Coordination Chemistry Reviews, 67 (1985) 109—170
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2. IRON

R. DAVIS

CONTENTS

INTRODUCTION

This review broadly follows the format established in the previous two years. The literature coverage continues where that of 1980 ceased. Thus, publications cited in *Chemical Abstracts* Vol. 93 (19–26), Vol. 94 and Vol. 95 (1–18) are 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 1981.

2.1 CARBONYL, THIOCARBONYL, ISONITRILE, NITROSYL AND RELATED COMPLEXES

One of the most interesting findings in this area involves a study of the reaction of the optically active complex, [FeMe(CO){(S)-NMe(CHMePh)}(cp)] with

0010-8545/85/$21.70

CO which yielded [Fe(COMe)(CO){(S)-NMe(CHMePh)}(cp)] with 90% stereoselectivity. This is compatible only with a mechanism involving the formation of an η^2-MeC=O intermediate rather than the well established methyl migration mechanism observed for the carbonylation of [MnMe(CO)$_5$] [1].

Interest in metal carbonyl radicals, radical anions and radical cations continues to grow. UV irradiation of [Fe(CO)$_5$] in pentane at -100 °C under dihydrogen (30 atm) yields [HFe$_2$(CO)$_8$]$^\bullet$, and one-electron oxidation of [HFe$_3$(CO)$_{11}$]$^-$ and [HFe$_4$(CO)$_{14}$]$^-$ gives [HFe$_3$(CO)$_{11}$]$^\bullet$ and [HFe$_4$(CO)$_{14}$]$^\bullet$, respectively [2]. When a dilute solution of [Fe(CO)$_5$] in rigorously dry, oxygen-free thf is treated with an excess of an alkali metal or an alkali-metal alloy, a red-brown coloration is developed and EPR spectroscopy shows the presence of [Fe$_2$(CO)$_8$]$^{\dot{-}}$, [Fe$_3$(CO)$_{11}$]$^{\dot{-}}$, [Fe$_3$(CO)$_{12}$]$^{\dot{-}}$ and [Fe$_4$(CO)$_{13}$]$^{\dot{-}}$ [3]. In a related study, [SFeCo$_2$(CO)$_9$]$^{\dot{-}}$ has been generated by both electrochemical and chemical means, and it was found that about 60% of the unpaired electron density resides on the two cobalt atoms [4].

The EPR spectrum of the species generated by γ-irradiation of single crystals of [Fe(CO)$_2$(NO)$_2$] is consistent with production of [Fe(CO)$_2$(NO)$_2$]$^{\dot{-}}$, which has C_{2v} symmetry; the unpaired electron density is largely confined to the nitrosyl ligands [5]. Electrochemical reduction of [FeX(CO)$_2$(cp)] (X = Cl, Br, I, SnCl$_3$, GeCl$_3$, SiPh$_3$, SnPh$_3$ or GePh$_3$) proceeds in two one-electron steps. The primary products of the first step, the $E_{\frac{1}{2}}$ of which depends slightly on X, are the anion X$^-$ and the kryptoradical [Fe(CO)$_2$(cp)]$^\bullet$, which is strongly attached to the surface of the mercury electrode. The second step corresponds to reduction of the dimer [Fe$_2$(CO)$_4$(cp)$_2$] which is formed by a complex sequence of reactions at the electrode. The LUMO in the [FeX(CO)$_2$(cp)] complexes is a σ*-orbital of the Fe-X bond [6].

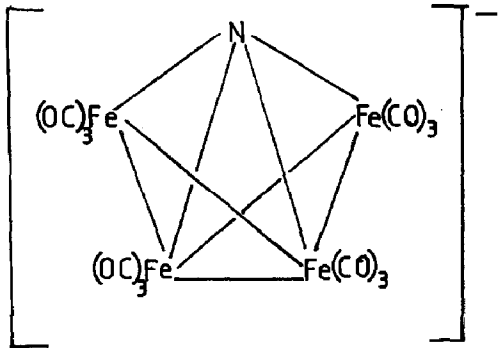
Electrochemical oxidation of [Fe(CO)$_4$L] and [Fe(CO)$_3$L$_2$] has been studied. At a platinum electrode, the 17-electron cations [Fe(CO)$_4$L]$^+$ and [Fe(CO)$_3$L$_2$]$^+$ (L = AsPh$_3$ or SbPh$_3$) which are generated initially are unstable in all solvents, although [Fe(CO)$_3$(PPh$_3$)$_2$]$^+$ shows some stability in dichloromethane. At a mercury electrode, the cations seem markedly more stable and chemically reversible behaviour can be observed, whereas the behaviour is irreversible at platinum. It seems that mercury-stabilised cations are responsible for this difference [7].

A study of the mechanism of the reaction of [FeI(CO)$_2$(cp)] with Ag[BF$_4$] has shown that the adduct [(cp)Fe(CO)$_2$IAg]$^+$ is formed initially and this decomposes to AgI and, in the presence of an excess of [FeI(CO)$_2$(cp)], the bridged cation [{Fe(CO)$_2$(cp)}$_2$I]$^+$. This dinuclear cation reacts with a further half equivalent of Ag[BF$_4$] to yield [Fe(BF$_4$)(CO)$_2$(cp)], in which the anion is coordinated to the metal. Oxidation of [Fe$_2$(CO)$_4$(cp)$_2$] with

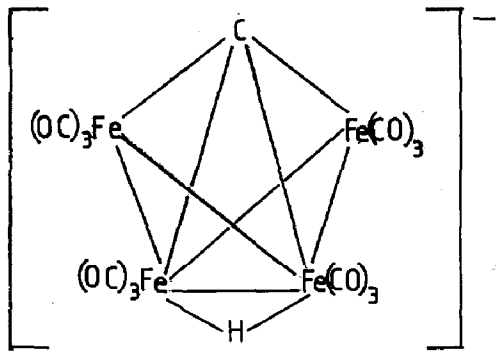
$[Fe(cp)_2]^+$ in propanone (presumably containing traces of water) gives $[Fe(CO)_2(H_2O)(cp)]^+$ [9]. The preparations of $[Fe(CO)_{3-n}(PMe_3)_n(cp)]^+$ (n = 1, 2 or 3) have also been described and the species (n = 2) yields $[Fe(PMe_3)_2(MeCN)(cp)]^+$ on photolysis in ethanenitrile. This cation is a useful precursor to $[FeX(PMe_3)_2(cp)]$ [10].

$K[Fe(CO)_2(cp)]$ is conveniently prepared by treating $[Fe_2(CO)_4(cp)_2]$ with potassium benzophenone ketyl in thf [11]. Irradiation of $[Fe_3(CO)_{11}]^{2-}$ in the presence of PPh_3 in MeCN gives $[Fe(CO)_4]^{2-}$ and $[Fe(CO)_3(PPh_3)_2]$. The reaction is inhibited by CO, and the suggested mechanism involves initial formation of $[Fe_3(CO)_{10}]^{2-}$ which is the immediate precursor of the products. It is proposed that the reason why cluster fragmentation does not occur in the primary photoprocess is that the face-bridged CO ligand inhibits geometric rearrangement of the photogenerated diradical species. UV irradiation of the $[Fe_3(CO)_{11}]^{2-}$ anion in NaOH solution gives $[Fe(CO)_4]^{2-}$, $Fe(OH)_2$, H_2 and CO; however, the initial step of this reaction is not known [12].

