO_2, Me or Cl)	preparations described	c
$[FeL_2].nH_2O$ (LH = 3-methylpyrazol-5-one; n = 0 or 2)	preparation described	d
$[FeL_2]$ (LH = 4'-methyl-4-hydroxy-3-carboxyazobenzene)	preparation described; tetrahedral Fe(II)	e
$[Fe(\text{4-benzoquinonediimine})X_2]$ (X = ClO_4, Cl or Br)	preparations described	f
$[Fe(\text{isonicotinic acid hydrazide})][SO_4].2H_2O$	preparation described; high-spin octahedral Fe(II)	g
$\{FeL\}_n$ (H_2L = *N*,*N'*-di(thiocarbamoyl)-hydrazine)	preparation described	h
$[Fe(tte)_2L_2]$ (tte = thiotheonyltrifluoroethanoate, L = py or 4-Mepy)	preparation described; high-spin octahedral Fe(II)	i
$[Fe(L)X_2]$ (L = vanillinthiocarbohydrazone)	preparation described	j
$\{Fe(\text{hydrazodithioamide})\}_n$, $\{Fe(\text{hydrazodicarbonamide})\}_n$	preparations described	k,l
$[Fe(PhCH{=}NNHCSNHNHCOCH_2Ph)_2X_2]$ (X = Cl, Br, I, NO_3 or NCS)	preparation described	m
$[Fe(\text{thiophen-2-aldoxime})_2X_2]$ (X = Cl, Br, I, I, NCS or NCSe)	preparation described; high-spin *trans*-octahedral Fe(II)	n
$[Fe(\text{pyridine-2-aldoxime})_2X_2]$ (X = Cl, Br, I, NCS)	preparation described; temperature dependent μ_{eff}	o
$[Fe(\text{2'-hydroxy-4-methoxy-5'-methylchalcone})_3]$	preparation described	p
$\{Fe(\text{hydrazodicarbonimide})\}_n$	preparation described	q
$[FeL_2]$ {LH = 2-amino-5-(2-phenoxy)-1,3,4-thiadiazole}	preparation described; octahedral Fe(II)	r
$\{FeL(H_2O)_2\}_n$ (LH = 5,5'-(4,4'-biphendiyl(bisazo(bis 8-hydroxyquinoline)	preparation described	s
$[FeL_2]X_2$ (L = 2-hydrazinoquinoxaline; X = Cl or $\frac{1}{2}[SO_4]$)	preparation described; tetrahedral Fe(II)	t
$[FeL_2Cl(H_2O)].2H_2O$ (LH = quinazoline-2-thione-4-one)	preparation described	u

TABLE 1 (continued)

Compound	Comments	Ref.
$[FeL_2]$ (LH_2 = 2-(*N*—α—furfuralideneimino)-benzoic acid)	preparation described	v
$H_2Fe_4L_5.xH_2O$ (L = eosine)	preparation described; polymeric	w
iron(II) complexes of 1-(2-pyridylazo)-2-naphthol	Mössbauer study	x
iron(II) complexes of Schiff bases from salicylaldehyde and sulphamethoxypyridazine	preparations described	y
iron(II) complexes of 2-(*N*—α—pyrrolyl-methyleneamino)benzenesulphonic or -ethane sulphonic acids	preparations described	z

(a) N.S. Gill and F.Y. Yang, *Aust. J. Chem.*, 32 (1979) 1669. (b) M. Goto, M. Takeshita and T. Sakai, *Bull. Chem. Soc. Jpn.*, 52 (1979) 2589. (c) C. Natarajan and R. Rengasamy, *Indian J. Chem. Sect. A*, 18 (1979) 356. (d) S.N. Podder and A.K. Das, *Indian J. Chem. Sect. A*, 18 (1979) 429. (e) S.D. Goswami, *Curr. Sci.*, 48 (1979) 812. (f) M. Zaghal and H.A. Tayim, *J. Inorg. Nucl. Chem.*, 41 (1979) 889. (g) C.B. Mahto, *J. Indian Chem. Soc.*, 57 (1980) 485. (h) K.C. Satpathy and T.D. Mahana, *J. Indian Chem. Soc.*, 56 (1979) 1173. (i) T. Maitani, T. Kobayashi and Y. Saito, *J. Inorg. Nucl. Chem.*, 41 (1979) 1689. (j) G. Macarovici and S. Barbu, *Rev. Roum. Chim.*, 24 (1979) 1039. (k) D.G. Batyr, B.M. Balogna, E.V. Popa and Y.Y. Karitonov, *Koord. Khim.*, 6 (1980) 968. (l) D.G. Batyr, B.M. Balogna, E.V. Popa and Y.Y. Kharitonov, *Koord. Khim.*, 6 (1980) 1125. (m) M.C. Jain, R.K. Sharma, K. Ram and P.C. Jain, *Gazz. Chim. Ital.*, 109 (1979) 601. (n) M. Mohan, *Gazz. Chim. Ital.*, 109 (1979) 655. (o) M. Mohan, G. Mittal, H.C. Khera and A.K. Sirivastava, *Monatsch. Chem.*, 111 (1980) 63. (p) N.S. Bhave and R.B. Kharat, *J. Indian Chem. Soc.*, 56 (1979) 244. (q) D.G. Batyr, B.M. Baloyan, E.V. Popa and Y.Y. Kharitonov, *Koord. Khim.*, 6 (1980) 807. (r) N.B. Singh, J. Singh, K.K. Pathak and N.K. Singh, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 60. (s) V. Banerjie and A.K. Dey, *Polym. Bull.*, 1 (1979) 685. (t) K.D. Schleinitz, G. Westphal, A. Surkau and D. Lochner, *J. Prakt. Chem.*, 322 (1980) 199. (u) B. Singh, M.M.P. Rukhayer, R.K. Mehra and R.J. Sinha, *Indian J. Chem. Sect. A*, 17 (1979) 520. (v) N.K. Sankha, D.C. Sehgal and R.K. Mehta, *J. Indian Chem. Soc.*, 56 (1979) 1030. (w) B. Agarwal, B.V. Agarwala and A.K. Dey, *Rev. Chem. Miner.*, 16 (1979) 535. (x) K.B. Pandeya, R.P. Singh, G.L. Sowhney and J.S. Baijal, *Solid State Commun.*, 32 (1979) 823. (y) K. Lal, *Rev. Roum. Chim.*, 25 (1980) 355. (z) C.P. Gupta, N.K. Sankhla and R.K. Mehta, *J. Prakt. Chem.*, 321 (1979) 691.

A structural study of $\{Fe(thiourea)_2(NCS)_2\}_n$ shows it to be polymeric with iron atoms in octahedral environments coordinated to four equatorial *S*(thiourea) atoms and two axial *N*(thiocyanate) atoms: each sulphur is shared by three iron atoms [175]. Mössbauer data shows the co-existence of two solid state isomers of $[FeL_6][ClO_4]_2$ (L = *N*,*N'*-dicyclohexylthiourea) between 200 and 300 K: these arise by alteration of the hydrogen bonding of the cation to the perchlorate anions [176].

The chelating *SS*-ligand, 2,4-dithiobuiret (Hdtb) forms the high-spin complexes $[\mathrm{Fe(Hdtb)}_n\mathrm{X}_2]$ (n = 1 or 3; X = Cl, Br, I or $\frac{1}{2}[\mathrm{SO_4}]$) [177]. Thiomalic acid ($\mathrm{H_3L}$) forms the octahedral complexes $\mathrm{A[FeL]}.n\mathrm{H_2O}$ (A = Li, Na or K) and $\mathrm{[Fe(LH)]}.n\mathrm{H_2O}$ [178].

1.6.3 *Complexes with P-donor ligands*

The secondary phosphine complexes, $\mathrm{[FeX(HPR_2)_4]Y}$ and $\mathrm{[Fe(HPR_2)_5]Y_2}$ (X = Cl, Br or I; Y = $\mathrm{BF_4}$ or $\mathrm{PF_6}$; $\mathrm{R_2}$ = MePh, EtPh or $\mathrm{Et_2}$) have been prepared. The first series have triplet ground states, but the second have magnetic moments in the range 1.4 to 2.5 μ_B. Reactions with CO give $\mathrm{[FeX(CO)(HPR_2)_3]^+}$ or $\mathrm{[Fe(CO)_2(HPR_2)_4]^{2+}}$ respectively [179].

The structures of *trans*-$[\mathrm{FeCl_2}(cis\text{-}\mathrm{Ph_2PCH{=}CHPPh_2})_2].\frac{1}{2}\mathrm{Me_2CO}$ [180] and $\mathrm{[FeCl_2\{PhP(CH_2CH_2PPh_2)_2\}_2]}.\frac{1}{2}\mathrm{Me_2CO}$ [181] have been determined, and both have octahedral geometry. $\mathrm{PhP(CH_2CH_2PPh_2)_2}$ reacts with $\mathrm{[Fe(H_2O)_6]^{2+}}$ and $\mathrm{H_2S}$ in propanone to form $\mathrm{[Fe_2(\mu\text{-}SH)_3\{PhP(CH_2CH_2PPh_2)_2\}_2][ClO_4].Me_2CO}$. The cation has a confacial bioctahedral structure in which each iron atom is bound to three phosphorus atoms of one ligand molecule, and three bridging SH groups [182].

Electron-poor organometallic cations always undergo hydride attack at a ligand. However, little is known of the behaviour of electron-rich cations. One of these, $\mathrm{[Fe\{PhP(CH_2CH_2PPh_2)_2\}(cp)]^+}$, has been prepared by reaction of $\mathrm{[FeCl_2\{PhP(CH_2CH_2PPh_2)_2\}]}$ and thallium(I) cyclopentadienide. Hydride attack on this cation gives $\mathrm{[Fe(H)\{PhP(CH_2CH_2)PPh_2)_2\}(cp)]}$, but deuteration studies show metal-cp hydrogen exchange to be occurring [183].

$\mathrm{[FeH_2(N_2)(PBuPh_2)_3]}$ reacts with $\mathrm{CO_2}$ under ambient conditions to give $\mathrm{[Fe(O_2CH)_2(PBuPh_2)_2]}$. This is less stable than the $\mathrm{PEtPh_2}$ analogue due to both the higher σ donor power and the large size of the $\mathrm{PBuPh_2}$ ligand. With $\mathrm{[FeH_2L_4]}$ (L = $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PEt_2Ph}$, $\mathrm{P(OEt)_2Ph}$ or $\mathrm{P(OEt)_3}$) and $\mathrm{[FeH_2(dppe)_2]}$, there was no reaction with $\mathrm{CO_2}$. This can be partly ascribed to the bulk of the ligands, but is also due to the absence of a readily available vacant site (*n.b.* such a site is formed in the earlier complexes by loss of $\mathrm{N_2}$) [184]. $\mathrm{CS_2}$ insertion into $\mathrm{[FeH(dppe)(cp)]}$ gives $\mathrm{[Fe(S_2CH)(dppe)(cp)]}$ [185].

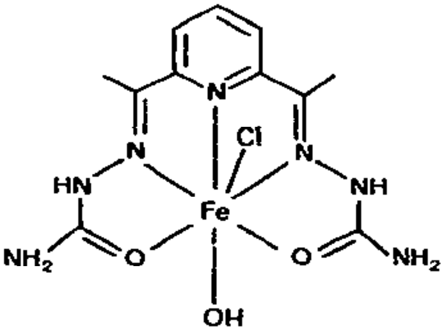
The electrochemical behaviour of $\mathrm{[Fe(dppe)_2L_2]^{2+}}$ (L = MeCN) shows two reduction steps giving $\mathrm{[Fe(dppe)_2(MeCN)]^+}$ and the rather labile $\mathrm{[Fe(dppe)_2(\eta^2\text{-}MeCN)]}$. In contrast, when L = CO, two electrons are taken up in a single step [186].

The structure of $\mathrm{[FeI\{(-)\text{-}diop\}(cp)]}$ has been determined and the conformation of the chelate ring compared with those observed in other diop complexes [187].

1.6.4 *Complexes with mixed donor ligands*

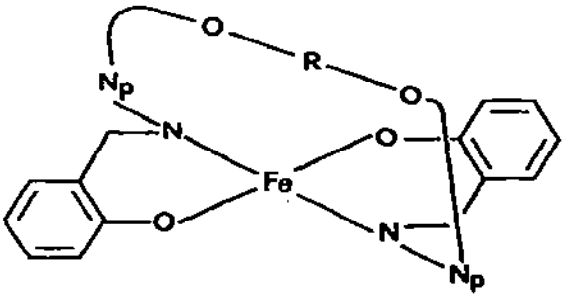
In view of the use of $\mathrm{edtaH_4}$ as an analytical reagent, it is perhaps surprising that little attention has been paid to complexes of simple derivatives such as esters and amides. However [Fe{edta(Me)$_4$}]Cl$_2$ has been obtained and contains octahedral coordination of the cation in solution. In the solid state, one or both of the chlorides are also coordinated [188a]. Stopped-flow kinetics of the reaction of O$_2$ with {Fe^{II}(edta)} in neutral or acidic solution indicates the formation of an intermediate O$_2$-complex, which then interacts with a proton and a second iron(II) atom. This leads to O$_2$ reduction by a radical mechanism with the intermediate formation of $HO_2^{\cdot}$. [188b].

A detailed study has been made of the magnetic and spectroscopic properties of the pentagonal bipyramidal complex, (36), and these have been reproduced by



(36)

MO calculations based on an angular overlap model [189]. There has been considerable interest in capped or basket handle porphyrins (see Section 1.9.1). In an attempt to restrict the size of the cavity under the handle, Schiff base complexes containing the linking atoms bonded directly to the ligating atoms have been prepared, (37) [190].



(37; Np = naphthyl)

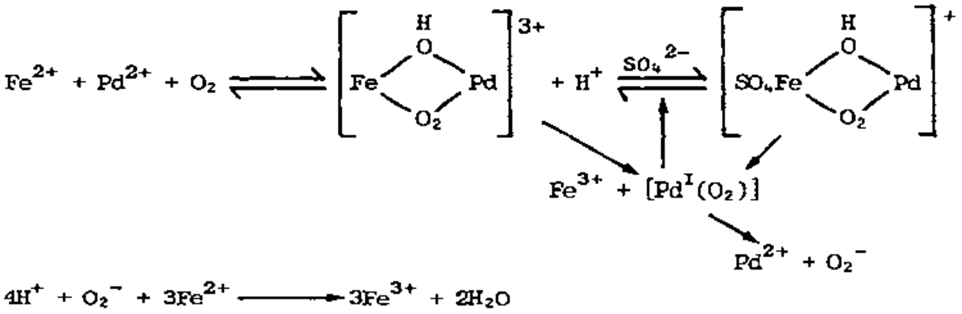
The complexes, $[Fe(\alpha\text{-diox})_3][M(dto)_2]$ (α-diox = condensation product of bipy or phen with diacetylbis(*N*-methylamine), dto = dithiooxalate, M = Ni^{II} or Pt^{II}) and $[Fe(bipy)_n][WS_4]$ (*n* = 2 or 3) have been prepared. Resonance Raman spectroscopy has been used to differentiate between the electronic absorption spectra of the two chromophores present in each compound, even when there is spectral overlap [191]. $[FeL_2(B)_2]$ (HL = α-furyldioxime; B = py, 3-HOpy, 2-Mepy or imidazole) showed changes in their electronic spectra, on standing, that were ascribed to hydrogenation of L [192].

A structural study on $[Fe(HL)_2(H_2O)_2]Cl_2.2H_2O$ (HL = 2-hydrazino-4-hydroxy-6-methylpyrimidine) has shown the ligand to be in the keto-form with the proton from the hydroxy group on N^1 of the ring [193]. 1-(2-hydroxyphenyl)iminomethyl-2-naphthol (H_2L) and *N*,*N*-bis-2-ethylaminoethyl)-2-hydroxyethylamine (L') form the dimeric complexes, $[Fe_2L_2]$ and $[Fe_2L'_2]^{2+}$ [194,195].