Reaction of $[Fe(CO)_3(NO)]^-$ and $[Fe_3(CO)_{12}]$ gives the anion (*1*), which has a butterfly structure with all metal atoms linked to the nitrogen atom. Protonation of (*1*) gives $[Fe_4N(CO)_{12}H]$. However, reaction with an excess of acid under CO yields $[Fe_4N(CO)_{11}(NO)]$, $[Fe_3(NH)(CO)_{10}]$ and $[Fe_3(NH)_2(CO)_9]$. Reaction with $[NO]^+$ leads to $[Fe_4N(CO)_{11}(NO)]$ [13]. Treatment of $[Fe_4(CO)_{13}]^-$ with CF_3SO_3H yields the closely related carbido-anion (*2*) [14]. Oxidation of



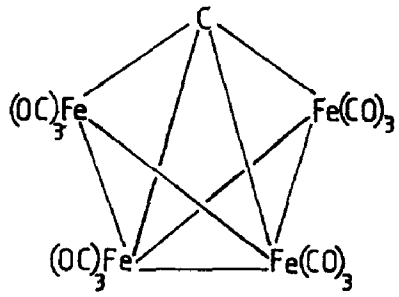
(*1*)



(*2*)

the dianion $[Fe_6C(CO)_{16}]^{2-}$ in methanol gives $[Fe_4(CO)_{12}C(CO_2Me)]^-$, which on treatment with CF_3SO_3H produces the carbide (*3*) [15].

The cluster compound $[Fe_4(CO)_4(cp)_4]$ is obtained in high yields by photolysis of $[Fe_2(CO)_4(cp)_2]$ in the presence of catalytic amounts of PPh_3. However, the use of 1,3-dimethylbenzene as solvent is said to be critical in obtaining high yields. In halocarbon solvents, PPh_3 is ineffective and the tetramer is obtained as the radical cation [16].



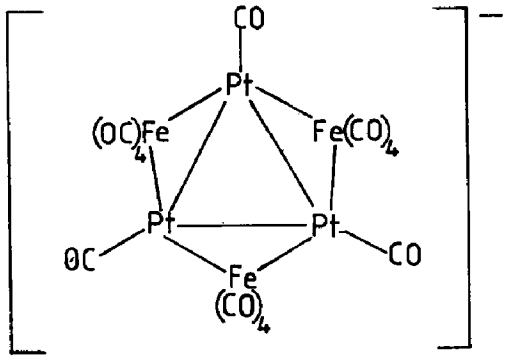
(3)

The fluxional behaviour of $[Fe_3(CO)_{11}L]$ {L = PR_3 or $P(OR)_3$} has been interpreted in terms of an icosahedral $\rightleftharpoons$ cubo-octahedral interchange of ligands, of the type previously postulated for the carbonyls $[M_4(CO)_{12}]$ (M = Co, Rh or Ir) [17]. The heats of formation of $[Fe_2Ru(CO)_{12}]$ and $[FeRu_2(CO)_{12}]$ are -1820 ± 14 kJ mol^{-1} and -1903 ± 18 kJ mol^{-1}, respectively. These values lead to an Fe–Ru bond enthalpy contribution of *ca.* 95 kJ mol^{-1} [18].

Substitution of $[H_2FeM_3(CO)_{13}]$ (M = Ru or Os) with PR_3 gives $[H_2FeM_3(CO)_{13-n}(PR_3)_n]$ {M = Os, R = Ph, n = 1; M = Ru, R_3 = Ph_3, Ph_2Me, $PhMe_2$, $PhEt_2$, $(OMe)_3$, $(OEt)_3$, $(OEt)_2Ph$, Me_3 or $(CHMe_2)_3$; n = 1}. The structure of $[H_2FeRu_3(CO)_{12}(PMe_2Ph)]$ has been determined and is basically the same as the unsubstituted complex, with the phosphine being attached to the ruthenium atom that is also bound to the two hydride ligands. Photolysis of $[H_2FeM_3(CO)_{13}]$ in the presence of H_2 gives $[H_4FeM_3(CO)_{12}]$, but similar treatment in the presence of CO leads to cluster fragmentation [19]. $[H_2FeRu_3(CO)_{13-n}(PR_3)_n]$ display fluxional processes which are basically the same as those of the unsubstituted complex. These involve bridge-terminal CO exchange localised on iron, cyclic exchange of CO ligands about the triangular face of the cluster which possesses the CO bridges, and metal framework rearrangement with corresponding shifts of hydride and carbonyl ligands [20]. Reaction of $[FeH(CO)_4]^-$ with $[Ru_3(CO)_{12}]$ or $[Fe_2Ru(CO)_{12}]$ gives $[HFeRu_3(CO)_{13}]^-$ or $[HFe_2Ru_2(CO)_{13}]^-$, respectively. The structures of these two anions are similar, in that they both contain a tetrahedral array of metal atoms. The $\{FeRu_3\}$ species has three terminal CO ligands on each ruthenium atom, two terminal CO ligands on the iron atom, and two semi-bridging CO groups between iron and ruthenium with the two hydride ligands bridging one Ru–Ru bond; the $\{Fe_2Ru_2\}$ species contains a fully bridging CO group between the iron atoms and no semi-bridging CO ligands [21]. $HC(PPh_2)_3$ reacts with $[HFeCo_3(CO)_{12}]$ with the replacement of three CO groups and the formation of a complex in which a

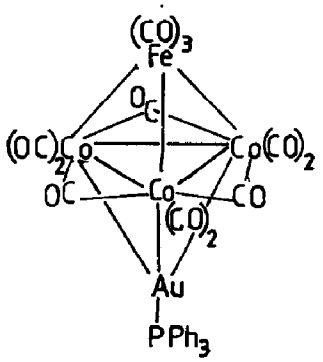
phosphorus atom coordinates to each of the three metal atoms forming a triangular face [22].

EPR spectra of the anion (*4*) show the unpaired electron to be located in a

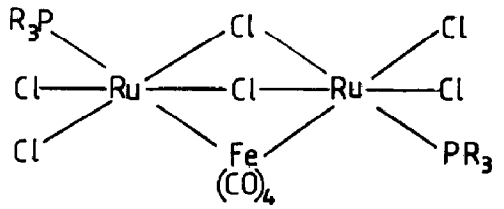


(*4*)

non-degenerate MO of the $\{Pt_3\}$ system [23]. The related anion, $[Pt_6Fe_4(CO)_{22}]^{2-}$, is obtained from reaction between $[Fe_4(CO)_{13}]^{2-}$ and a platinum(II) salt in thf [24]. The recognition that $\{Au(PPh_3)\}$ is isolobal with the hydride ligand has led to an increase in interest in clusters containing this group. It has been found that $[FeCo_3(CO)_{12}]^-$ reacts with $[Au(NO_3)(PPh_3)]$ to produce (*5*), which contains the first example of a triply-bridging gold atom and is analogous to $[HFeCo_3(CO)_{12}]$ in which the hydride bridges the three cobalt atoms [25].

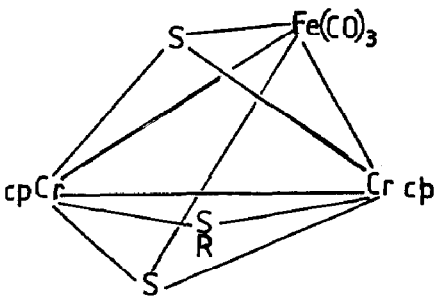


(*5*)

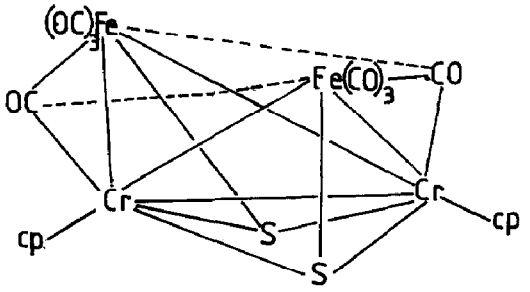


(*6*; R = Me or Ph)

$[Fe_2(CO)_9]$ reacts with $[RuCl_2(PR_3)(arene)]$ to give (*6*) [26]. Treatment of $[\{Cr(SCMe_3)(cp)\}_2S]$ with $[Fe(CO)_5]$ under photochemical conditions leads to (*7*), whereas the related compound (*8*) is obtained from reaction between $[Fe_2(CO)_6S_2]$ and $[Cr_2(CO)_6(cp)_2]$ [27].



(7)



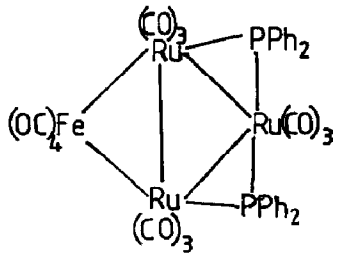
(8)

Reaction of $[HfX_2(cp)_2]$ (X = Cl or I) with $Na_2[Fe(CO)_4]$ leads to $[(cp)_2HfFe(CO)_4]$ [28] and treatment of $[Fe(CO)_5]$ with $[Cd(O_2CMe)_2]$ in the presence of *N,N'*-dimethyl-1,2-diaminoethane or 1,3-diaminopropane (L_2) and NH_4OH yields $[L_2CdFe(CO)_4]$ [29].

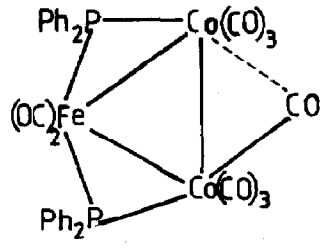
The complex $[Fe(CO)_4(AsMe_2X)]$ reacts further with $AsMe_2X$ to give $[Fe(CO)_3(AsMe_2X)_2]$ (X = NMe_2 or $SiMe_3$). Reaction of the bis(dimethylaminoarsine) complex with HCl yields $[Fe(CO)_3(AsMe_2Cl)_2]$ and reaction of the bis(trimethylsilylarsine) complex with MeOH, Me_2PCl and Me_2AsCl produces $[Fe(CO)_3(AsMe_2X)_2]$ (X = H, PMe_2 or $AsMe_2$). Benzilideneacetonetricarbonyliron reacts with $[(OC)MAsMe_2]$ {M = $Mn(CO)_3PMe_3$, $Fe(CO)(cp)$, *etc.*} to form $[(OC)_4\overline{FeAsMe_2M}]$ [30]. $[(OC)_4\overline{FeAsMe_2M}(CO)_n]$ (M = Mn, n = 4; M = Co, n = 3) undergoes reaction with $[M'AsMe_2]$ (M' = $Mn(CO)_4L$, $Re(CO)_3L_2$, $Fe(CO)(NO)L_2$ or $Co(CO)_2L_2$ {L = Co, PMe_3 or $P(OMe)_3$}) to give the chain compounds $[(OC)_4Fe-AsMe_2-M-AsMe_2-M']$ [31]. A kinetic study of the reaction of $[(OC)_4\overline{FeAsMe_2Co}(CO)_3]$ with P-, As- and Sb-donor ligands suggests that a concerted, largely I_d, process is occurring with the less nucleophilic reagents, but that the reactions have an increasingly greater I_a character as the ligand nucleophilicity increases. The products have L attached to the cobalt atom [32].

Reaction of $[Fe(CO)_4(PPh_2PPh_2)]$ with $[Ru_3(CO)_{12}]$ produces (*9*) and a similar reaction of $[Co_2(CO)_8]$ gives (*10*). The latter product undergoes three one-electron electrochemical oxidation reactions and yields an anion on treatment with sodium amalgam [33].

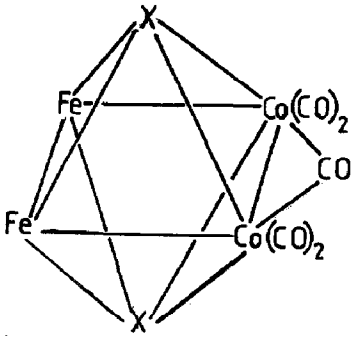
Treatment of $[Fe_2(CO)_6(\mu\text{-}X)_2]$ (X = S or PPhH) with $[Co_2(CO)_8]$ leads to (*11*) [34a]. However, a similar reaction between $[Fe_2(CO)_6(\mu\text{-}S)_2]$ and $[Mn_2(CO)_{10}]$ under photochemical conditions gives $[Fe_2Mn_2S_2(CO)_{14}]$, the most likely structure for which is (*12*), although it is difficult to distinguish between the iron and manganese atoms by X-ray methods [34b]. When a mixture



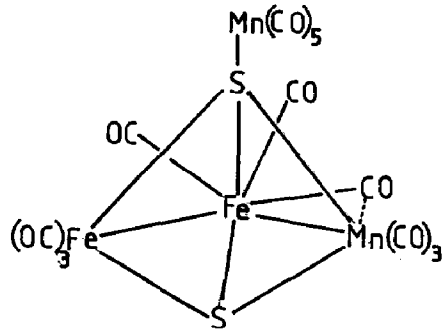
(9)



(10)

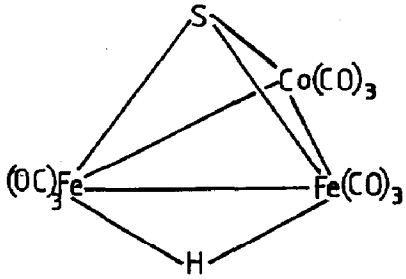


(11)

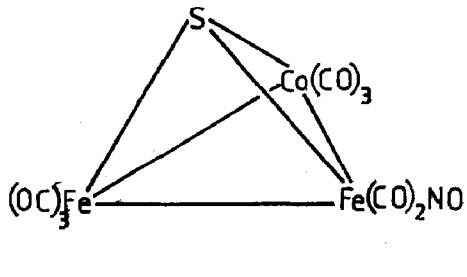


(12)

of $[Fe(CO)_5]$ and $[Co_2(CO)_8]$ is treated with Na_2S or Na[SEt] under CO (150 atm), $[Fe_2Co(CO)_9S]^-$ is formed. This anion undergoes protonation to form (*13*), a reaction which is reversed when (*13*) is treated with polar solvents. The anion also reacts with acidified nitrite solution to yield (*14*) [35].