Cysteine forms the complexes $[Fe(cys)(H_2O)_{1.5}]$ and $Na_2[Fe(cys)_2H_2O]$. The former contains {*SNO*}-ligand chelation, whereas the latter (and $[Fe(Mecys)_2(H_2O)_{1.5}]$) both contain only {*SN*} chelation [196]. The high-spin complex, $[FeL(ClO_4)(H_2O)_2(EtOH)]$ (HL = adenine) has been prepared by warming hydrated $[Fe(ClO_4)_2]$ in $(EtO)_3CH$ and EtOH for 2 h, followed by boiling with HL for 48 h [197]. Other studies on iron(II) mixed donor ligand complexes are given in Table 1.

1.6.5 *Miscellaneous*

The kinetics of the oxidation of $[Fe(H_2O)_6]^{2+}$ by iodate has been investigated. The reactions were performed in the presence of allyl alcohol to remove any complications of Fe(II) oxidation by iodine arising from iodate reduction. A mechanism involving the $[IO_2]^-$ ion was tentatively advanced [198]. The oxidation of $[Fe(H_2O)_6]^{2+}$ by O_2 in the presence of catalytic amounts of Pd(II) follows the mechanism shown in Scheme VI [199]. A kinetic study has also been



SCHEME VI: The mechanism for the oxidation of $[Fe(H_2O)_6]^{2+}$ by O_2 in the presence of Pd(II).

made of the oxidation of $[Fe(H_2O)_6]^{2+}$ by nitric acid (equation 6), which is the

$$3Fe^{2+} + 4H^+ + NO_3^- \rightleftharpoons 3Fe^{3+} + 2H_2O + NO \qquad (6)$$

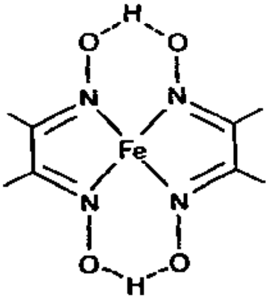
basis of the brown ring test [200]. Photooxidation of $FeSO_4$ in H_2SO_4 gives iron(III) and dihydrogen in a 2:1 mole ratio [201].

1.7 IRON(III)

1.7.1 Complexes with N-donor ligands

Reaction of $FeCl_3$ with $K(NPh_2)(dioxan)_3$ gives $K[Fe(NPh_2)_4]$ [134]. A Mössbauer study of $[Fe(NCSe)_6]^{3-}$ indicates the participation of ligand π-orbitals in bonding to the metal [135].

Charge-transfer photochemistry of $[Fe\{(28)\}(OMe)(MeOH)]^{2+}$ and $[Fe(dmg)_2(OMe)(MeOH)]$ (38) can be described as photooxidation of coordinated methanol and reduction of the metal atom as shown in Scheme VII [202].



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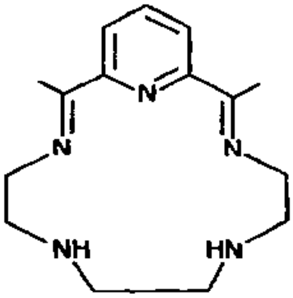

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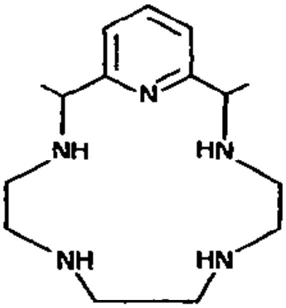

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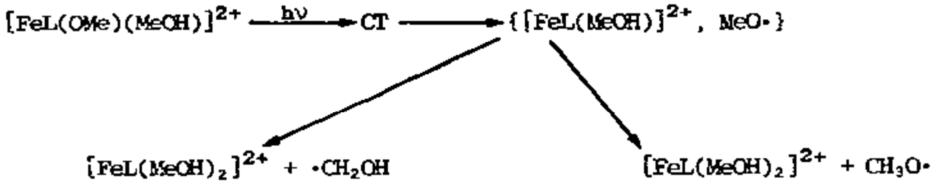


$$[FeL(OMe)(MeOH)]^{2+} \xrightarrow{h\nu} CT \longrightarrow \{[FeL(MeOH)]^{2+}, MeO\bullet\}$$

$$CH_3O\bullet + CH_3OH \longrightarrow CH_3OH + \bullet CH_2OH$$

$$2\bullet CH_2OH \longrightarrow CH_2O + CH_3OH$$

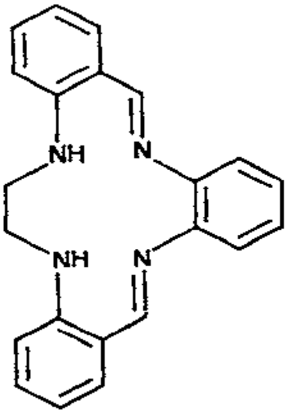
$$\bullet CH_2OH \longrightarrow CH_2O\bullet + H$$

$$CH_2O\bullet + FeL(OMe)(MeOH)]^{2+} \longrightarrow CH_2O + [FeL(MeOH)_2]^{2+}$$

SCHEME VII: Mechanism for the photooxidation of coordinated methanol.

Photochemical activity of $[Fe(L)X_2]^+$ (L = (39) or (40); X = Cl, Br, I, N_3 or NCS) also involves reduction of the metal with concurrent oxidation of X [203].

The complex $[FeL(O_2CMe)]$ (L = (41)), when held in dmf at 80 °C for 6 h, gives



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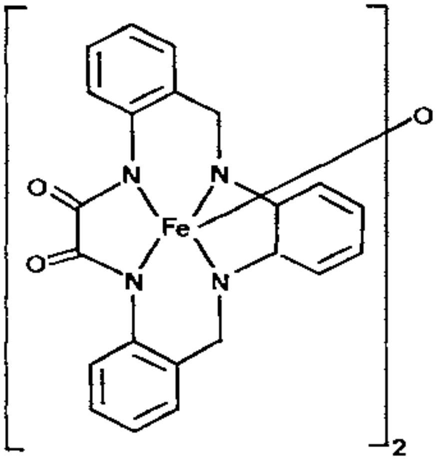
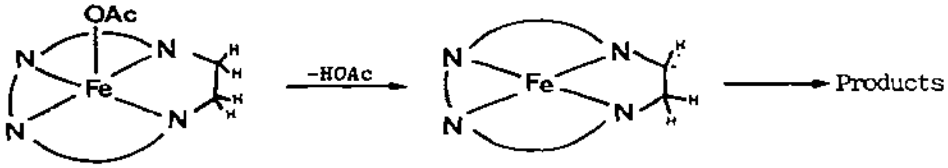


(42)

rise to ligand oxidation and metal-oxo dimer formation yielding (42). The reaction is believed to proceed *via* the radical mechanism shown in Scheme VIII [204].



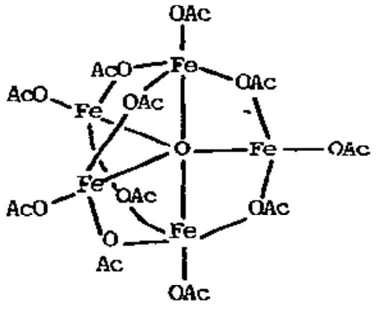
SCHEME VIII: Mechanism for the formation of (42).

The ligand (30) forms the complex $[\{Fe[(30)]Cl_2\}_2O].2H_2O$ [153]. The complexes $[Fe_2OL_4]Cl_4$ (L = bipy or phen) catalyse the conversion of water to oxygen [205]. Iron(III) 4,4',4'',4'''-tetracarboxyphthalocyanine also shows this catalase-like activity and is much more efficient than the above complexes, hemin or other metal phthalocyanines [206]. Similar behaviour has been observed with iron(III) phthalocyanine bound to polystyrene [207]. 3,3',3'',3''',4,4',4'',4'''-octacarboxyphthalocyanine iron(III) shows peroxidase-like activity in catalysing the oxidation of guiaiacol by H_2O_2 [208]. $H_3[FeL].8H_2O$, $Na_3[FeL].\frac{1}{2}NaOH.4H_2O$, $K_3[FeL].\frac{1}{2}KOH.4H_2O$ and $Cs_3[FeL].1.5CsOH.2H_2O$ (L = 4,4',4'',4'''-tetrasulphophthalocyanine) have been prepared. The first of these exists in low-spin and intermediate-spin forms, whereas the three salts all exist as two different low-spin isomers. In solution, the sodium salt is high-spin at low concentration, and low-spin at high concentration. No evidence was found for the formation of Fe–O–Fe bridged species in this study [209]. A separate study has shown this [FeL]$^{3-}$ anion to be low spin in aqueous solution of low pH containing about 20% (v/v) dmf, and to be reduced by [BH$_4$]$^-$ to [Fe^{I}L]$^{5-}$. Reduction with pyridine gives a species which is EPR inactive, and is thought to be an Fe(I)-ligand radical anion complex. This can be reoxidised to the starting material by O$_2$. With NH$_2$OH, [FeL]$^{3-}$ forms [Fe(NO)L] [210].

A structural study on high spin [FeCl$_3$(4-CNpy)$_2$] shows it to be a rare example of trigonal-bipyramidal coordination of iron(III). The only other known example is [Fe(N$_3$)$_5$]$^{2-}$ [211]. FeCl$_3$ reacts with S$_4$N$_4$ in CCl$_4$ to give α-FeCl$_3$.S$_4$N$_4$, which has a tetrahedral $\{Cl_3N\}$ coordination sphere [212]. Other *N*-donor ligand complexes of iron(III) are listed in Table 2.

1.7.2 Complexes with O-donor ligands

The structures of Rb$_5$[Fe$_3$O(SO$_4$)$_6$].5H$_2$O and K$_{2.64}$Tl$_{2.36}$[Fe$_3$O(SO$_4$)$_6$].5H$_2$O have been reported. Both contain three $\{FeO_6\}$ octahedra sharing common corners the oxo atom, and are further linked by three pairs of bridging SO$_4$ ligands [213]. The related complexes [Fe$_2$MO(O$_2$CCH$_2$I)$_6$(H$_2$O)$_3$] (M = Fe, Mn, Co, Ni, Cu or Zn) have been prepared from MCl$_2$, FeCl$_3$ and [ICH$_2$CO$_2$]K in ICH$_2$CO$_2$H [214]. On the basis of a magnetic study it has been suggested that [Fe$_5$O(O$_2$CMe)$_{12}$][O$_2$CMe] contains a trigonal bipyramidal array of metal atoms linked to a central oxo atom. Each metal atom is bonded to one terminal ethanoate, and the bridging ethanoate ligands are arranged as shown in (43) [215].



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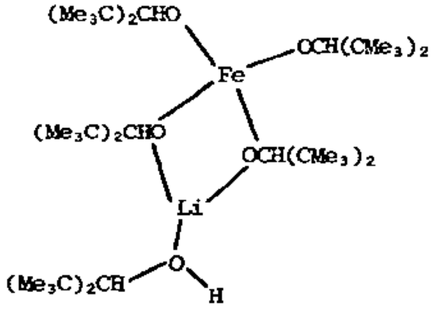


(44)

Reaction of FeCl$_3$ with Li[OCH(CMe$_3$)$_2$] did not lead to [Fe{OCH(CMe$_3$)$_2$}$_3$], but gave (44) [216].

[Fe(acac)$_3$] reacts with RCO$_2$H (R = CHCl$_2$, CH$_2$Cl, CCl$_3$, *etc.*) or with X$_2$

TABLE 2

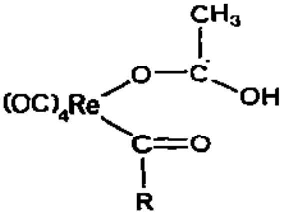
Miscellaneous Studies on some Iron(III) complexes

Compound	Comment	Ref.
$[\mathrm{FeL_2X_2}]\mathrm{X}$, $[\mathrm{FeLCl_3}]$ (L = melamine; X = Cl or $\mathrm{NO_3}$)	preparation described; octahedral Fe(III)	a
$[\mathrm{FeL_3}]$ (HL = 2-oxocyclopentanoic acid ethyl ester)	preparation described	b
$[\mathrm{Fe(quinNO)_4Br_2}][\mathrm{FeBr_4}]$ (quinNO = quinoline *N*-oxide)	preparation described	c
$[\mathrm{FeL_3}]$ (L = 4,6-dihydroxycoumaran-3-one	preparation described	d
$[\mathrm{FeCl_3(OAsPh_3)_{1.5}}]$, $[\mathrm{FeCl_3(OAsPh_3)_2}]$	preparation from $\mathrm{AsPh_3}$ described	e
$[\mathrm{Fe(SbCl_3)Cl_5}]^{2-}$, $[\mathrm{Fe(SbCl_3)_2Cl_4}]^{2-}$	preparation described	f
iron(III) complexes of nicotinaldehyde-thiocarbohydrazone	preparation described	g
$[\mathrm{FeL_3}].6\mathrm{H_2O}$ (LH = 2'-hydroxy-4-methoxy-5'-methylchalcone oxime)	preparation described	h
iron(III) complexes of 2-amino-5-phenyl-1,3,4-oxadiazole	preparation described	i
iron(III) complexes of 2-HO-4-$\mathrm{ROC_6H_3CPh{=}N(CH_2)_\mathit{n}N{=}CPhC_6H_3}$4-OR-2-OH ($n$ = 2 or 3)	preparation described	j
iron(III) complexes of 3-diphenylaminomethyl)-5-(2-hydroxyphenyl)-1,3,4-oxadiazole-2-thione	preparation described	k
$[\mathrm{FeL_2}][\mathrm{ClO_4}].2\mathrm{H_2O}$ (HL = 1-(2-pyridylazo)-2-naphthol or -2-phenanthrol	preparation described; complexes exhibit a doublet ground state	l
$[\mathrm{FeL_3}]$ (HL = 4-(4-dimethylanilino)-3-penten-2-one)	preparation described	m
iron(III) complexes of phenylphthalimic acid	preparation described	n
$[\mathrm{Fe(2\text{-}picolylamine)_3}]\mathrm{Cl_2}.2\mathrm{H_2O}$	structure reported	o
iron(III) complexes of cinnamoylhydrazine	preparation described	p
$[\mathrm{Fe(HL)L}]$, $[\mathrm{Fe(HL)_2}]\mathrm{X}$ ($\mathrm{H_2L}$ = 2-$\mathrm{HOC_6H_4CH{=}NN{=}C(SMe)NH_2}$; X = Cl, Br or $\mathrm{NO_3}$)	preparation described	q
$[\mathrm{FeL_3}]$ (HL = 8-HO-5-quinolinyl-COCH=CHPh)	preparation described	r
$[\mathrm{Fe_2L(OH)_2}]$ ($\mathrm{H_4L} = \{\mathrm{HO_2CCH_2CH(CO_2H)}\}_2\mathrm{S}$)	preparation described	s

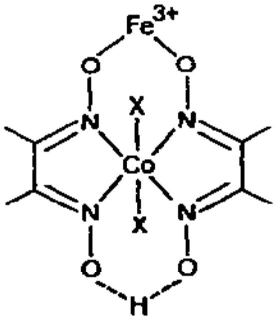
TABLE 2 (continued)

(a) C. Gheorghiu, M. Bicher, C. Marculescu, L. Diamandescu and D. Barb, *Rev. Roum. Chim.*, 24 (1979) 815. (b) M.A. Banares, C.A. Angos and A.S. Yanez, *An. Quim.*, 75 (1979) 795 [*Chem. Abstr.*, 93 (1980) 36081]. (c) [172a]. (d) R. Raina and M.L.D. Lar, *J. Indian Chem. Soc.*, 57 (1980) 673. (e) V. Vancova, M. Melnik, G. Ondrejovic and J. Gazo, *Z. Anorg. Allg. Chem.*, 455 (1979) 93. (f) M. Dinculescu, *Bul. Inst. Politch. "Gheorghe Gheorghiu-Dej" Bucuresti Ser. Chim. Metal.*, 40 (1978) 83 [*Chem. Abstr.*, 92 (1980) 103551]. (g) S. Barbu and G. Macarovici, *Rev. Roum. Chim.*, 25 (1980) 207. (h) N.S. Bhave and R.V. Kharat, *J. Indian Chem. Soc.*, 56 (1979) 244. (i) N.B. Singh and J. Singh, *Indian J. Chem. Sect. A*, 17 (1979) 424. (j) U. Dinju, H. Stahl and E. Uhlig, *Z. Anorg. Allg. Chem.*, 464 (1980) 37. (k) R.A. Rai and U. Agarwala, *Indian J. Chem. Sect. A*, 18 (1979) 426. (l) Y.K. Bhoon, K.B. Pandeya and R.P. Singh, *J. Indian Chem. Soc.*, 57 (1980) 286. (m) S.K. Agarwal and R.C. Saxena, *J. Indian Chem. Soc.*, 56 (1979) 925. (n) V.V. Korshak, E.E. Danilenko, V.V. Trachevskii, M.T. Bryk, G.M. Tseitlin and M.S. Ustinova, *Dokl. Akad. Nauk, SSSR*, 248 (1979) 1160. (o) M. Mikami, M. Junno and Y. Saito, *Koen Yoshishu-Bunshi Kozo Sogo Tornokai*, (1979) 24 [*Chem. Abstr.*, 93 (1980) 159428]. (p) M.M. Mostafa, S.M. Hasson and A.A. El-Asmy, *J. Indian Chem. Soc.*, 57 (1980) 127. (q) N.V. Gerebeleu, K.I. Turta, V.M. Canic, V.M. Leovac and V.B. Arion, *Koord. Khim.*, 6 (1980) 446. (r) S.S. Misra, P.C. Dwivedi, R.K. Upadhyaya, V.P. Singh and D.R. Gupta, *J. Indian Chem. Soc.*, 57 (1980) 107. (s) S.K. Tiwari and D.P.S. Rathore, *Natl. Acad. Sci. Lett. (India)*, 2 (1979) 293.

(X = Cl or Br) in CCl_4 or CS_2 to give $[Fe(acac)_2(O_2CR)]$ or a mixture of $[Fe(acac)_2X]$ and $[Fe(acac)X_2]$ respectively [217]. The electrochemistry of $[Fe(acac)_3]$ and $[Fe(hfacac)_3]$ have been studied [218]. The rhenium complexes, (45), react with $[Fe(OEt)_3]$ to give a tris-metallo chelate of iron [219].



(45; R = Me or $CHMe_2$)



(46)

Iron(III) also undergoes reversible association with $[Co(dmg)_2X(H_2O)]^{n+}$ (X = Me, n = 0; X = H_2O, n = 1) in which the iron atom replaces the proton of the O-H...O group (46) [220].

$[Fe(sal_2en)]$ reacts with 1,2-naphthaquinone, 9,10-phenanthraquinone or 3,5-di-*t*-butyl-1,2-benzoquinone to give $[Fe^{III}(salen)(1,2\text{-}sq)]$ (sq = a semiquinone radical anion). All of these are high-spin complexes with $\mu_{eff} \sim 4.9\ \mu_B$, and can be viewed as containing coordinated semiquinone radical anions, the unpaired electron of which is antiferromagnetically coupled with the five unpaired electrons of iron(III) to give an $S = 2$ ground state [221].

The high-spin complexes $[FeL_6]X_3$ {L = urea, 1,3-Me_2-urea, 1,3-Et_2-urea, 1,3-$(CH_2)_3$-urea (*i.e.* perhydro-pyrimidin-2-one) or imidazolidin-2-one; X = ClO_4 or Br} and *cis*-$[FeL_4(H_2O)_2]Cl_3.2H_2O$ {L = 1,3-$(CH_2)_3$-urea} have been prepared, and the crystal structure of the last of these reported [222].

Direct oxidation of metallic iron in the donor-acceptor media, CCl_4/L (L = dmso or dmf) gives *cis*-$[FeCl_2(dmso)_4]$, $2FeCl_3.3dmso$, $[FeCl(dmso)_5][FeCl_4]_2$, $[FeCl(dmso)_5][Fe_2Cl_6O]$, *cis*-$[FeCl_2(dmf)_4][FeCl_4]$ [137b]. $[Fe(NO_3)_3(dihexylsulphoxide)_3]$ has also been reported. The octahedral complex contains unidentate nitrate groups [223].

The polymeric complexes, $[FeL_nX_3]$ (L = triallylphosphate; n = 1, 2 or 3; X = ClO_4, Cl, NCS or NO_3) have been prepared by reaction of poly(triallylphosphate) with the appropriate metal salt [173]. $[FeL_3]$ (L = monoisooctylphenyl-, monoisooctylmethyl- or ethoxymethylphosphonate) have also been reported [224]. Other *O*-donor ligand complexes of iron(III) are listed in Table 2.

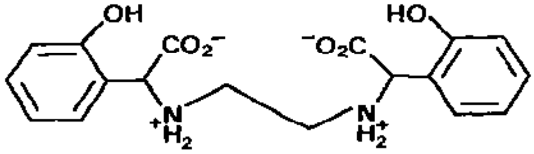
1.7.3 Complexes with S-donor ligands

Electrochemical studies of $[Fe(S_2CNR_2)_3]$ (NR_2 = pyrrolidino) have shown that both one-electron oxidation and one-electron reduction can occur in most solvents [225]. The complexes $[FeX(S_2CNR_2)_2]$ (X = Cl or I), $[FeI_2(S_2CNR_2)]$ (NR_2 = pyrrolidino) and $[Fe(SOCNR'_2)_3]$ (NR'_2 = morpholino, pyrrolidino) have been prepared. The last of these shows a spin equilibrium [226]. A structural study on $[FeI_2\{S_2C(pyrollidino)\}_2]$ has shown the compound should be formulated as $[FeI\{S_2C(pyrollidino)\}_2].0.5I_2$ containing a distorted square pyramidal coordination sphere, with the iodine atom in the apical position [227]. A similar structure has been demonstrated for $[Fe(NCS)(S_2CNEt_2)_2]$ [228]. MO calculations for $[FeX(S_2CNR_2)_2]$ complexes, showing the existence of both low-spin and intermediate-spin ground states, have been reported [229].

The low-spin complexes, $[Fe(Hdtb)_nX_3]$ (Hdtb = 2,4-dithiobiuret; n = 1 or 3; X = Cl, Br, I or $\frac{1}{2}[SO_4]$) have been isolated and contain chelating Hdtb ligands [177].

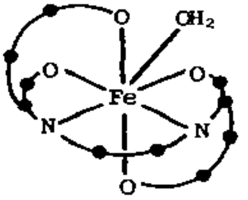
1.7.4 Complexes with mixed donor ligands

The ligand (47; H_2L) forms the very stable complex $[Fe(HL)Cl_2]$, which on the



(47)

basis of a stability constant of *ca*. 10^{30} has been suggested as a model for biological iron carriers (see Section 1.9.4). The molecule may exhibit octahedral $[N_2O(phenolic)Cl_2(OH_2)]$ coordination or may be an octahedral dimer [230]. *Rac*-en-*N*,*N'*-disuccinic acid (H_4L') forms the complex $Na[FeL'].2H_2O$ for which the seven-coordinate structure (48) has been suggested [231].



(48)

The Schiff base formed from substituted salicylaldehydes (substituents = 5-Br, 4-MeO, 3-EtO or 3,5-Cl_2) and 2-aminobenzyl alcohol (H_2L) form the complexes [Fe(L)Cl] in which the Schiff base is tridentate {*ONO*}. The complexes are, however, dimeric with bridging alcoholic *O* atoms completing square pyramidal geometry at each metal atom, and display antiferromagnetic exchange (μ_{eff} = 4.37-4.55 μ_B) [232]. The Schiff base formed from 5-phenylazosalicylaldehyde and aniline (HL') forms a four coordinate [Fe(L')Cl]Cl complex in which the chromophore is {Fe*NONCl*}, rather than the expected {FeN_2O_2}. Again the compound is either dimeric or polymeric [233].

Reaction of aqueous or alcoholic $FeCl_3$ with glycine (Hgly) in the presence of glycinate gives $[Fe_3O(gly)_6(H_2O)_3]Cl.3H_2O$. IR data suggest the complex contains bidentate *NO*-bonded glycinate ligands [334]. Other mixed donor ligand complexes of iron(III) are listed in Table 2.

1.7.5 Miscellaneous

Experiments have been performed to test whether the widely reported reduction of iron(III) compounds under combined hydrostatic pressure and shear stress is due to either one or both of these factors. With $K_3[Fe(CN)_6]$, there is no evidence for hydrostatic reduction, and thus the phenomenon must be due to shear [235].

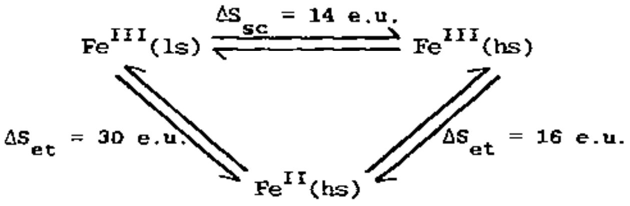
1.8 COMPLEXES EXHIBITING SPIN EQUILIBRIA

This year has seen a number of important and detailed studies on spin equilibria in iron complexes, and these are gathered together here. The six-coordinate complex $[Fe(phy)_2][ClO_4]_2$ (phy = 1,10-pheanthroline-2-carbaldehydephenylhydrazone) exhibits a $^5T_2 \rightleftharpoons {}^1A_1$ spin change in the solid state that is accompanied by a crystallographic change. This crystallographic change arises from formation of independent domains by both $^5T_2$ and $^1A_1$ molecules. The magnitude of the domains is about 5000 Å [236]. Complexes such as $[Fe(S_2CNR_2)_3]$ (NR_2 = morpholino) have previously been shown to exhibit a plateau in the transition from $S = \frac{5}{2}$ to $S = \frac{1}{2}$ at $S = \frac{3}{2}$. A detailed study of such behaviour in the complexes $[Fe(Xsal_2eenH)_2]Y$ {$Xsal_2eenH_2$ = Schiff base formed from condensation of salicylaldehyde (X = H), or its methoxy derivative (X = OMe), with *N*-ethyl-1,2-diaminoethane; Y = $[NO_3]$, $[PF_6]$ or $[BPh_4]$} has now been reported. For the complex with X = H, Y = $[PF_6]$ there is a gradual, but complete crossover from $S = \frac{5}{2}$ to $S = \frac{1}{2}$, but those complexes with X = H, Y = $[NO_3]$ or X = OMe, Y = $[BF_4]$ show plateaux at 3.03 μ_B (below 77 K) corresponding to $S = \frac{3}{2}$. It was found that the plateaux could be induced by grinding the samples, although it is not observed in the samples when originally prepared. The plateau could also be removed from a sample by dissolving and reprecipitating the ground sample. It was suggested that formation of a plateau in a spin transition can be explained by the nucleation and growth mechanism of phase transitions of solids [237].

There have been a number of closely related studies of the $[Fe(2\text{-picolylamine})_3]^{2+}$ cation. A structural study of the dichloride dihydrate, which has the *fac*-geometry and is low-spin, shows an average Fe-N distance of 199.7 pm at 115 K. The structure has an extensive three-dimensional hydrogen bonding network linking uncoordinated water molecules, chloride ions and all six amine hydrogen atoms. The diiodide shows two crystallographically independent isomers. The unsymmetric *mer*-isomer is high-spin with an average Fe-N distance of 220.0 pm, while the *fac*-isomer has an average Fe-N distance of 206.4 pm and exists as an interconverting mixture of high- and low-spin species at room temperature. In this case the *mer* and *fac* isomeric cations are linked by hydrogen bonding between iodide ions and amine hydrogen atoms. The dichloride monomethanolate has been examined by X-ray crystallography at five different temperatures. Spin isomers have been resolved by their Fe-N distances at intermediate temperatures and these are in excellent agreement with the values obtained at the high and low temperature limits {$\bar{r}$(Fe-N) = 201.6 pm at 115 K and 219.8 pm at 227 K}. At 115 K and 227 K, the sample was 96.4% and 16.4%, respectively, in the low-spin state [239a]. A similar study of the dichloride monoethanolate at 298 K shows it to be high-spin {$\bar{r}$(Fe-N) = 219.5 pm}, while at 90 K it is low-spin {$\bar{r}$(Fe-N) = 201.3 pm}. The solvate ethanol molecule is hydrogen bonded to the chloride ions which, in turn are hydrogen bonded to the amine hydrogen atoms. In the high-spin form, ethanol exhibits orientational disorder, while in the low-spin state it adopts a regular arrangement. The structure has also been determined at 150 K, at which temperature the spin transition begins to take place. Here the dominant site of disordered ethanol molecules has about 80% occupancy, but the Fe-N bond lengths have changed very little. It was suggested that ordering of the ethanol molecules appears to act as a trigger to the spin transition. In the case of the methanolate discussed above, the spin state transformation occurs more gradually. It is thought that the ethanol solvate contains domains composed of like spin states, consisting of about five hundred complex cations [239b].

NMR studies on a range of iron(III) porphyrin perchlorates in non-coordinating solvents are anomalous when compared to other iron(III) porphyrin species. Measurements supported earlier solid state studies, suggesting a quantum mechanical admixture of $S = 3/2$ and $S = 5/2$ spin states rather than a thermal mixture. The most likely ground state configuration for the $S = 3/2$ state is $(d_{xy})^2(d_{z^2})^1\ (d_{xz},d_{yz})^2$. Such an intermediate-spin quantum mechanical admixture has been previously invoked to explain the unusual EPR spectrum of ferric cytochrome c• [240].

Electroreduction of $[Fe\{(Xsal)_2trien\}]^+$ (X = H, NO_2, OMe, Br, Cl; $(Xsal)_2trienH_2$ = Schiff base formed by condensation of substituted salicylaldehydes and triethylenetetramine) has led to the behaviour outlined in Scheme IX [241].



(sc = spin change, et = electron transfer, ls = low-spin, hs = high-spin; e.u. = J mol^{-1} K^{-1})

SCHEME IX: Spin equilibria for $[Fe\{(Xsal)_2trien\}]^+$.

$[Fe(HBPz_3)]$ $\{HBPz_3$ = hydrotris(pyrazol-1-yl)borate$\}$ shows a reverse spin equilibrium at high temperature, (298–463 K). That is, it is transformed from low-spin to high-spin [242]. Use of isotopically labelled iron has allowed assignments of the Fe–N stretching frequencies of both high- and low-spin forms. At intermediate temperatures, bands arising from both spin forms are observed.

1.9 INORGANIC BIOCHEMISTRY OF IRON

Work in this area has continued to increase in volume and, as last year, the coverage given here is aimed towards those studies that illuminate the rôle of the metal in natural systems, as well as work on model compounds. For convenience, all work or iron porphyrin complexes is included in this section.