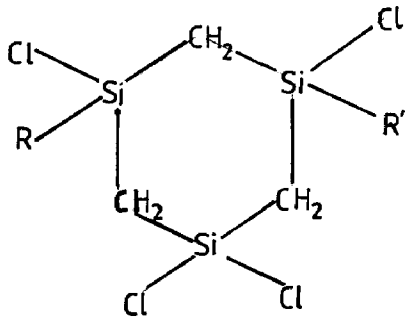
(13)



(14)

The anion $[Fe(CO)_4]^{2-}$ reacts with $[SiMe_3Br]$ in petroleum ether to give *cis*-$[Fe(CO)_4(SiMe_3)_2]$. However, when the reaction of the potassium salt of the anion is carried out in thf, $K[Fe(CO)_4(SiMe_3)]$ is obtained. This salt is

also obtained by treating $[Fe(H)(SiMe_3)(CO)_4]$ with KH. Oxidation of the salt with the tropylium ion or treatment of the bis(trimethylsilyl) derivative with benzaldehyde gives the dimer $[Fe_2(CO)_8(SiMe_3)_2]$ [36]. The structures of (*15*) (R = $Fe(CO)_2cp$, R' = Cl; R = R' = $Fe(CO)_2cp$) have been reported. In both

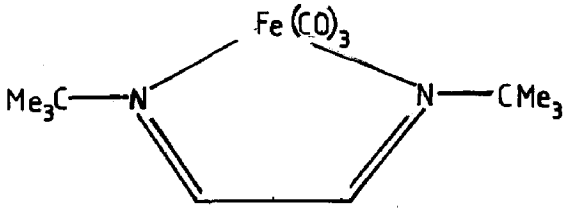


(*15*)

complexes the six-membered rings adopt a skew-boat conformation [37].

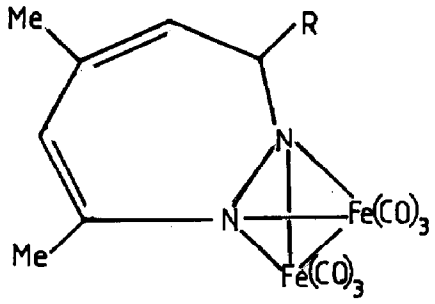
When $[\{Fe(CO)_4(\mu\text{-}SnR_2)\}_2]$ is dissolved in strong Lewis bases, L, an equilibrium is established with the unbridged monomer adduct, $[Fe(CO)_4(SnR_2)L]$ (L = thf, py or $4\text{-}MeC_5H_4NO$). These adducts undergo two-electron reduction in the presence of NaH or sodium-amalgam to give $[Fe(CO)_4(SnR_2)]^{2-}$ in which the electrons reside in the lone-pair orbital on the tin atom [38]. Reaction between $[Fe(MgBr)(diphos)(cp)]$ and $[GeBrPh_3]$ produces $[Fe(GePh_3)(diphos)(cp)]$ [39]. $[Sn(Cl)\{Co(CO)_4\}\{Fe(CO)_2(cp)\}_2]$ has also been prepared [40].

$Me_3CN{=}CHCH{=}NCMe_3$ (dab) reacts with $[Fe_2(CO)_9]$ to form $[Fe(CO)_3(dab)]$ (*16*) and $[Fe(CO)_5]$ in equimolar amounts. The dab complex contains the ligand in

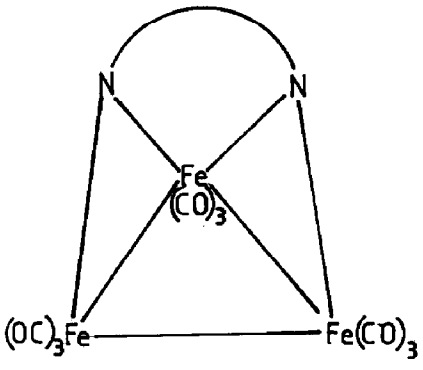


(*16*)

the σ,σ coordination mode, which is in contrast to an earlier assumption of σ,π coordination. The diazacyclopentene can also be obtained by carbonylation of dab in the presence of catalytic amounts of $[Fe_2(CO)_9]$, although the turnover is poor [41]. $[Fe(CO)_3(MeN{=}N{-}N{=}NMe)]$ reacts with a wide range of tertiary phosphines and arsines, L, to form $[Fe(CO)_2L(MeN{=}N{-}N{=}NMe)]$ and with Me_3CNC, L', to yield $[Fe(CO)_{3-n}L'_n(MeN{=}N{-}N{=}NMe)]$ (n = 1, 2 or 3) [42]. Reaction between 3H-1,2-diazepines and $[Fe_2(CO)_9]$ gives (*17*; R = Et, $CHMe_2$ or $PhCH_2CH_2$) [43]. The structure of *syn*-$[Fe_2(CO)_6(\mu\text{-}N{=}CHCH_3)_2]$ has been reported



(17)



(18)

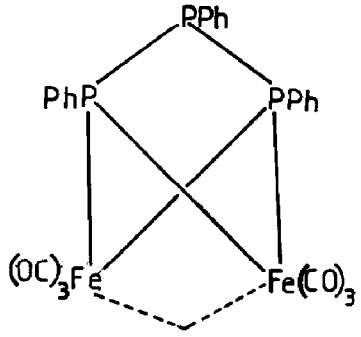
[44], as has that of $[Fe_3(CO)_9(2,3\text{-diazonorbornene})]$, (*18*) [45].

It has been found that $CoCl_2.2H_2O$ and $CoI_2.4H_2O$ catalyse the reaction between $[Fe(CO)_5]$ and PR_3 giving good yields of $[Fe(CO)_4(PR_3)]$. The reaction rate follows the order: $PPh_3 \sim AsPh_3 \sim P(OPh)_3 > SbPh_3 > PPh_2Me > PPhMe_2 > P(cych)_3 > P(OEt)_3 > PBu_3 > P(OMe)_3$ [46]. The electrochemical synthesis of phosphite substituted iron carbonyl complexes using metal anodes has also been reported [47].

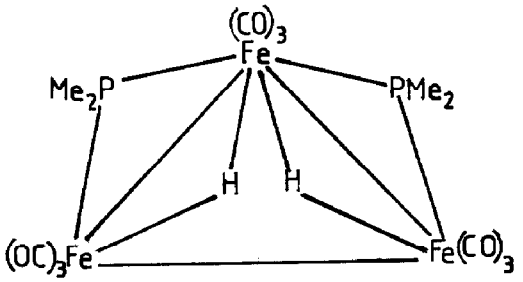
Reaction between $[Fe_2(CO)_3\{P(OR)_3\}(cp)_2]$ (R = Me or Et) and an excess of $P(OR)_3$ gives $[Fe(CO)\{P(OR)_3\}\{P(O)(OR)_2\}(cp)]$, $[Fe(COR)(CO)\{P(OR)_3\}(cp)]$ and $[Fe(OR)(CO)\{P(OR)_3\}(cp)]$ (R = Me only). A similar reaction between $[Fe_2(CO)_3(PPr_3)(cp)_2]$ and excess PR_3 produces ferrocene and $[FeH(CO)(PR_3)(cp)]$ [48].