1.9.1 Complexes and enzymes containing iron porphyrins

[Fe(TPP)], a porphyrin complex with an $S = 1$ spin state (μ_{eff}~4.4 μ_B), was first reported some years ago by Collman and coworkers, but an understanding of the details of the electronic arrangement for this spin state remains sparse. For example, it is not known why μ_{eff} is so high. Two groups have now reported detailed examinations of this problem. Buckingham and coworkers have measured the magnetic susceptibility and magnetic anisotropy of single crystals in the range 4–300 K. Detailed ligand field calculations give a satisfactory explanation of the data, and indicate d_{z^2} is the lowest lying orbital with a ground state of $^3A_2$, followed by the ^3E and ^3B levels in ascending order of energy [243]. Mispelter *et al.* have investigated the temperature dependence of the paramagnetic shifts in the ^1H NMR spectra of a range of newly synthesised, substituted TPP complexes in which both faces of the tetrapyrollic ring are strictly controlled. Pseudocontact and contact contributions to the hyperfine shifts and their temperature dependence have been interpreted in terms of a model with two possible electronic ground states. The nature of the ground state depends critically on the energy of d_{z^2} relative to the degenerate d_{xy} and d_{yz} orbitals, and in most cases the ground state is $^3A_{2g}$, strongly perturbed by the close lying ^3E_g excited state [244].

Enthalpies and free energies of ligand addition to [Fe(TPP)] has been determined by variable temperature electrochemistry and these show a linear relationship to the pK_a values of the ligands (py, 4-Mepy or 3-Xpy (X = CN, Cl, Br or Me)), while the entropy values remain constant [245].

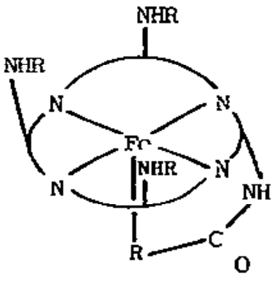
A structural study on [Fe(*meso*-TPP)(thf)$_2$] has shown the complex to be six coordinate with the metal atom located rigorously in the plane of the $\{N_4\}$-core. This is thus the first exception to the generality that high iron(II) porphyrins are five coordinate with large out-of-plane iron displacements [246]. [Fe(TBzP)(py)$_2$] (TBzPH$_2$ = tetrabenzylporphyrin) undergoes one electron oxidation to [Fe(TBzP)(py)$_2$]$^+$ [247]. The complex, [Fe^{II}(Me-*N*-TPP)Cl] has been prepared and this has a methyl group bonded to one of ligating *N*-atoms, thereby restricting axial coordination of the iron atom on one side of the ring and stabilising Fe(II) with respect to Fe(III) (its oxidation potential is +0.49 V (*vs.* SCE) compared to −0.29 V for [Fe(TPP)Cl]). Cyclic voltammetry shows that, unlike for [Fe(TPP)], oxidation is reversible. A structural study shows distorted square-pyramidal coordination with r(Fe–NMe) = 232.9 pm and r(Fe–N$_{others}$) = 210 pm [248].

Molecular mechanisms of Hb cooperativity have been studied by flash photolysis, and the results imply that either the spin state of the iron atom is not the only major factor in the determination of its position with respect to the heme plane, or the change with conformation of the protein, exerted *via* the proximal histidine on the iron, is less than 50% of that expected from models [249]. A systematic correlation of the visible and Soret spectra of five-coordinate porphyrin complexes and their O_2 and CO adducts with those of Hb, Hb(O_2) and Hb(CO) suggests that the iron atom is more easily distorted from the heme plane in the O_2 complexes than in those with CO. Also the proximal histidine is restrained by the protein in both the liganded R states of Hb and Mb giving relatively weak Fe–N bonds. Coordination of O_2 or CO and transition to the T state results in the iron atom being forced towards the histidine, thereby strengthening the Fe–N bond and introducing strain in both the heme complex and the protein [250].

Measurements of the rates of CO binding to iron(II) porphyrins have been used to examine the different factors proposed for protein control on heme reactivity. The results indicate that electronic control through π donor-acceptor interactions with the porphyrin ring are not important, but that hydrogen bonding to the metal bound imidazole can have a powerful influence on reactivity [251]. The ratios of $P_{\frac{1}{2}}$(CO)/$P_{\frac{1}{2}}$(NO) have been measured for horse Mb and (*N*-Meimid)protoheme and are vastly different to that for model systems, providing further evidence for the interaction of CO with the protein chain in Mb [252]. ^{13}C NMR spectra of crystalline and solution state samples of [Hb(A)(CO)] suggest that the structure is the same in both states, in accord with previous IR studies [253].

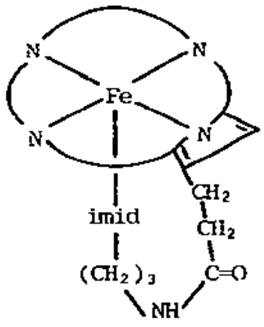
The structures of the picket-fence porphyrin complex, [Fe(TPivPP)(2-Meimid)].EtOH and its O_2 adduct have been reported. In the deoxy compound, $r(\text{Fe–N}_{\text{por}})$ = 206.8 and 207.5 and $r(\text{Fe–N}_{\text{imid}})$ = 209.5 pm. In the oxy complex, $r(\text{Fe–N}_{\text{por}})$ = 199.7 and 199.5 and $r(\text{Fe–N}_{\text{imid}})$ = 210.7 pm. The iron atom is 39.9 pm out of the $\{N_4\}$ plane in the former complex, whereas this value is reduced to 8.6 pm in the oxy form. The important parameters of the {Fe(O_2)} unit are r(Fe–O) = 189.8, r(O–O) = 122 pm and $\text{Fe}\hat{\text{O}}\text{O} = 129^{\circ}$. In the presence of ethanol, the deoxy compound binds O_2 reversibly and non-cooperatively, and with a lower affinity than when the sample is desolvated. In the latter case, binding in cooperative. Thus, these are possible models for the T-state deoxy and oxy forms of Hb [254]. Resonance Raman spectroscopy has been used to assign the Fe–O stretching frequencies in [Fe(TPivPP)(L)(O_2)] (L = 1-Meimid, 2-Meimid, 1,2-Me imid) at 25° and -70 °C. The results suggest that the O_2 affinity is similar to that of Mb or R-state Hb when L = 1-Meimid, and similar to that of T-state Hb in the other cases [255].

Collman and coworkers have now moved to the synthesis of tailed picket fence porphyrin complexes, (49). Adducts with O_2, CO and *N*-Meimid have been prepared [256a]. Traylor *et al.* have reported a similar complex (50) in which the pendant ligand is linked to one of the pyrrole rings and which displays properties similar to those of R-state Hb [256b]. [Fe{*meso*-tetra(anthracenyl)por}(imid)$_2$]



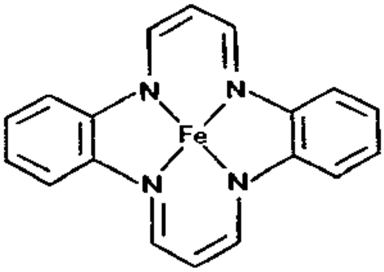
(49)

R = $(CH_2)_4$imid, $(CH_2)_3$imid,
$(CH_2)_4$SMe, or $NH(CH_2)_3$imid



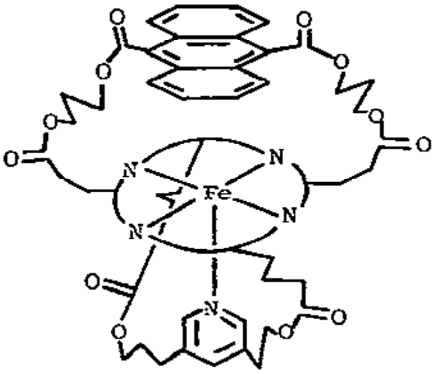
(50)

takes up dioxygen at room temperature with oxidation to iron(III): at low temperature an O_2 adduct is formed [257]. Iron(II) deuteroporphyrin has been attached, *via* an imidazole axial base, to polystyrene and undergoes several reversible dioxygen uptake cycles without noticeable irreversible oxidation to iron(III) [258]. An attempt has been made to use globin as a sterically hindered environment for $Fe{-}O_2$ complex formation by binding in the simple macrocycle (51). This was achieved by treating globin with $[FeL(O_2CMe)]$, and



(51)

one molecule of iron complex only was bound to one globin unit. Cooperativity is observed for the binding of {FeL} to apohemoglobin, an observation not previously demonstrated for heme binding. The {FeL} unit was shown to occupy the same site in globin as a heme and to take up O_2 and CO [259]. Oxygenation equilibrium curves have been reported for a tetrametric Hb with iron(II) in the α sub-units and cobalt(II) in the β sub-units, and *vice versa* [260]. There has been considerable interest in capped porphyrin complexes. Thus, the complex (52) with an anthracene bridge across one face of the porphyrin and a pyridine bridge across the other has been synthesised. This mimics Hb in that it has a



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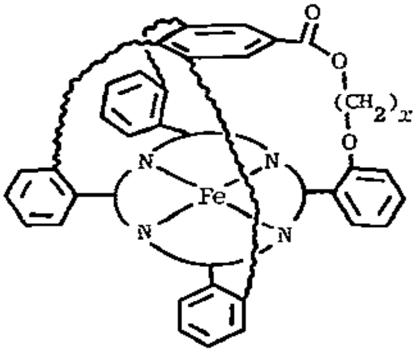
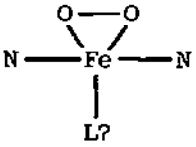


(53)

hydrophobic pocket and takes up dioxygen reversibly. It also takes up CO, but like natural systems (and unlike other model systems) this CO can be replaced by O_2 [261]. The complex [Fe(cap)] {cap = (53; x = 2)} contains a capped porphyrin ligand and can bind an axial ligand only on the vacant side of the porphyrin plane, but if the volume of the cap is increased by using the homologous capped ligand, {homcap = (53; x = 3)}, then two small ligands can be bound in axial positions to the metal atom. The O_2 binding constant of [Fe(cap)] is larger than that of [Fe(homcap)], but in both cases the O_2 affinities are appreciably lower than those of other porphyrin complexes. It is thought that this is because the caps provide a steric constraint on movement of the metal atom from the stable out-of-plane position to the in-plane O_2-bound position. Evidence was found for the novel seven-coordinate complexes [Fe(homcap)$L_2(O_2)$] (L = 1-Meimid) and its CO analogue and it is believed that one L ligand and O_2 (or CO) occupy axial sites with the other L ligand showing off-axial binding [262]. The low spin adducts [Fe(cap)L] (L = PBu_3, $P(OEt)_3$, or $PhCH_2NC$) have been isolated and add to the previously small number (only [Fe(TPP)(NO)] and [Fe(TPP)(CO)]) of low-spin five-coordinate iron porphyrin adducts [263].

Addition of excess pyridine to aqueous protoheme leads initially to the formation of a bis(pyridine)heme dimer which does not fully monomerise until the pyridine concentration is between 2 *M* and 3 *M*. Reaction of the dimer with dioxygen was examined and this leads to formation of an iron(III)-containing product, formed by an outer sphere mechanism with no evidence for the intermediacy of an Fe(II)-O_2 complex [265].

The reaction of superoxide ion with [Fe(Por)Cl] (Por = TPP or OEP) in dmso, dmso-py, MeCN-py or $PhCH_3$-py gives [Fe(Por)L_2] (L = dmso or py) and O_2. However, at −50 °C in dmf–py, $[Fe(TPP)(py)(O_2)]$ is formed, and in wet solvents at ambient temperatures, $[\{Fe(Por)\}_2O]$ is obtained. A new species was also observed from the reaction of iron(II) and $[O_2]^-$ and, although it could not be isolated, some of its reactions suggest it could be the high-spin iron(III) peroxo complex (54) [266]. Ferryl-Mb is a peroxide hemoprotein that contains iron(IV), and this



(54)

can be reduced by γ-irradiation at 77 K to a novel low-spin iron(III) compound. This, in turn, underwent a higher temperature transition to high-spin iron(III) probably *via* transient low-spin and $S = \frac{3}{2}$ forms [267]. A kinetic study of the reaction of aqua-Fe(III)Mb with H_2O_2 at pH 8 suggests the reaction mechanism shown in equations (7)–(9) in which the intermediate R is believed to be the

$$\text{Mb(III)} + H_2O_2 \longrightarrow \text{Intermediate X} \tag{7}$$

$$\text{Intermediate X} + H_2O_2 \longrightarrow \text{Intermediate R} \tag{8}$$

$$\text{Intermediate R} \longrightarrow \text{Mb(III)} \tag{9}$$

iron(IV) species. Resonance Raman spectroscopy of the intermediate R suggests that the iron(IV) centre is low-spin, and a comparison with similar spectra of model compounds indicates that $r(\text{Fe–N}_{\text{por}}) = 208$ and $r(\text{Fe–N}_{\text{imid}}) = 209$ pm, and that the iron atom is 53 pm above the $\{N_4\}$ plane [268].

Traylor and Berzinis have prepared the iron(III) cationic form of their tailed-porphyrin complex (50) and this mimics the behaviour of horseradish peroxidase [269]. Two further studies of tailed-porphyrin iron(III) complexes have appeared. In these cases the tails are $C_6H_4NHCO(CH_2)_2$imid and $C_6H_4O(CH_2)_4$imid groups which replace aryl groups in tetraarylporphyrins. NMR studies on these complexes indicate that the tension in the tail is important in dictating the electronic properties of the complex [270].

The X-ray crystallographic structural study of $[Fe(OEP)(ClO_4)]$ has shown it to be composed of dimeric units in which the two iron(III) porphyrins have a face-to-face contact with a closest approach distance of 356 pm between *meso*-C and pyrrolic α-C atoms on different porphyrin molecules. The iron atoms are displaced 26 pm from the mean $\{N_4\}$ planes. This dimerisation is explained by a weak π–π* interaction. The complex has an $S = \frac{3}{2}$ ground state [271]. The EPR spectra of high-spin iron(III) porphyrins show an absorption, in addition to the main signal, which is remarkably sensitive to concentration, solvent, pH and temperature, and this has been interpreted as belonging to a dimeric form. In the case of some porphyrins, a further signal is observed in alkaline solutions which is assigned to a dimer with a very long Fe...Fe distance, as well as a skew angle [272].

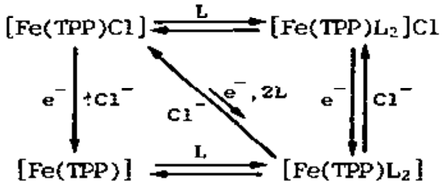
$[Fe(OEP)(3\text{-}Clpy)_2][ClO_4]$ also shows a high-spin $\rightleftharpoons$ low-spin equilibrium and a structure determination at 298 K has shown that the $Fe\text{–}N_{por}$ distances are midway between those of typical high-spin and low-spin complexes [273]. The new type of mixed axial ligand complexes, $[Fe(OEP)(ROH)(amine)]Cl$ (R = Me, Et or Pr; amine = pip, pyrrolidine, Et_3N, aziridine, 4-Mepy or 1,2-Me imid), have been reported and suggested as models for aquamethemoglobin and aquametmyoglobin [274]. Stability constants for the interaction of $[Fe(PPIXDME)Cl]$ and imidazoles have been determined [275].

A complete assignment of the ^{13}C NMR spectra of $[Fe(TPP)X]$ (X = Cl or I) has been made [276]. Examination of the ^{1}H NMR spectra of a series of five- and six-coordinate high-spin iron(III) porphyrins has led to the suggestion that the ratio of shift of the pyrrole protons to that of the methyl protons may serve as a useful indicator of the state of occupation of the sixth site in high-spin hemoproteins [277]. A kinetic study using ^{17}O NMR has been made of the exchange of water with water soluble iron(III) porphyrins [278].

In an examination of the possible importance of partially or totally deprotonated imidazole ligands in hemoproteins, Reed and coworkers have isolated $[Fe^{III}(TPP)(imid)_2]^-$, $[Fe^{II}(TPP)(imid)_2]^{2-}$ and $[Fe^{II}(TPP)(2\text{-}Meimid)]^-$ (imidH = imidazole) [279].