When $[FeX(CO)_2(cp)]$ (X = Cl or Br) is treated with $[Li\{P(SiMe_3)_2\}]$, $[Fe\{P(SiMe_3)_2\}(CO)_2(cp)]$ is formed. This compound reacts with $[Ni(CO)_4]$ and $[Fe_2(CO)_9]$ to give $[(cp)(OC)_2Fe\{\mu\text{-}P(SiMe_3)_2\}M(CO)_n]$ (M = Ni, n = 3; M = Fe, n = 4) respectively. Photolysis of the di-iron complex leads to $[(cp)(OC)Fe\{\mu\text{-}P(SiMe_3)_2\}(\mu\text{-}CO)Fe(CO)_3]$ and treatment with methanol gives $[(cp)(OC)_2Fe(\mu\text{-}PH_2)Fe(CO)_4]$ [49]. Reaction of $[Fe(CO)_5]$ with $[PPhH_2]$ at 90-120 °C gives three stereoisomers of $[Fe_2(CO)_6(\mu\text{-}PPhH)_2]$ differing in the mutual positions of the Ph group and the H atom on the phosphido bridges. Further treatment of the bridged dimer with $[PPhCl_2]$ in the presence of Et_3N gives $[(PhHP)Fe_2(CO)_6(PPh)_3Fe_2(CO)_6(PHPh)]$ and (*19*) [50]. Treatment of $[Fe(CO)_4(PMe_2H)]$ with $[Ni(\eta^3\text{-}C_3H_5)_2]$ or photolysis of $[Fe_3(CO)_{12}]$ in the presence of $[PMe_2H]$ leads to (*20*) [51].

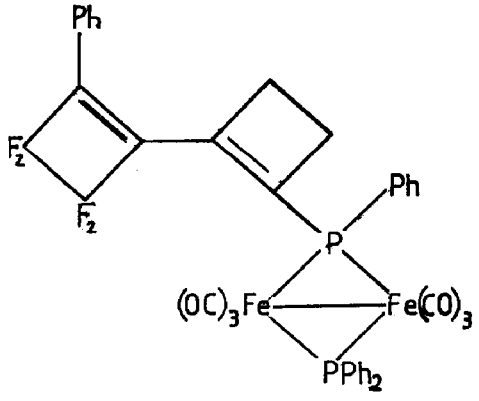
$(C_6H_{11})_2P\overline{C=CP(C_6H_{11})_2(CF_2)}_n$ (LL, n = 2; LL', n = 3) react with iron carbonyls to yield $[Fe(CO)_3(LL)]$, $[Fe(CO)_3(LL')]$, $[Fe_2(CO)_6(LL)]$, and $[Fe_2(CO)_8(LL')]$; (*21*) and (*22*) are formed from $(Ph_2P)\overline{C=C(CF_2)_2C=C(PPh_2)(CF_2)_2}(LL')$ [52].



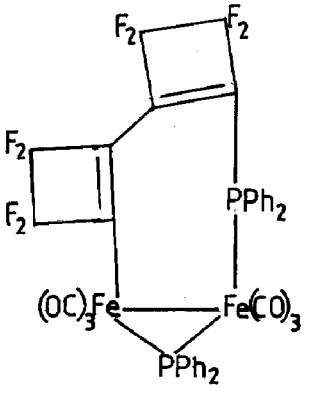
(19)



(20)

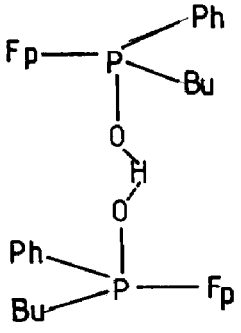


(21)



(22)

When $[Fe(CO)_2(PPhRCl)(cp)]^+$ is treated with aqueous triethylamine in propanone, the complexes $[\{Fe(CO)_2(PPhRO)(cp)\}_2H]^+$ are formed. These are acids of moderate strength and a structural study on the butyl derivative shows it to adopt structure (*23*) in which the O···H···O distance of 240.3 pm is



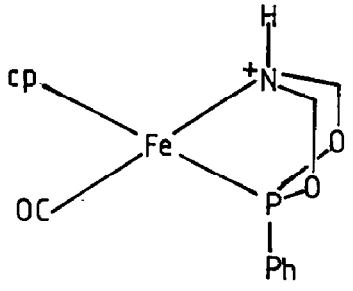
(23; Fp = {Fe(cp)(CO)$_2$})

somewhat shorter than average. Reaction with gaseous HBr gives $[Fe(CO)_2\{PPhR(OH)\}(cp)]$ and treatment with Et_3N leads to $[Fe(CO)_2\{PPhR(O)\}(cp)]$ [53]. A structural study on $[(OC)_3Fe(\mu\text{-}PMe_2)(\mu\text{-}I)Fe(CO)_3]$ shows the Fe-Fe

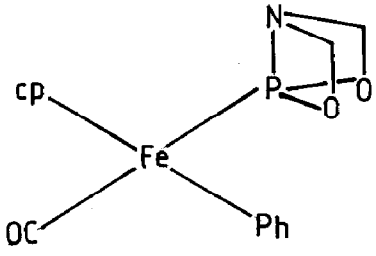
distance to be considerably shorter than expected at 258.8 pm [54].

Reaction between $[Fe(CO)_4(PR_2Cl)]$ and $AlCl_3$ gives $[Fe(CO)_4(PR_2)]^+$ (R_2 = $(Me_2N)Cl$, $(Et_2N)Cl$, $\{(CHMe_2)_2N\}Cl$, $(Me_3Si)_2$, $(Me_2N)CMe_3$) [55]. Treatment of $[Fe_2(CO)_4(cp)_2]$ with SbF_3 gives $[\{Fe(CO)_2(cp)\}_2SbF_3]^+$ or $[\{Fe(CO)_2(cp)\}_3SbOSb\{Fe(CO)_2(cp)\}_3]^{2+}$, whereas AsF_3 yields $[\{Fe(CO)_2(cp)\}_2AsF_2]^+$. With $RAsX_2$ and R_2AsX, $[\{Fe(CO)_2(cp)\}_2As(R)X]^+$ and $[\{Fe(CO)_2(cp)\}_2AsR_2]^+$ are formed respectively [56]. $[Fe_2(CO)_9]$ reacts with substituted stibanes, R_2SbSbR_2, to yield $[Fe(CO)_4(SbR_2SbR_2)]$ (R = Et or CMe_3), $[Fe(CO)_3(\mu\text{-}SbR_2)_2Fe(CO)_3]$ (R = Et or Ph) and $[Fe(CO)_4(\mu\text{-}SbPh)_2Fe(CO)_4]$ [57]. Reaction of $[FeBr(CO)_2(cp)]$ with $[Ph_2PCH_2CH_2S]^-$ gives $[Fe(PPh_2CH_2CH_2S)(CO)(cp)]$ [58].

When the cation (*24*) is treated with base, simple *N*-deprotonation was not observed, but was accompanied by the unexpected migration of the phenyl group to the metal atom to give (*25*). Even more surprisingly, this reaction could be reversed by treating (*25*) with acid [59].