$[\{(TPP)Fe\}_2N]$ is the only μ-nitrido complex of the first row transition metals, and its resonance Raman spectrum suggests that both iron atoms are trivalent, whilst its EPR spectrum locates the single unpaired electron in an orbital of essentially (μ-N) character [280]. In the absence of any added base, this dimer is electrochemically reduced at +0.17 V (*vs*. SCE) to $[\{(TPP)Fe\}_2N]^-$, and at −1.19 V (*vs*. SCE) to the dianion. Addition of substituted pyridines causes negative shifts in the potentials of the first reduction wave [281]. The Fe $2p_{3/2}$ and N 1s binding energies of $[\{(TPP)Fe\}_2N]$, $[\{(TPP)Fe\}_2O]$ and $[Fe(TPP)X]$ (X = Cl, Br, N_3 or $[ClO_4]$) have been determined by XPES and correlate well with $E_{\frac{1}{2}}$ values for reduction of the complexes in non-coordinating solvents. On the basis of this study, the μ-nitrido complex is assigned a low-spin configuration [282].

Electrochemical oxidation of $[\{(TPP)Fe\}_2O]$ to both a mono- and dication has been achieved. The former contains an $\{Fe^{III}\text{–}O\text{–}Fe^{IV}\}$ unit, but the latter may be either $\{Fe^{IV}$–O–$Fe^{IV}\}$ or $\{Fe^{IV}$–O–Fe^{III}–$(Por^{\cdot +})\}$. Similarly, oxidation of [Fe{TPP(OMe)}Cl] leads to a species, the magnetic moment of which is consistent with the presence of iron(IV). However, the formation of an iron(III)-porphyrin radical cation could not be ruled out [283]. Previous studies have suggested that $[\{(TPP)Fe\}_2O]^+$ can be formed by chemical oxidation of the neutral dimer with $H[BF_4]$; however, it has now been shown that the product of this reaction is a mixture of [Fe(TPP)F] and $[Fe(TPP)(BF_4)]$ [284]. Electroreduction of [Fe(TPP)X] (X = Cl, $[ClO_3]$ or $[ClO_4]$) in the presence of substituted pyridines, L, can be summarised as shown in Scheme X [285]. Treatment of $[\{(TPP)Fe\}_2O]$ with $H_2[SO_4]$ gives the high-spin complex, $[Fe(TPP(SO_4)_{\frac{1}{2}}]$ [286].



SCHEME X: The electrochemistry of [Fe(TPP)Cl].

The monooxygenase enzyme cytochrome P-450, and models for its behaviour, continue to attract considerable attention. An analysis of the spectral and ligation data for native cytochrome P-450_{cam} from *Pseudomonas putida* and four synthetic analogues has been presented, and this emphasised the unique characteristics of the thiolate ligated heme: a simple method for the purification of the heme centre from cytochrome P-450 was also reported [287]. An ENDOR study on cytochrome P-450_{cam} obtained from *Pseudomonas putida* has examined the native, substrate-free, low-spin iron(III) centre and the high-spin iron(III) unit in the enzyme-substrate component. The former shows the presence of at least one strongly coupled exchangeable proton attached to an axial ligand, while the latter shows no evidence for the presence of coordinated histidine or water, indicating this is a five-coordinate iron(III) centre [288]. Examination of the spin equilibria and redox potentials of cytochrome P-450 from rat liver microsomes has shown that the main effect of drug binding is alteration of the redox potential by modification of the iron(III)-heme spin equilibrium [289].

The reduced state of chloroperoxidase has spectral properties very similar to those of reduced cytochrome P-450, and their CO adducts are also very similar. These properties are modelled by $[Fe(TPP)(SEt)]^-$ and $[Fe(TPP)(SEt)(CO)]^-$ respectively. The former model is high-spin and five-coordinate, and the metal atom is 52 pm above the $\{N_4\}$ plane towards the SEt ligand. The latter is low-spin and six-coordinate, with the iron atom in the plane. The Fe–S distances are very similar in both models [290]. Ullrich and coworkers have reported a study of hemin coordinated with a mercaptide ligand at the fifth site, and various ligands at the sixth site, as possible models for cytochrome P-450. Mixing hemin and the mercaptide below −60 °C prevented reduction of the metal atom and these spectral comparisons suggest the sixth ligand may be a hydroxyl group rather than an imidazole [291].

The model complex [Fe(TPP)(SPh)(SHPh)] exhibits at least two magnetic sites, each of which shows a temperature dependent spin change. At 300 K, iron(III) is high-spin ($S = {}^5\!/_2$), and at lower temperatures the spin state is lower or the complex possesses a reduced moment due to dimerisation or a cooperative magnetic exchange phenomenon ($\mu_{eff} = 5.7\ \mu_B$ at 300 K, $3.7\ \mu_B$ at 20 K, $2.7\ \mu_B$ below 20 K). This compound corresponds to the oxidised state of cytochrome P-450. On substrate binding in the natural system, about 70% of the metal becomes low-spin iron(III) and nothing is known of the structural factors involved in this conversion. Preliminary X-ray data on this model show it to exhibit thermally driven changes in coordination that may be relevant to this. That is, at high temperature the complex is high-spin and five-coordinate with the PhSH molecule not bound to the metal; on lowering the temperature this is converted to a six-coordinate low-spin form [292].

^{1}H NMR spectroscopy has shown that ligand exchange of both natural and synthetic high-spin iron(II) porphyrin-$[RS]^-$ complexes is slow on the NMR time scale [293]. Attempts to measure stability constants for complex formation between iron porphyrins and a range of *S*-donor ligands were successful only for thiolates [294].

Both [Fe(TPP)Cl] and the analogous compound with the tailed porphyrin based on (50) are active as catalysts in the oxygenation of cyclohexene, in both the presence and absence of PhSH. Maximum activity is observed for [Fe(TPP)Cl] in the presence of both imidazole and PhSH [295].

Two groups have reported the stabilisation of the oxyferryl form of cytochrome P-450, from two different mammalian sources, at −30 °C [296]. By use of isotopic tracer methods it has been shown that during cytochrome P-450 hydroxylation, dihydrolipoic acid acylates the coordinated O_2 molecule to form a transient acyl peroxide intermediate. This undergoes facile O–O bond cleavage. When $^{18}O_2$ is used, one oxygen atom is incorporated into the lipoic acid and the second enters the substrate, indicating the involvement of a ferryl or peracid mechanism [297].

Balch and coworkers have shown that addition of dioxygen to toluene solutions of [Fe(T-3-TP)] (T-3-TP = tetra-3-tolylporphyrin) at −80 °C gives the new intermediate [{(T-3-Tp)Fe}O_2{Fe(T-3-TP)}], which on warming gives [{(T-3-TP)Fe}$_2$O] and O_2. On the basis of labelling studies, the mechanism of formation and decomposition outlined in Scheme XI was advanced. Similar behaviour was observed for TPP, T-4(MeO)-PP, OEP and DPIXDME. The ferryl intermediate [Fe(Por)O] has

$$[\mathrm{Fe^{II}(Por)}] + \mathrm{O_2} \rightleftharpoons [\mathrm{Fe^{II}(Por)O_2}] \xrightarrow{[\mathrm{Fe^{II}(Por)}]} [\mathrm{(Por)Fe{-}O{-}O{-}Fe(Por)}]$$

$$[\mathrm{(Por)Fe{-}O{-}O{-}Fe(Por)}] \longrightarrow 2[\mathrm{Fe^{IV}(Por)O}]$$

$$[\mathrm{Fe^{IV}(Por)O}] + [\mathrm{(Por)Fe{-}O{-}O{-}Fe(Por)}] \longrightarrow [\mathrm{(Por)Fe^{III}{-}O{-}Fe^{III}(Por)}] + [\mathrm{Fe^{II}(Por)O_2}]$$

$$[\mathrm{Fe^{II}(Por)O_2}] \rightleftharpoons [\mathrm{Fe^{II}(Por)}] + \mathrm{O_2}$$

$$[\mathrm{Fe^{IV}(Por)O}] + [\mathrm{Fe^{II}(Por)}] \longrightarrow [\mathrm{(Por)Fe^{III}{-}O{-}Fe^{III}(Por)}]$$

$$[\mathrm{Fe^{IV}(Por)O}] + [\mathrm{Fe^{II}(Por)O_2}] \longrightarrow [\mathrm{(Por)Fe^{III}{-}O{-}Fe^{III}(Por)}] + \mathrm{O_2}$$

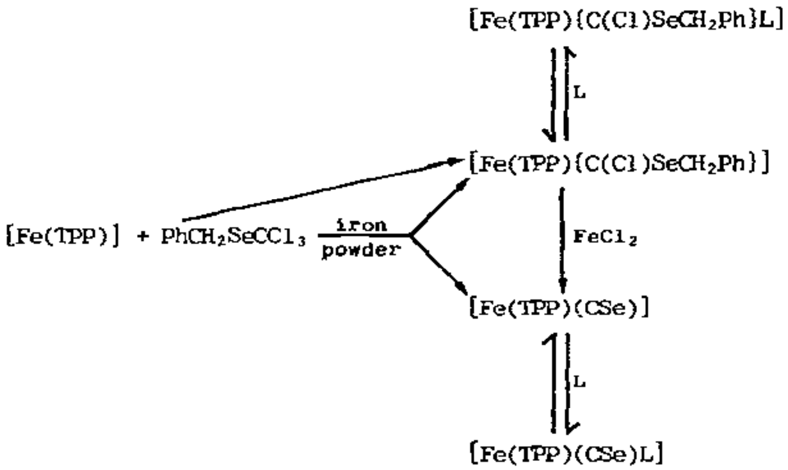
SCHEME XI: Mechanism for the formation of $[\{\mathrm{(T\text{-}3\text{-}TP)Fe}\}_2\mathrm{O}]$.

been isolated at low temperature, and shows a magnetic moment in solution of 2.9 μ_B at −52 °C, which is invariant down to −90 °C: no EPR signals were observed for a frozen solution at 77 K. The derivatives, [LFe(Por)O] (L = py, pip or *N*-Meimid) were also prepared. At −80 °C, this ferryl complex quantitatively converts PPh_3 to $OPPh_3$. At 25 °C, [Fe(Por)] catalyses the oxidation of PPh_3 by molecular oxygen, the final metal containing product from this catalysed reaction being [(Por)Fe–O–Fe(Por)]. Both [Fe(Por)Cl] and $[Fe(Por)L_2]$ are inactive in this reaction and the involvement of the ferryl intermediate as the active species is postulated [298].

Groves has studied the cumene hydroperoxide dependent oxidation of cyclohexane, catalysed by cytochrome P-450, and yielding cyclohexene oxide and cyclohexenol. Use of [FeCl(TPP)(PhIO)] and [CrCl(TPP)(PhIO)] give the same products and on the basis the scrambling of deuterium labels when deuterated C_6H_{10} is used; a mechanism involving caged radical intermediates has been advanced [299].

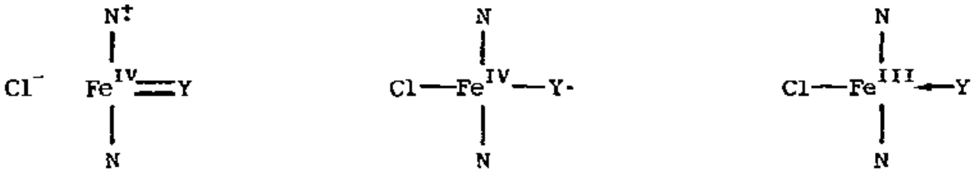
It is possible that cytochrome P-450 can metabolise halogenated compounds by initial formation of R-X=O and this reaction has been demonstrated with labelled PhI [300a]. Others have shown the $[Me_2\dot{C}(OH)]$ radical to reduce $[Fe(DPIX)]^+$ to [Fe(DPIX)], but that the iron(III) cation does not react with $[CH_{3-n}Cl_n]\cdot$ radicals from CCl_4, $CHCl_3$ and CH_2Cl_2. However, the iron(II) porphyrin does react rapidly with these radicals, and this has led to the alternative suggestion that this may be the method of detoxification of polychlorocarbons [300b]. Two studies of $[Fe(Por)(CX_2)]$ complexes suggest that such carbene intermediates may also be involved [301]. [Fe(TPP)] has also been shown to react with $PhCH_2SCCl_3$

to form the carbene $[Fe(TPP)\{C(Cl)SCH_2Ph\}]$. On treatment with iron(II) chloride, this yields $[Fe(TPP)(CS)]$, which can also be obtained from $[Fe(TPP)]$ and Cl_2CS. Such behaviour has now been extended to the selenium analogue as shown in Scheme XII [302].



SCHEME XII: The formation of some carbene and CSe derivatives of $[Fe(TPP)]$ (L = EtOH, *N*-Meimid or py).

Compound II of horseradish peroxidase and compound II of catalyse are both believed to contain an iron(IV) porphyrin in the form an $\{FeO\}$ or $\{Fe(OH)\}$ complex. Compound I of both enzymes can be considered either as radical cations of the porphyrin of compound II, or as a formally iron(V) species. $[Fe(TPP)\{C{=}C(C_6H_4\text{-}4\text{-}Cl)_2\}]$ has been suggested as an analogue to the compounds II and this can be oxidised by iron(III) or copper(II) chloride to a complex with spectra analogous to the compounds I. However, the structural details of this oxidised complex are still not clear, the choice lying between those shown in (55) [303].



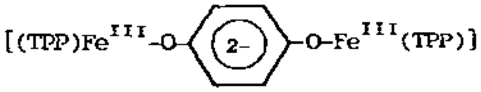
(55; $Y = \{C{=}C(C_6H_4\text{-}4\text{-}Cl)_2\}$)

NMR has been used to study the metal environment in iron(III)-horseradish peroxidase and indicates five coordination with a distal imidazole, but no H_2O or OH group at the sixth site [304]. High field ^1H NMR of the iron(III) resting state of horseradish peroxidase is consistent with appreciable $S = {}^3/_2$ character in a quantum mechanically mixed spin state (see also Section 1.8). All the resolved resonances were accounted for by the porphyrin and the imidazole ligand, although these workers could not definitely rule out the presence of a sixth ligand. The extremely slow exchange of bulk water with the histidine proton of the imidazole, and the absence of deviations from Curie behaviour of the porphyrin vinyl and propanoic acid proton hyperfine shifts, indicate a buried heme crevice which is more rigid than that in metmyoglobin [305].

Resonance Raman spectroscopy of the yeast cytochrome c-peroxidase – H_2O_2 compound support previous studies that indicate the presence of a low-spin iron(IV) heme centre [306]. On the basis of a 2.5 Å electron density map of cytochrome c-oxidase, a histidine side chain has been identified as the fifth ligand with tryptophan, histidine and arginine side chains near the sixth site, but water as the sixth ligand. The iron atom is 30-50 pm out of the $\{N_4\}$ plane towards the histidine [307].

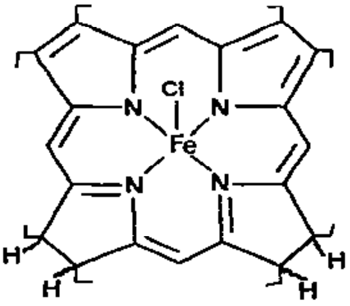
A resonance Raman study of $[Fe(OEP)L(ClO_4)]$ (L = py, py-4-CHO or py-4-CN) and $[Fe(OEP)(dmso)_2]^+$ suggests that the unusual spectrum obtained from neutral cytochrome c' can be attributed to coordination of a carbonyl or carboxyl group at the sixth site with histidine as the fifth ligand [308].