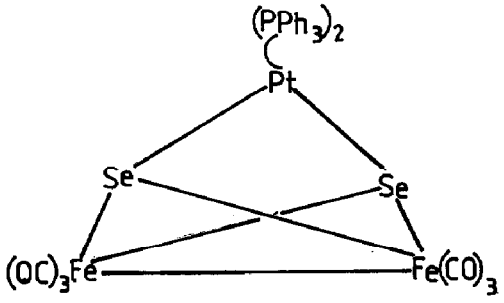


(*24*)



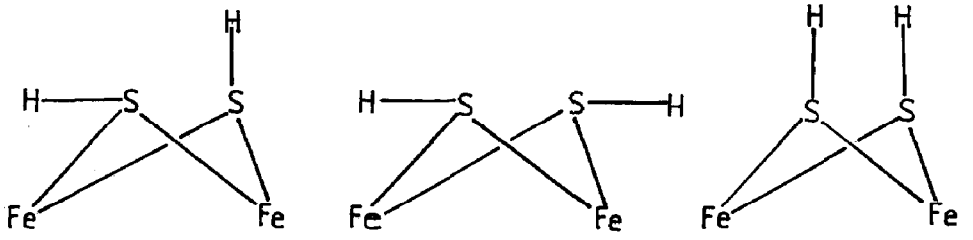
(*25*)

He(I) and He(II) PES and MO calculations of $[Fe_2(CO)_6L_2]$ (L = S or $SCHMe_2$) have been reported [60]. $[Fe_2(CO)_6(\mu\text{-}Se)_2]$ reacts with electrophiles in a manner similar to organic diselenides. Thus, treatment with $Li[BEt_3H]$ or RLi gives $[Fe_2(CO)_6(\mu\text{-}SeLi)_2]$ or $[Fe_2(CO)_6(\mu\text{-}SeR)(\mu\text{-}SeLi)]$ respectively. Reaction with $[Pt(PPh_3)_2]$ gives (*26*) and with $[Co_2(CO)_8]$, $[FeCo_2(CO)_9(\mu_3\text{-}Se)]$ is obtained [61]. Roussin's Red Salt, $[Fe_2(NO)_4(\mu\text{-}S)_2]^{2-}$, behaves similarly,



(*26*)

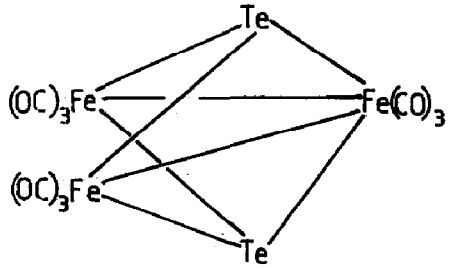
reacting with electrophiles to give $[Fe_2(NO)_4(\mu\text{-}SR)_2]$ {R = Me, Et, $CHMe_2$, $PhCH_2$, Me_3Sn, Ph_3Sn, Ph_3Pb, PhHg or $Fe(CO)_2(cp)$} and with $[Pt(PPh_3)_2Cl_2]$ to form the analogue to (*26*) [62]. The same research group have prepared $[Fe_2(CO)_6(\mu\text{-}SH)_2]$ by reaction of $[Fe_2(CO)_6(\mu\text{-}S)_2]$ with KH to form $[Fe_2(CO)_6(\mu\text{-}S)]^{2-}$, followed by protonation of the dianion with CF_3CO_2H. NMR studies suggest the di-(μ-SH) complex exists as a mixture of three isomers differing in the relative orientations of the SH groups as shown in (*27*).



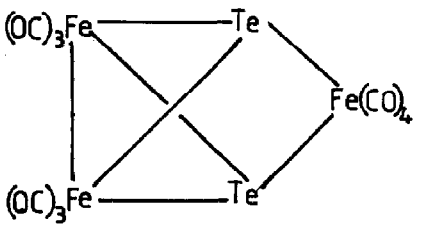
(27; CO groups omitted)

This molecule mimics organic thiols reacting with $I(CH_2)_nI$ and Et_3N to yield $[Fe_2(CO)_6\{\mu\text{-}S(CH_2)_nS\}]$ (n = 1 or 2) [63]. It has been proposed that *syn*- and *anti*-isomers of $[\{Fe(CO)_3(\mu\text{-}SMe)\}_2]$ interconvert *via* a mechanism involving Fe-S bond rupture and reformation [64].

Reaction of $[Fe_2(CO)_6(\mu\text{-}Te)_2]$ with $[Fe(CO)_5]$ in the presence of base or Me_3NO or reaction of $[Fe(CO)_5]$ with $[TeO_3]^{2-}$ and hydroxide ion gives (*28*). The first of these routes also gives (*29*) [65]. The structures of the two



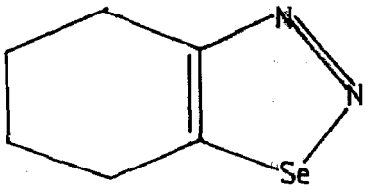
(28)



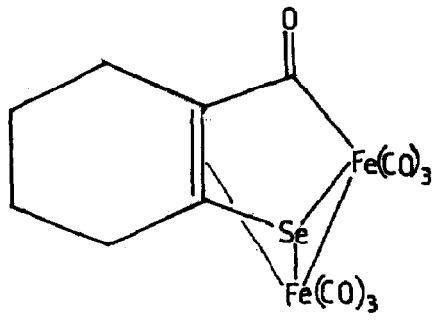
(29)

isomers of $[\{Fe(CO)(cp)\}_2(\mu\text{-}TeC_6H_4\text{-}4\text{-}OEt)_2]$ have been determined. Both contain slightly puckered TeFeTeFe rings, the iron atoms being tetrahedrally coordinated and the tellurium atoms having irregular trigonal pyramidal coordination. One isomer has the two cp rings *cis* to one another and to the puckering of the ring, whereas they are mutually *trans* in the other [66]. The structure of $[Fe_2(CO)_6(\mu\text{-}SPh)(\mu\text{-}PPh_2)]$, obtained from photolysis of $[Fe(CO)_5]$ and Ph_2PSPh, has also been determined {r(Fe-Fe) = 261.0 pm} [67].

Reaction of $[Fe_2(CO)_9]$ with cyclohexeno-1,2,3-selenadiazole, (*30*), gives (*31*) {r(Fe-Fe) = 263.1 pm} [68]. The complexes $[Fe(XYCNMe_2)(CO)(cp)]$ and

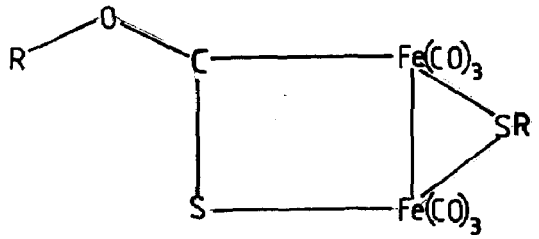


(30)



(31)

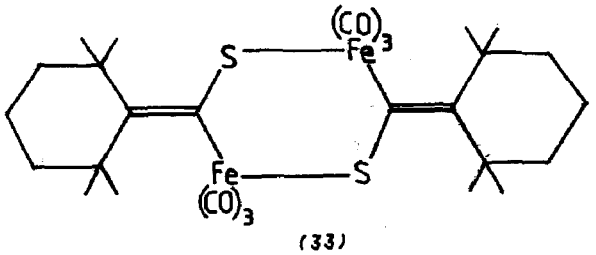
$[Fe\{X(Y)NMe_2\}(CO)_2(cp)]$ {XY = SeSe, SeS or SS; X(Y) = Se(Se), S(Se), S(S), Se(O) or S(O)} all undergo a one-electron oxidation to the corresponding cation. The shifts in the oxidation potentials indicate the order of electron donor power, Se > S > O [69]. ^{13}C NMR spectra of $[Fe_2(CO)_5L(\mu\text{-}SR)(\mu\text{-}X)]$ {X = *S*-alkyldithiocarbamate, L = CO or $P(OMe)_3$} over the temperature range -100 °C to +50 °C shows one $\{Fe(CO)_3\}$ unit to be static while the other is fluxional [70]. $[Fe_2(CO)_9]$ reacts with *O*-alkyl-*S*-alkyldithiocarbonates to give (*32*).