A comparison of the kinetics of the reactions of $[CN]^-$ and $[N_3]^-$ with Mb, and with the octapeptide model system derived from cytochrome c, has shown that (contrary to previous suggestions) steric effects appear to be energetically unimportant in these systems, while electrostatic effects and conformational effects dominate the ligation kinetics [309]. In a study related to the function of electron transport chains, [Fe(TPP)] has been shown to react with 1,4-quinones to give iron(III)-containing dimers of the form shown in (56) [310].



(56)

Two groups have examined model compounds for the iron isobacteriochlorin prosthetic group (siroheme) observed in nitrite and sulphite reductases, which have been shown to be the site of interaction of the substrate and the electron transport chain. Holm and coworkers have prepared chloroiron(III) octaethylisobacteriochlorin, (57), and have shown that the complex obtained by replacement of Cl by SAr gives rise to an EPR spectrum that is closer to that of the



(57)

natural system [311]. Chang and Fajer have prepared dimethyl-*gem*-octaethylisobacteriochlorin (LH_2) and have isolated the iron derivatives, $[Fe^{III}(L)Cl]$, $[Fe^{II}(L)(py)_2]$, $[Fe^{II}(L)(py)(CO)]$, $[Fe^{II}(L)(1\text{-Meimid})_2]$ and $[Fe^{II}(L)(1\text{-Meimid})(CO)]$. This macrocyclic skeleton has an extremely low oxidation potential, and so oxidation of the iron complexes may involve loss of an electron from the ring rather than from the metal. Thus, the reductases may utilise π-radical cations similar to those suggested in catalyse and horseradish peroxidase [312].

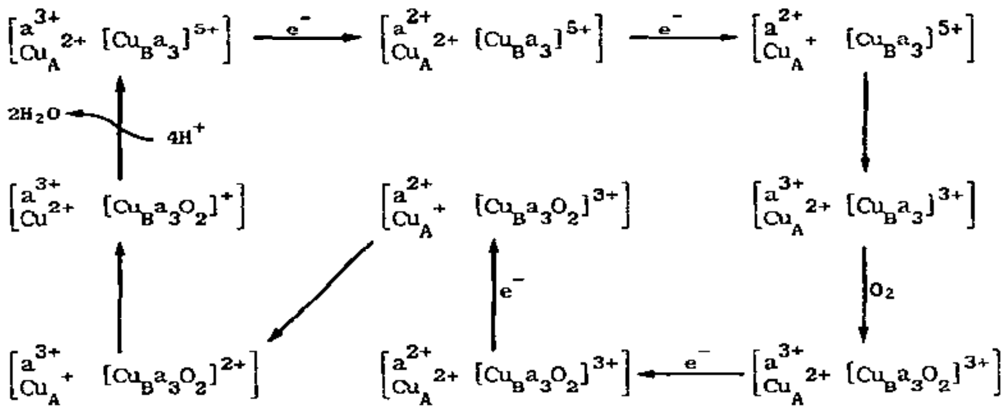
Finally, in this section, discrepancies in the observed and calculated diamagnetic corrections for TPP have been ascribed to iron impurity in commercial samples of the ligand [313].

1.9.2 Cytochrome oxidase and Fe-Cu containing model compounds

Cytochrome oxidase is a two heme centre, two copper centre containing enzyme. Low temperature EPR spectroscopy accompanying the reaction of fully reduced cytochrome-c-oxidase with dioxygen has shown the presence of only two signals. These are attributable to low-spin (cytochrome a)$^{3+}$ and $(Cu_A)^{2+}$. At the completion of the reaction, 100% of Cu_A is in the 2+ state, but only 40% of cytochrome a was present as low-spin Fe^{3+}. A mechanism for the reaction involving four intermediates has been advanced. The initial intermediate (I) contains (cytochrome a)$^{2+}$ and $(Cu_A)^{+}$; intermediate (IIA) contains low-spin (cytochrome a)$^{3+}$ and $(Cu_A)^{+}$ and intermediate (IIB) contains (cytochrome a)$^{2+}$ and $(Cu_A)^{2+}$ (*i.e.* identical total electron counts). Intermediate (IIB) is stable, but (IIA) proceeds to (III), which contains low-spin (cytochrome a)$^{3+}$ and $(Cu_A)^{2+}$ [314,315].

A similar study of the low temperature reaction of mixed valence state cytochrome-c-oxidase $\{a^{3+}.Cu_A{}^{2+}.Cu_B{}^{+}.a_3{}^{2+}\}$ indicates that cytochrome a and Cu_A

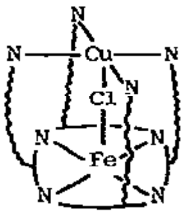
remain as a^{3+} and Cu_A^{2+} in a reaction involving three intermediates. On the basis of these studies a mechanism of the action of cytochrome-c-oxidase has been advanced, and this is shown in Scheme XIII [314,315].



SCHEME XIII: Proposed mechanism for the action of cytochrome-c-oxidase.

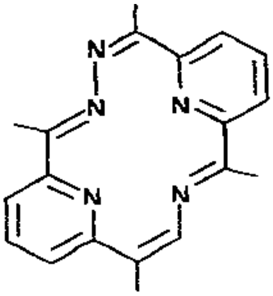
On the basis of EPR and other evidence, it has been suggested that an alternative model may be appropriate for cytochrome-c-oxidase, in which cytochrome a acts as a two electron redox centre (Fe(II)$\leftrightarrow$Fe(III)$\leftrightarrow$Fe(IV)). This model does not require an antiferromagnetic coupling scheme [317].

Three inorganic systems have been examined as models for cytochrome-c-oxidase. Buckingham and coworkers have prepared {α,α,α,α-tetra(2-nicotinamidophenyl)-porphyrin}chloroiron(III), in which the ends of the picket-fence type chains are capable as acting as donor ligands to a second metal atom. Reaction of this with copper(II) perchlorate gives (58). A structural study on this dimetallic



(58)

product shows very long Fe-Cl and Cu-Cl distances, indicating the presence of weak bridging between the two metals. Magnetic measurements are consistent with the iron atom either being high-spin, or having a ground state with quantum mechanical $(S = \frac{3}{2})$–$(S = \frac{5}{2})$ mixing: the copper has an $S = \frac{1}{2}$ ground state. EPR data support a high-spin iron(III) configuration. Physical data show that copper incorporation markedly effects the electronic state of the iron atom [318]. An alternative approach has been the preparation of $\{Fe^{II}(\mu\text{-bipyrimidine})Cu^{II}\}$ complexes, which are proposed as models of $[(\text{cytochrome } a_3)^{3+} (\text{imidazole})Cu_B^{2+}]$. The macrocycle (59) is capable of folding, and this can form the *cis*-complex



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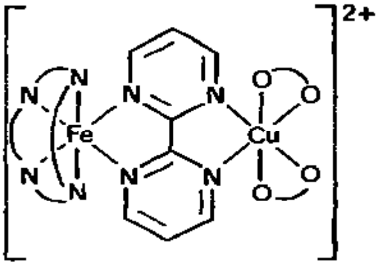
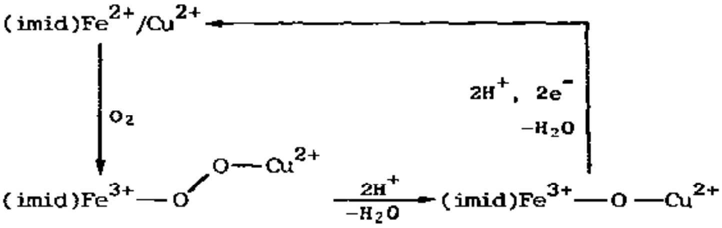


(60)

$[Fe\{(59)\}(bipym)]^{2+}$, which reacts with $[Cu(acac)_2]$ to form (60). The cation $[Fe\{(59)\}(bipym)]^{2+}$ is low-spin; in the dinuclear complex, the iron is high-spin at room temperature. A variable temperature susceptibility study shows the dimer to contain magnetically isolated Fe(II) (S = 2) and Cu(II) (S = ½) ions, with J = 0 through the bipyrimidine bridge. The $E_{½}$ value for the Fe(III)/Fe(II) couple is +0.6 V (*vs*. SCE) which is 700 mV lower than that of the low-spin monomer. The $E_{½}$ value for the Cu(II)/Cu(I) couple is ~0.24 V (*vs*. SCE). In the natural system, J>200 cm^{-1} and thus these authors suggest the possibility of O_2 bridging rather than imidazole bridging (see Scheme XIV) [319].



SCHEME XIV: A proposed scheme for cytochrome-c-oxidase.

The third approach has been reaction of [Cu(salen)] with anhydrous $FeCl_3$ to give the binuclear compound $[Cu(salen)FeCl_3]$, which has a magnetic moment of only 1.34 μ_B, suggesting very strong antiferromagnetic interaction. $[Cu(salen)Fe(ClO_4)_2].2H_2O$ was also prepared. Again, formation of dimers lowered redox potentials and the chemical effects of this were demonstrated by the fact that the Cu^{II}-Fe^{III} dimer is reduced by ascorbic acid, although neither

[Cu(salen)] or the iron compounds alone are effected [320].

1.9.3 Rubredoxin, Ferredoxins and Fe-Mo-S cluster compounds

An X-ray crystallographic refinement of rubredoxin from *Clostridium pasteurianium* at 1.2 Å resolution has been published. The Fe–S distances are found to be in the range 224 to 233 pm (at an average of 229 pm). The B parameters (which measure the distribution of atoms around their mean positions) are relatively large, implying that there are relatively large amplitudes of atomic motion and thus the molecule is pliable and readily deformed [321].

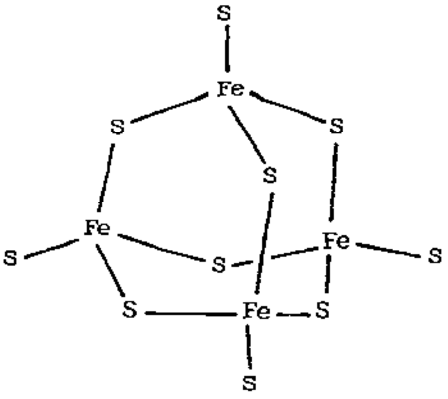
Improved syntheses of the model complexes, $[Fe_2X_2(S_2\text{-xyl})_2]^{2-}$ and $[Fe_2X_2(SC_6H_4Y)_4]^{2-}$ (X = S or Se; S_2-xyl = $[1,2\text{-}C_6H_4(CH_2S)_2]^{2-}$; Y = H or Me) have been developed. These involve reaction of $FeCl_3$, elemental X and $[S_2\text{-xyl}]^{2-}$ (1:1:2) or $[S_2C_6H_4Y]^-$ (1:1:4) in the presence of tetraalkylammonium ions. In the absence of these large cations, $[Fe_4S_4(SR)_4]^{2-}$ clusters are formed. The selenium compounds have not been previously reported, but exhibit spectra and redox properties every similar to their sulphur-containing analogues [322].

A kinetic study of the reaction of $[Fe_2S_2(SR)_4]$ clusters with [HgMe(X)] (X = O_2CMe or SCH_2CO_2K) shows the rate of sulphur extrusion to be much faster in the case of the ethanoate. Initial attack by the mercury complex is on the labile sulphur, ultimately yielding $[(MeHg)_2S]$ and $[\{(RS)HgMe\}_4]$ [323].

Antiferromagnetic exchange in the $\{Fe_2S_2\}$-ferredoxin from a blue green alga has been studied with a very highly sensitive magnetic balance. Values of $-J$ = 182 and 98 cm^{-1} were found for the oxidised and reduced forms, respectively. This antiferromagnetic coupling has been studied by Xα-VB calculations. Other MO calculations upon $[Fe_2S_2(SH)_4]^{n-}$ (n = 2 or 3) favour a ground state configuration with ten unpaired electrons both high-spin iron(III) for the oxidised form, and the reduced form containing Fe(II) and Fe(III) with longer Fe–S bonds to the Fe(II) centres [324].

Important papers have appeared on three iron ferredoxins containing $\{Fe_3S_3\}$ cores. Both X-ray structural and EPR evidence on the Fe-S clusters from *Azobacter vinlandii* are consistent with the presence of $\{Fe_4S_4(SR)_4\}$ and $\{Fe_3S_3\}$ clusters separated by about 11 Å. The protein makes six contacts to the $\{Fe_3S_3\}$ unit [325]. The ferredoxin from *Desulphovibrio gigas* mediates electron-transfer between cytochrome c_3 and sulphite reductase. A Mössbauer and EPR study of this shows the presence of three iron atoms per monomer unit, and a spin concentration of 0.9 spins per monomer unit. The Mössbauer spectrum is very similar, if not identical, to that of the low potential centre from *Azobacter vinelandii* and indicates the presence of an $\{Fe_3S_3\}$ cluster here also [326].

Christou and Garner have reported a convenient synthesis of $[Fe_4S_4(SR)_4]^{2-}$ (R = Ph, CMe_3 or CH_2CH_2OH) clusters from iron(II) or iron(III) chlorides, elemental sulphur and M[SR] (M = Li or Na) [327]. Holm and coworkers have reported that $FeCl_2.2H_2O$ reacts with Na[SPh] in methanol to give $[Fe_4(SPh)_{10}]^{2-}$ (61), an intermediate in the synthesis of $[Fe_4S_4(SPh)_4]^{2-}$. This novel cluster has been isolated and characterised by X-ray methods; the anion (61) consists of a tetrahedron of {Fe(SPh)} units linked to an octahedron of bridging {SPh} units. It reacts smoothly with elemental sulphur to give the $[Fe_4S_4(SPh)_4]^{2-}$ ion in 80% yield [328].



(61; Ph groups omitted for clarity)

$[Fe_4S_4(SCMe_3)_4]^{2-}$ reacts with $MeC(O)(Gly)_2(CysGly_2)_nCysGlyNH_2$ (n = 0–3) with exchange of $SCMe_3$ groups and formation of the peptide bound cluster. For the n = 0 peptide, four successive equilibrium constants were evaluated for the four binding sites of the cluster [329]. The cluster $[Fe_4S_4(thiocyclodextrin)_4]^{2-}$ has been prepared and it was found that the presence of the hydroxyl groups of the thiodextrin increased the ease of reduction of the $\{Fe_4S_4\}$ core. The reduction potential is intermediate between those of $\{Fe_4S_4\}$ in water, and those of $\{Fe_4S_4\}$ bound to alkylthiolate ligands in aprotic solvents [330].

Holm has now completed his important structural analysis of $[Fe_4S_4(SR)_4]^{n-}$ (n = 2 or 3) clusters. In the solid state $[Fe_4S_4(SR)_4]^{3-}$ clusters appear to divide into two groups, those containing tetragonal cores, and those containing non-tetragonal cores. However, all exhibit the same structure in frozen solution - an elongated tetragonal core. Thus the above differences are purely crystallographic effects. These findings together with similar core uniformity in the Fd_{ox} analogues, $[Fe_4S_4(SR)_4]^{2-}$, provide substantial experimental evidence for an elongated D_{2d} core as the stable configuration of the trianion and a change to compressed D_{2d} structure on oxidation [331].

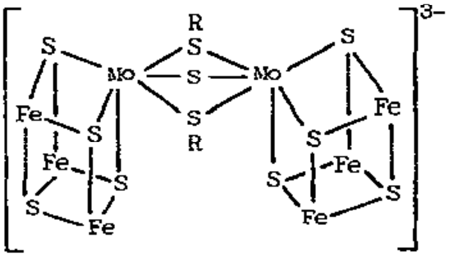
Holm has also studied the electron exchange kinetics for $[Fe_4S_4(SR)_4]^{n-}$ and $[Fe_4Se_4(SC_6H_4Me)_4]^{n-}$ (R = $PhCH_2$ or 4-MeC_6H_4; n = 2 or 3) by NMR methods. Rate constants of the order of 10^6 to 10^7 ℓ mol^{-1} s^{-1} place these among the faster inorganic self-exchange reactions. Thus, the slow rates observed for natural systems can be attributed to the retarding influences of the protein rather than to intrinsically slow reactions of the clusters [332]. The kinetics of $[Cr^{II}(edtaH_2)]$ reduction of $[Fe_4S_4(SCH_2CH_2CO_2)_4]^{6-}$ shows reduction to the heptaanion is too fast to be followed by stopped flow methods. With an excess of $[Cr(edtaH_2)]$, production of an octaanion was monitored by stopped flow. $[Cr(edtaH_2)]$ was incapable of producing super-reduced forms of $[Fe_4S_4]$ protein from *Clostridium pasteurianum* or of the HIPIP protein from *Chromatium vinosum* [333]. The kinetics of oxidation of $[Fe_4S_4(SR)_4]^{3-}$ clusters by a number of inorganic oxidants has also been reported [334]. Photo-induced electron-transfer from $[Fe_4S_4(SR)_4]^{2-}$ to methyl viologen, acenaphthaquinone or TCNE has been published. In some cases, $[\{MoO(H_2O)(cys)(\mu\text{-}O)\}_2]$ was used as a catalyst [335]. Electrochemical studies of ferrodoxins absorbed onto a mercury electrode have been reported [336].

Ethyne has been used as a substitute for N_2 in probing nitrogen fixation and it has now been shown that $[Fe_4S_4(SPh)_4]^{3-}$ together with ethanoic acid and ethanoic anhydride in *N*-methylpyrrolidone at 25 °C effects homogeneous reduction of ethyne to ethene (60% conversion). Deuterium incorporation is stereoselective giving *cis*-CHD=CHD. The system is not catalytic, and departed from the strict stoicheiometry of equation (10), primarily because of a competing cluster

$$2[Fe_4S_4(SR)_4]^{3-} + C_2H_2 + 2H^+ \longrightarrow 2[Fe_4S_4(SR)_4]^{2-} + C_2H_4 \qquad (10)$$

oxidation reaction [337]. The cluster $[Fe_4S_4Cl_4]^{2-}$ containing labile terminal chloride ligands, after treatment with PhLi, is active in the hydrogenation of *cis*- and *trans*-stilbines. PhLi treated $[Fe_4S_4(SPh)_4]^{2-}$ exhibits no activity [338]. $[Fe_4S_4(SR)_4]$ does, however, catalyse the oxidation of RSH to RSSR by oxygen. The rate determining step of this process is believed to be electron-transfer from the cluster to O_2 [339].

The observation of an $\{Fe_3MoS_4\}$ core in nitrogenase has generated considerable activity in modelling iron-molybdenum-sulphur clusters, principally by the groups of Garner and Holm. Holm and coworkers have reported that the reactions of $[MS_4]^{2-}$, $FeCl_3$, RSH and Na[OMe] in an alcoholic solvent at room temperature give $[M_2Fe_6S_9(SR)_8]^{3-}$ (M = Mo or W), $[Mo_2Fe_6S_8(SR)_9]^{3-}$, $[M_2Fe_7S_8(SR)_{12}]^{3-}$ and $[M_2Fe_7S_8(SR)_{12}]^{4-}$ (M = Mo or W), which adopt the structures **(62)**-**(64)**. X-ray crystallography shows **(62)** and **(63)** are almost isodimensional, with Mo....Mo distances of 366.8 and 330.6 pm respectively. Complexes **(64a)** and **(64b)** display trigonal antiprismatic coordination of the central iron atoms. The electronic difference between the last two anions lies in the oxidation state of these central iron atoms; iron(III), probably low-spin, in **(64a)** and high-spin iron(II) in **(64b)**. EXAFS data for these clusters is in good agreement with the Mo-S and



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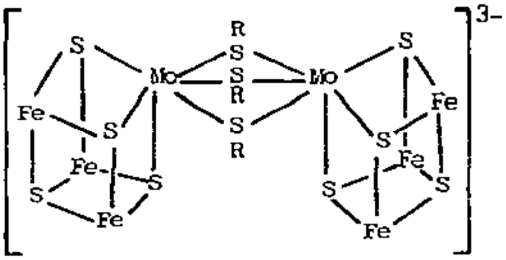

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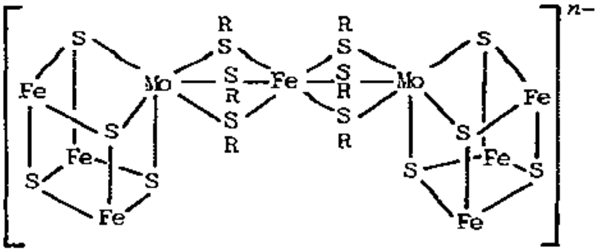


(64a; $n = 3$)

(64b; $n = 4$)

Mo-Fe distances obtained by crystallography, but is not too close to the EXAFS data for nitrogenase. NMR spectroscopy indicates that (62), (64a) and (64b) all exist in single isomeric forms in solution. (62) and (63) both show three-membered electron-transfer series, whereas (64a) shows a four-membered series with initial reduction of the bridging iron, giving (64b), followed by reduction in the clusters. The $\{Fe_3Mo\}$ clusters are electronically delocalised and all iron atoms are virtually identical, with a mean oxidation state of 2.67. The formal definitions of the cluster oxidation states are $[\{Mo^{IV}Fe_2{}^{III}Fe^{II}S_4\}^{4+}$ $\{Mo^{III}Fe_2{}^{III}Fe^{II}S_4\}^{3+}]$ in (62) and $[\{Mo^{III}Fe_2{}^{III}Fe^{II}S_4\}_2{}^{3+}]$ in (63), (64a) and (64b) [340].

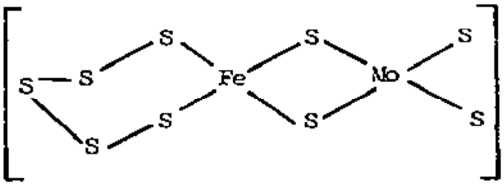
Garner and coworkers have also reported $[Fe_6W_2S_8(SEt)_9]^{3-}$, which is isomorphous with the molybdenum analogue. This anion undergoes two one-electron reduction steps at −0.46 V (−0.51 V) and −1.56 V (−1.76 V) (*vs.* Ag/Ag^+; values for the molybdenum analogue in parentheses), but unlike the molybdenum analogue these reductions are reversible. This may be relevant to the low activity observed when nitrogenase is reconstituted with tungsten in place of molybdenum [341]. These workers have also reported $[Fe_6MoS_3(SR)_9]^{3-}$ (R = Ph, Cl-4-C_6H_4, Me-4-C_6H_4 or Et) and presented detailed NMR, Mössbauer and electrochemical studies. On the basis of the isomer shifts, iron is assigned an oxidation state of 2.5, thus giving the molybdenum or tungsten atoms formal oxidation states between 3 and 4 [342]. The complexes $[Fe_6M_2S_8(SPh)_6(OMe)_3]^{3-}$ (M = Mo or W) have also been prepared and in these cases, the two $\{Fe_3MS_4\}$ cubes are linked by three methoxy groups [342,343]. Reaction of $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (R = Et, $PhCH_2$ or CH_2CH_2OH) with PhCOX (X = Cl or Br) leads to replacement of all Fe-bonded terminal SR groups to give $[Fe_6Mo_2S_8(SR)_3X_6]^{6-}$, the bridging SR groups being unaffected [344].

Hydrogenase contains $\{Fe_4S_4\}$ and $\{Fe_2S_2\}$ ferredoxin units, but treatment of $[Fe_4S_4(SPh)_4]^{3-}$ with weak acids gives oxidation without dihydrogen formation, and the use of strong acids gives rise to cluster decomposition. However, $[Fe_4S_4(SPh)_4]^{3-}$ in dma with PhSH gives $[Fe_4S_4(SPh)_4]^{2-}$, $[PhS]^-$ and H_2 (11-31% after 24 h). With $[Fe_6Mo_2S_8(SPh)_9]^{5-}$ (formed by reduction of the trianion) and PhSH, dihydrogen is produced in 80-100% yield after 600 min, according to equation (11). This demonstrated that this reduction needs a low potential two-electron reductant [345].

$$[Fe_6Mo_2S_8(SPh)_9]^{5-} + 2PhSH \longrightarrow [Fe_6Mo_2S_8(SPh)_9]^{3-} + 2[PhS]^- + H_2 \qquad (11)$$

$[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]^{3-}$, $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ and $[Fe_4Se_4(SCH_2CH_2OH)_4]^{2-}$ have all been used to replace the ferredoxin in *Clostridium pasteurianum*, and have mediated electron-transfer in hydrogenase activity [346].

A number of simpler Fe-Mo-S compounds have been prepared. Two groups have reported the preparation of $[Cl_2Fe(\mu\text{-}S)_2MoS_2]^{2-}$ from $[MoS_4]^{2-}$ and anhydrous $FeCl_2$ [347,348]. A structural study of this anion confirms the tetrahedral geometry of both metal ions {r(Fe....Mo) = 277.5 pm} [347]. Although covered in detail elsewhere, those working in this area may be interested in the preparation of a number of Mo-Cu-S clusters as part of this work [347]. Treatment of $[Cl_2Fe(\mu\text{-}S)_2MoS_2]^{2-}$ with RSH (R = Ph or $4\text{-}MeC_6H_4$) and Et_3N gives $[(RS)_2Fe(\mu\text{-}S)_2MoS\ ]^{2-}$ [348]. This anion, and its tungsten analogue, have also been prepared starting with $[Fe(SPh)_4]^{2-}$ in dmf. X-ray structural studies have also been performed on the molybdenum complex [348,349]. Reaction of the molybdenum and tungsten anions with ten equivalents of $[(C_7H_7S)_2]$ gives $[(S_5)Fe(\mu\text{-}S_2)MS_2]^{2-}$. The structure of the molybdenum containing anion (65) has



(65)

also been reported, and its electronic spectrum is very similar to the spectrum of acid-treated, reneutralised Fe-Mo protein from *Clostridium pasteurianum* [349].

$[MoS_4]^{2-}$ reacts with $[Fe(S_2COEt)_3]$ in dmf-MeCN to yield $[S_2Mo(\mu\text{-}S)_2Fe(\mu\text{-}S)_2MoS_2]^{3-}$, which contains tetrahedrally coordinated metal atoms with a slight bend in the Mo...Fe...Mo backbone {$Mo\hat{Fe}Mo$ = 173°; r(Fe-S) = 225.6; $r(Mo\text{-}S_{term})$ = 217.1; $r(Mo\text{-}S_{br})$ = 225.6 pm}. The previously reported $[Fe_4Mo_4S_{28}]$ anion is, in fact, this anion [350].

$[Fe_2S_2(SPh)_4]^{2-}$ reacts with $[MoS_4]^{2-}$ in MeCN at room temperature to give $[(PhS)_2Fe(\mu\text{-}S)_2Fe(\mu\text{-}S)_2MoS_2]^{3-}$, which contains antiferromagnetically coupled Fe^{3+} (S = 5/2) and an $[Fe^{2+}S_2Mo^{6+}S_2]$ (S = 2) unit giving a net S = ½ ground state [351]. $[Fe_4S_4(SCMe_3)_4]^{2-}$ reacts with $[MoS_4]^{2-}$ in MeCN-HCONHMe to form $[Fe_4(\mu\text{-}S)_4(MoS_4)_4]^{6-}$, which retains the $\{Fe_4S_4\}$ core, but has a bidentate $[MoS_4]^{2-}$ ion linked to each iron atom [352].

1.9.4 Iron storage and transport

Three iron-containing non-heme components of the cytosol have been identified from rabbit reticulocytes. These are ferritin, transferrin and a third, as yet uncharacterised component termed "binding protein I" [353]. It, therefore, seems that further development in the elucidation of the details of iron storage can be expected. The K-absorption edge EXAFS spectrum of human diferric transferrin has been compared with those of some model compounds. The results suggested the iron(III) sites are not tetrahedral, but could not distinguish between six- and seven-coordination. EPR spectroscopy suggests, however, they are not simple octahedral sites [354].

Enterobactin, the microbial iron transport compound containing three catechol groups, has been isolated from *Klebsiella pneumoniae*. The stability constant for the addition of Fe^{3+} to enterobactin (ent) has been determined and the value of 10^{52} is the largest for any known iron(III) complex. $[Fe(ent)]^{3-}$ undergoes three sequential protonations that correspond to the conversion of catecholate to salicylate. The complex anion can also be reduced electrochemically at pH>10, but the reduction potential (−1.230 V *vs.* SCE) is consistent with suggestions that it is too low for physiological reduction, and consequently the complex must be hydrolysed to permit iron reduction and removal [355]. Ferrous enterobactin has been isolated from *E. Coli* and its Mössbauer and electronic spectra examined [356].

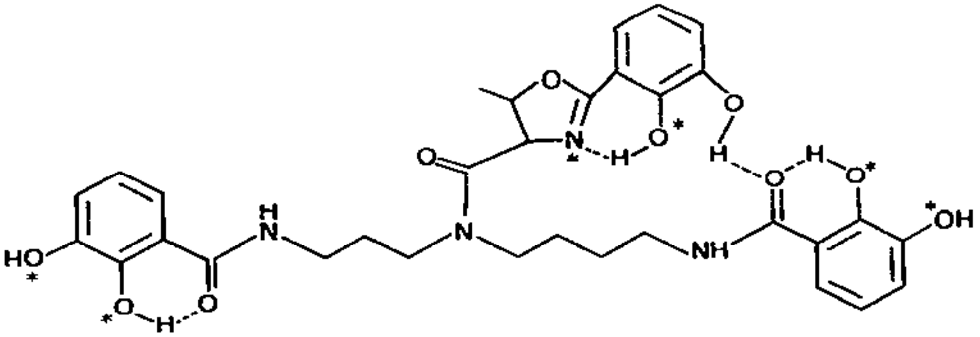
Formation constants for iron(III) complexes of the enterobactin analogues 1,5,9-N,N',N''-tris-(2,3-dihydroxybenzoyl)cyclotriazatridecane and 1,3,5-N,N',N''-tris-(2,3-dihydroxybenzoyl)triaminomethylbenzene are 10^{46} and 10^{40} respectively, and these are the largest measured values for any synthetic iron(III) complex. Both complexes undergo a series of protonations which shift the mode of ligation from use of two phenolic sites to use of carbonyl and phenolate sites. The relevance of these results to chelation therapy of chronic iron overload, as in Cooley's anaemia, were discussed [357].

Studies have been made that were aimed at finding *in vitro* chemical criteria which can be used as indicators of bilogical activity with the eventual aim of designing metal chelates as suitable sources of various trace elements essential to mammalian nutrition. A previous study of acetohydroxamate has now been supplemented by examination of iron(III) glycinehydroxamate. The results showed no production of polymeric species, a fact felt to be important for rapid transfer. The complex donates iron rapidly to apo-transferrin and the free ligand effectively depolymerises iron citrate polymers, a reaction used as a model for the requirement of abstracting iron from ferritin. The potential was thus indicated for the transfer ferritin ⟶ transfer agent ⟶ transferrin sequence [358].

The thiohydroxamate $[Fe\{ONR'CR(=S)\}_3]$ (R = H, R' = Me) can be obtained from *Pseudomonas fluorescens* and displays antibiotic and iron transport properties. The related compounds with (R = H, Ph, Me-4-C_6H_4 or $PhCH_2$; R' = H, Me, Ph or cych) have been synthesised and have been shown by electrochemical studies to undergo rapid one-electron reduction [359]. The complexes $[Fe\{R'C(O)N(O)R''\}(H_2O)_4]^{2+}$ (R' = Me or Ph; R'' = H, Me or Ph) have also been prepared [360].