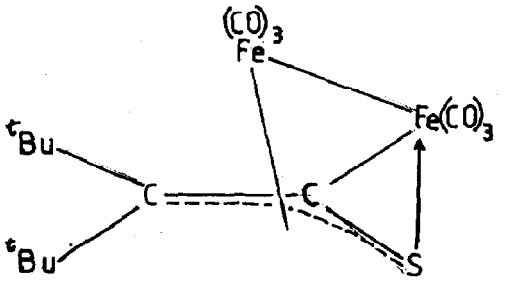
(32)

One or two CO ligands can be replaced by $P(OMe)_3$ [71]. Reaction between $[Fe(CO)_2(thf)(cp)]^+$ and PhSH gives $[Fe(CO)_2(SHPh)(cp)]^+$, which is a strong acid and can be deprotonated by base yielding $[Fe(SPh)(CO)_2(cp)]$ [72]. A structural study of $[Fe\{OC(O)H\}(CO)_2(cp)]$ confirms the presence of monodentate methanoate [73].

Dialkylthioketenes react with $[Fe_2(CO)_9]$ to give (*33*) and (*34*) [74].



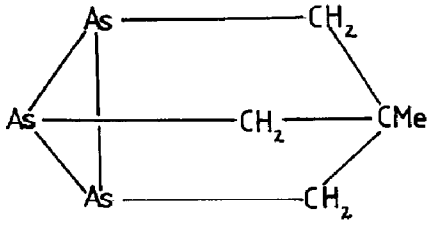
(33)



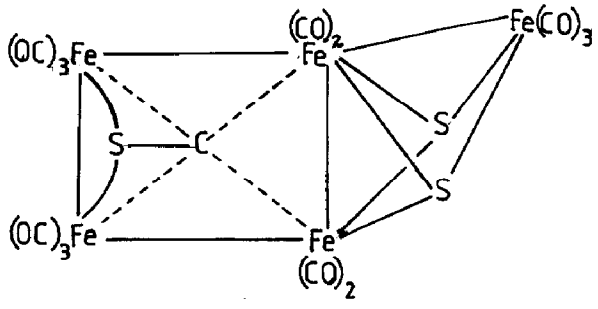
(34)

Treatment of $[Fe(CO)_4(cp)_2]$ with Et_2S_x (x = 3 or 4) gives $[Fe_2(S_2)(SEt)_2(cp)_2]$, $[Fe_3S_2(SEt)(cp)_3]$, $[Fe_4S_4(cp)_4]$, $[Fe_4S_5(cp)_4]$ and $[Fe_4S_6(cp)_4]$. A similar reaction of $[\{Fe(CO)(SEt)(cp)\}_2]$ and S_8 gives all these compounds except $[Fe_3S_2(SEt)(cp)_3]$ and treatment of $[Fe_2(CO)_4(cp)_2]$ with S_8 gives a mixture of the three tetranuclear species: all of these compounds contain the S_2 unit. Electrochemical oxidation of $[Fe_2(S_2)(SEt)_2(cp)_2]$ gives the corresponding monocation, whereas similar treatment of $[Fe_4S_5(cp)_4]$ gives both mono- and di-cations. $[Fe_4S_5(cp)_4]^{n+}$ (n = 0 or 1) are both fluxional [75]. $[(cp)Fe(CO)(\mu\text{-}CO)(\mu\text{-}CS)Fe(CO)(cp)]$ reacts with PR_3, MeNC and halo-organics as shown in Scheme 1 [76]. Reaction of $[Fe(CO)_4(CS)]$ with $[C(NMe_2)_4]$ gives $[Fe(CO)_4\{C(S)NMe_2\}]^-$, which on treatment with magic methyl yields the carbene complex $[Fe(CO)_4\{C(SMe)NMe_2\}]$ [77]. Reaction of $[Fe(CO)_2(CS)(cp)]^+$ with (*35*; L) in propanone under photolysis gives $[Fe(CS)L(Me_2CO)(cp)]^+$ [78].

When $[Fe_3(CO)_{12}]$ is treated with CS_2 in hexane at 80 °C under CO/Ar (1:1, 10 atm), $[Fe_3(CO)_9S_2]$, $[Fe_4(CO)_{12}(C_4S_4)]$, $[Fe_4(CO)_{12}(CS)S]$ and (*36*) are obtained [79].



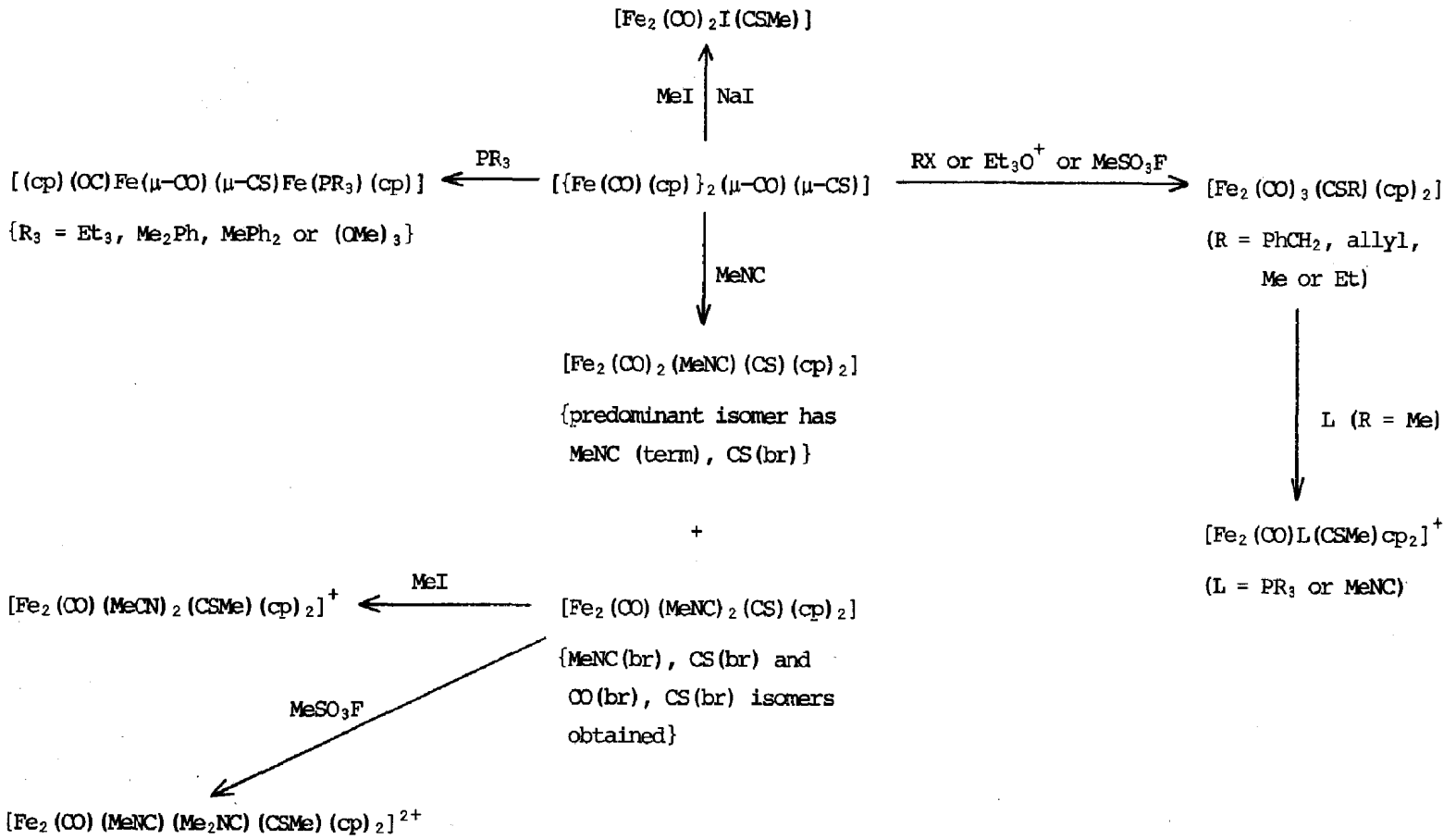
(35)