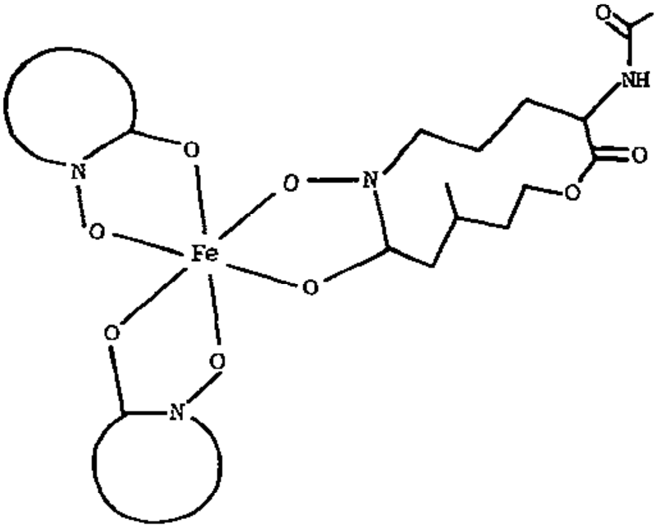
A study has also been made of the interaction of desferrioxamine B and a polymeric hydroxamine acid containing thirty-three hydroxamic acid groups with hydrosols consisting of uniform spherical α-Fe_2O_3 particles [361].

An X-ray structural study on tris-(*N*-methylthiobenzohydroxamto)iron(III) shows a *cis* arrangement of ligands in a trigonally distorted octahedral coordination sphere (twist angle = 42.9°, away from the trigonal prism) [362]. The structure of the linear tricatechol siderophore, agrobactin has also been determined. This coordinates iron(III) at the six sites marked * in (66) [363].



(66)

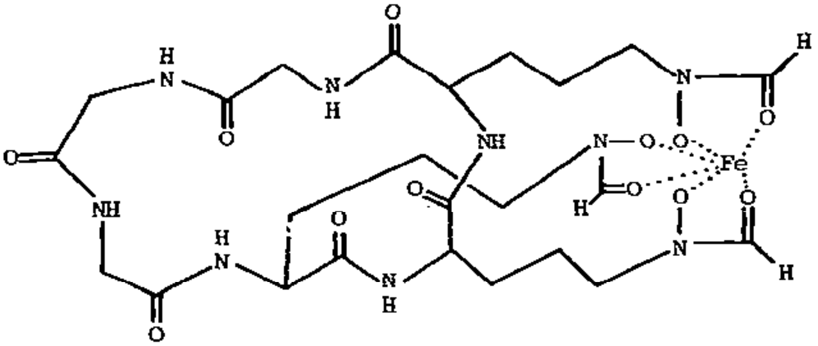
Fusarinines are one of the seven known families of siderophores (the others are ferrichromes, ferrioxamines, rhodorulic acids, aerobactins, enterobactins and mycobactins), and one of these, ferric-*N*,*N*',*N*''-triacetylfusarinine has been isolated from a *Penicillium* strain and studied by X-ray crystallography (67).



(67)

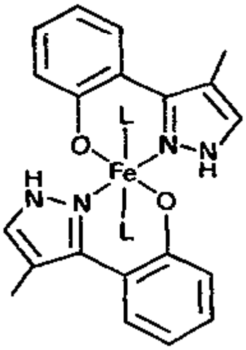
The molecule displays distorted octahedral coordination, and is relatively disc-like with a total thickness of *ca*. 450 pm. The molecules obtained from C_6H_6-EtOH assume the Λ-*cis* absolute configuration but molecules obtained from $CHCl_3$, and all molecules when in solution, are in the Δ-*cis* form [364].

Ferrichrome has been isolated from the smut fungus *Ustilago sphaerogena* and its structure determined (68). The six oxygen atoms of the N^{δ}-acetyl-N^{δ}-hydroxy-L-ornithine residue are coordinated to iron(III) in a distorted octahedral array [365].



(68)

Lactoferrin occurs in high concentration in human milk and although its physiological rôle has not been defined, it is thought to bind iron strongly and be responsible for iron depletion. It has a molecular weight of about 80000 Daltons, and binds two high-spin iron(III) ions and two hydrogencarbonate ions. Some evidence suggests the iron is bound to two or three tyrosine residues and a water molecule. A study has been reported of iron(III) phenolates as models for lactoferrin that have an $\{FeO_2N_2O'_2\}$ core (O=phenolate; N=aliphatic or aromatic N; O'=carboxylate or alkoxy). The structure of one of these, (69), has been determined, and others have been characterised spectroscopically.



(69; L = MeOH)

Collectively, these data support a structure for diferric lactoferrin in which the metal atoms occupy sites of rhombic symmetry, being bound to three tyrosines and two *cis* histadinyl residues: the hydrogencarbonate ions may hydrogen bond to the coordinated water molecule [366].

1.9.5 Other studies

Hemerythin is an invertebrate respiratory protein containing two non-heme iron atoms at each O_2-binding site. In both oxyhemerythin and methemerythin, the pairs of iron atoms are present as antiferromagnetically coupled high-spin iron(III). Previous X-ray crystallographic studies suggested that both iron atoms were octahedral, but the resolution was not high enough to determine the degree of regularity. Electronic spectroscopy suggests, however, that the iron atoms are inequivalently ligated by two and three histadine residues respectively [367]. The complex formed between sulphide and methemerythin has been characterised by resonance Raman spectroscopy, and at pH 8.0 probably contains $\{Fe^{III}\text{-}S\text{-}Fe^{III}\}$ units [368].

The iron centre in ribonucleotide reductase from *E. Coli* consists of two non-identical subunits, B_1 and B_2, both subunits constituting the active site.

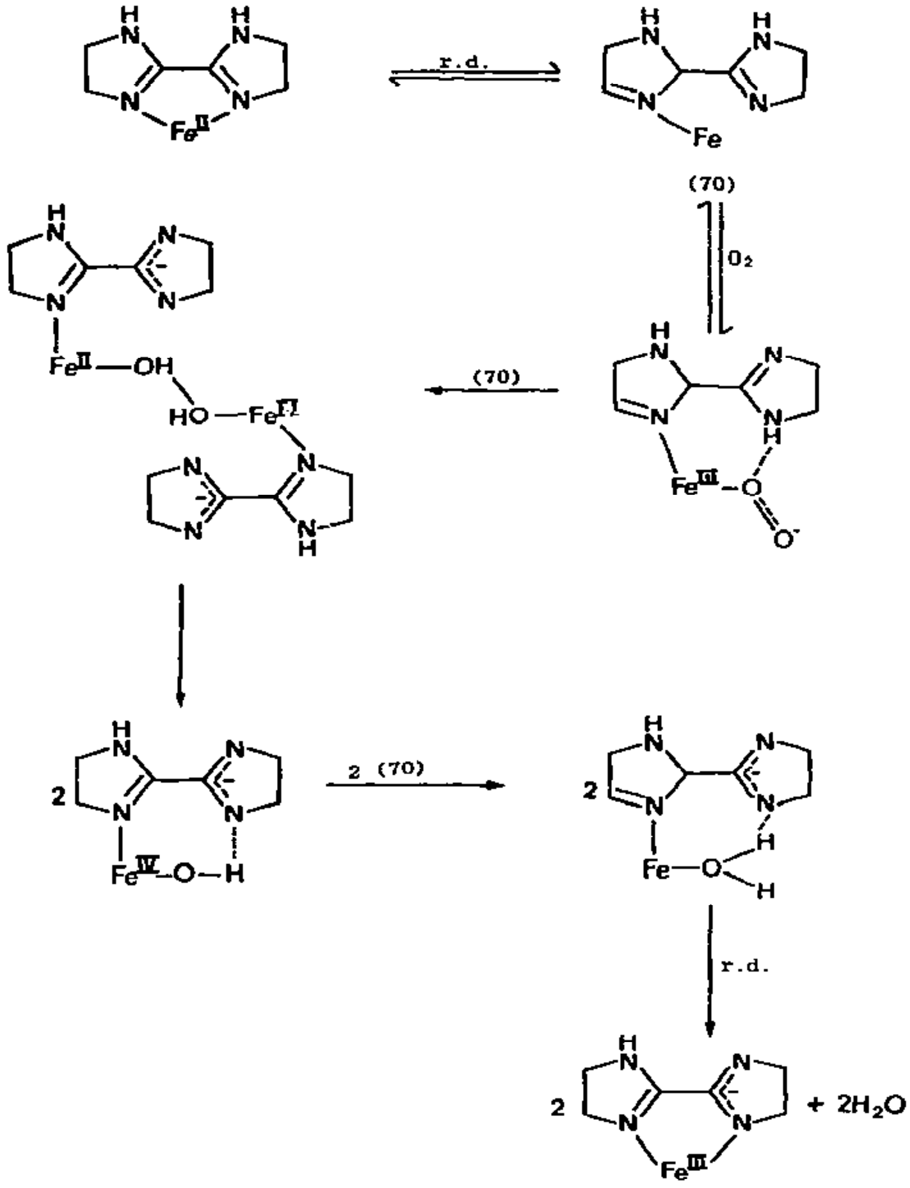
Unit B_2 contains two iron atoms and a tyrosinyl free radical, the metal probably being present as an $\{Fe^{III}\text{-}O\text{-}Fe^{III}\}$ unit [369].

The high-spin cation $[FeL_3]^{2+}$ (L = biimH) reacts with O_2 in aprotic media to produce an iron(III) complex in which one L ligand has been deprotonated, a finding relevant to the speculation on the rôle of the distal imidazole ligand in the reversible binding of O_2 to Hb or Mb, and in particular whether the imidazole hydrogen bonds to O_2. Production of the high-spin iron(III) complex is accompanied by that of water, and the mechanism in Scheme XV has been suggested [370]. An equilibrium study on tryptophan binding to iron(II) and iron(III) enzymes has led to the suggestion that the principal pathway of indoleamine-2,3-dioxygenase involves initial Fe^{II}-tryptophan binding followed by reaction with O_2 [371]. Oxidative ring cleavage of 3,5-di-*tert*-butylcatechol with total incorporation of O_2 is catalysed by $FeCl_2$ in the presence of bipy and py [372].

A system designed to mimic mixed-function oxidases in the hydroxylation of alkanes, based on iron(II), O_2 and *N*-alkyl-2-hydroxybenzylammonium chlorides, has been developed. However, alkane oxidation proceeded with minimal selectivity. The oxidation of anisole and toluene takes place with a selectivity dependent upon the nature of the *N*-alkylammonium chloride [373]. Hydroxylation of aniline has been achieved by systems based on iron(II) complexes and thiols [374]. Contrary to previous claims, it has been found that aqueous $FeCl_3$ is, at best, a feeble catalyst for the aerial oxidation of indole-3-ethanoic acid, and thus it is not a good model for peroxidase [375]. In contrast, *trans*-$[Fe(terpy)(OH)_2]^+$ bound to poly D- or poly L-glutamate is a good catalyst for the oxidation of ascorbic acid by H_2O_2 [376]. Iron(III) corrole complexes catalyse the hydration of alkenes with concomitant reduction to iron(II) species: re-oxidation of the metal is achieved by O_2 [377].

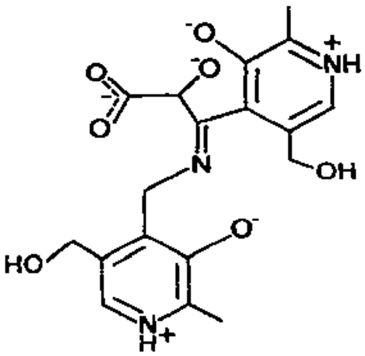
There has been some interest in vitamin B_6 related complexes of iron. Pyridoxal is important in enzymatic transamination and the reaction is catalysed by iron(III) among other metals. The complexes $[Fe(L')]^{2+}$ and $[Fe(LH)(L'H)]^{3+}$ (LH = pyridoxal, L'H = picolinic acid) have been studied [378]. Iron(III) complexes of pyridoxylideneglycine (H_2plgly) and 5'-phosphopyridoxylideneglycine (H_2plpgly) have been prepared. The monomeric five-coordinate high-spin species $[Fe(plgly)(H_2O)X]$ (X = Cl, Br or O_2CMe) and $[Fe(plpgly)(H_2O)(O_2CMe)]$ were obtained and IR data indicate coordination through azomethine *N*, phenolic *O* and carboxylic *O* in both cases [379]. Slow aerial evaporation of an aqueous mixture of pyridoxal, alanine and $Fe(ClO_4)_2$ gives the binuclear iron(III) complex of the ligand (71) [380].

Bleomycins (BLM) are a family of histidine containing glycopeptide antibiotics with anti-tumour properties. This anti-tumour activity is believed to involve iron(II) and oxygen and is believed to occur by reducing O_2 to a more reactive species in the vicinity of a susceptible DNA bond, thereby leading to its cleavage.

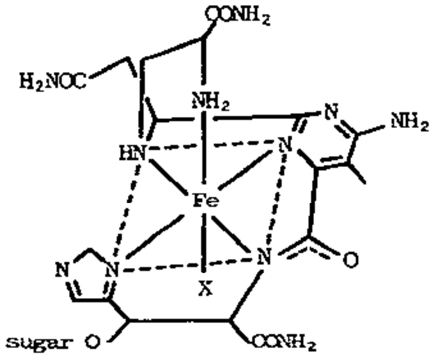


SCHEME XV: The reaction of $[Fe(BiimH)_3]^{2+}$ with O_2 (rd = rate determining step).

Fe(II)-BLM complexes also form low-spin adducts with CO, RNC and NO which inhibit their activity (Scheme XVI). However, with cyanide a high-spin BLM-Fe^{II}-CN adduct is formed, as well as a low-spin BLM-Fe^{III}-CN adduct. It has been reported that the Fe^{II}-O_2-BLM-$[CN]^-$ system is more efficient in producing the active $[O_2]^{\dot{-}}$ and [OH]· radicals than Fe-BLM-O_2 alone [381]. Studies

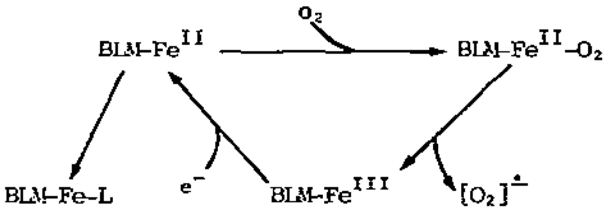


(71)



(72)

on iron belomycin complexes have established the coordination geometry shown in (72) and the iron(II) complexes have been shown to complex with dioxygen and efficiently form $[O_2]^{\dot{-}}$ and $[OH]^{\cdot}$ radicals [382].



SCHEME XVI: The activity of Fe(II)-BLM complexes (L = CO, RNC or NO).

Aconitase is an enzyme which catalyses the dehydration of citrate, and which requires iron(II) and a reducing agent to attain maximum activity. An equilibrium study of iron(II) citrate complexes is therefore relevant to the action of this enzyme, as well as to gastrointenstinal absorption of essential metals. Stability constants for $[Fe_2(citH)_2]$ and $[Mn_2(citH)_2]$ show that the complexes have very similar stabilities, a fact in accord with manganese inhibition of aconitase activity [383].

There has been considerable interest in metal riboflavin complexes, but riboflavin-5'-phosphate (H_2L) has not been previously studied. It has now been shown that the complex $[FeL(OH)].3H_2O$ can be isolated [384]. Camoquin (L'), which is more active than quinine against malaria, forms the complex $[\{Fe(SO_4)\}_2L'].4H_2O$ [385].

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