(36)

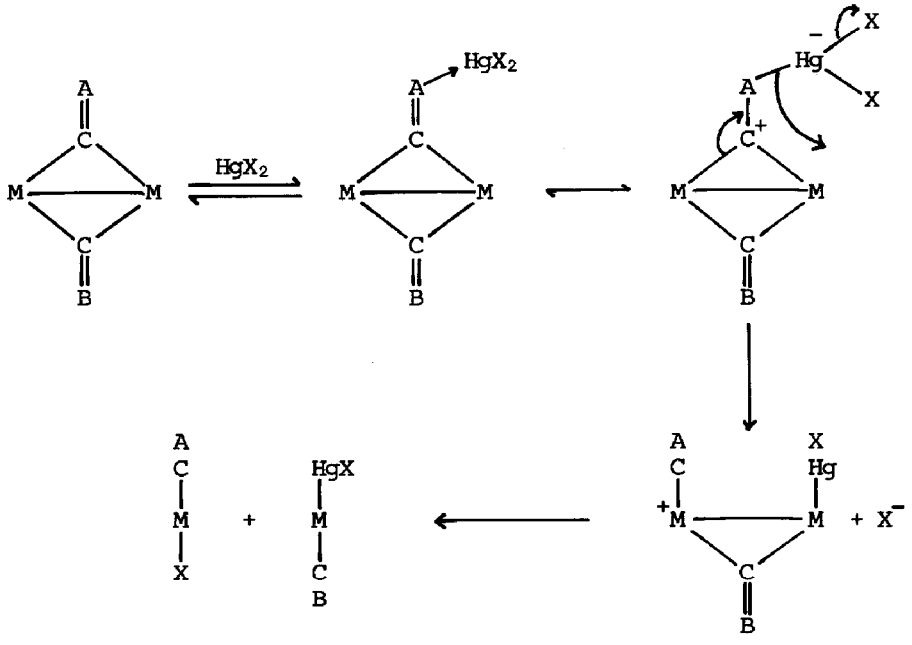
Photolysis of $[Fe(CNR)_5]$ gives $[Fe_2(CNR)_9]$ (R = Et or CHMe). A structural study of the CNEt compound shows it to be similar to $[Fe_2(CO)_9]$ {r(Fe-Fe) = 246.1 pm}. It shows bridge-terminal ligand exchange, occurring by a synchronous pair-wise mechanism. Reaction with RI (R = Me or Et) gives $[Fe_2(CNEt)_7\{CNEt(R)\}_2]I_2$ which contains bridging carbyne ligands. Photolysis of $[Fe(CNMe_3)_5]$ gives $[Fe(CNCMe_3)_4(CN)_2]$, and in the presence of cyclooctatetraene $[Fe(CNCMe_3)_3(\eta^4\text{-cot})]$ [80].

In solution, $[Fe_2(CO)_n(CNR)_{4-n}(cp)_2]$ (R = Ph, 4-$ClC_6H_4CH_2$, $PhCH_2$, 4-$MeC_6H_4CH_2$, 4-$MeOC_6H_4CH_2$, D(+)-PhMeCH, Me,Et,Bu,$CHMe_2$, C_6H_{11} or CMe_3, n = 2; R = Me, Et or $CHMe_2$, n = 1) exist as rapidly interconverting isomers. When n = 2, RNC is less likely to adopt a bridging position as R is varied along the above series. The isomer distribution is a consequence of the electron-withdrawing power of the R group, which as it increases favours a bridging CNR position. Steric effects are less important, but the more bulky



SCHEME 1. Some reaction of [{Fe(CO)(cp)}$_2$(μ-CO)(μ-CS)] [76].

R groups do favour a terminal CNR. When n = 1, only one predominant isomer is observed in solution [81]. Reaction of $[Fe_2(CO)_2L(CNMe)(cp)_2]$ (L = CO or CNMe) with $[HgX_2]$ (X = Cl, Br or I) gives $[Fe(CO)(HgX)(cp)]$ and $[Fe(NCMe)(L)X(cp)]$. This provides confirmation of a reaction mechanism in which the electrophile initially attacks a bridging ligand (Scheme 2) [82]. Treatment of



SCHEME 2. Mechanism of the reaction of $[Fe_2(CO)_2L(CNMe)(cp)_2]$ (L = Co or CNMe) with HgX_2 [82].

$[Fe_2(CO)_4(cp)_2]$ with $CN(CH_2)_nNC$ (n = 2, 3, 4 or 6) gives the complexes $[\{Fe_2(CO)_3(cp)_2\}_2\{CN(CH_2)_nNC\}]$, which are fluxional in solution and exist in three isomeric forms (bridged-bridged, bridged-terminal and terminal, terminal) with respect to the bonding mode of the bidentate isonitrile. Protonation gives $[\{Fe_2(CO)_3(cp)_2\}\{CN(H)(CH_2)_n(H)NC\}]^{2+}$ and reaction with iodine leads to $[FeI(CO)_2(cp)]$ and $[\{FeI(CO)(cp)\}_2\{CN(CH_2)_nNC\}]$ [83].

Sonochemistry of $[Fe(CO)_5]$ with intense ultrasound has been reported. Sonication produces very high local temperatures and pressures for very brief periods and may induce different chemistry to thermal or photochemical methods. For example, $[Fe(CO)_5]$ gives only $[Fe_3(CO)_{12}]$, not $[Fe_2(CO)_9]$ as is observed on photolysis. Furthermore, sonochemistry of $[Fe(CO)_5]$ produces a species capable of acting as an alkene isomerisation catalyst [84].

Intercalation compounds of $[Fe(CO)_5]$, $Na_2[Fe(CO)_4]$ and $[Fe_3(CO)_{12}]$ in graphite have been prepared [85]. When $[Fe(CO)_5]$ and $[W(CO)_6]$ in dmf or dmso

are exposed to air $[FeW(CO)_5O_3(dmf)]$ and $[(OC)_2(dmso)OFeOWO(CO)_2(H_2O)]$ are formed [86].

2.2 HALIDES, OXOHALIDES AND HALIDE COMPLEXES

Mössbauer spectra of $FeCl_3.nH_2O$ (n = 2, 2.5, 3.5 or 6) show all to contain $[FeCl_2(H_2O)_4]^+$ cations [87]. Mössbauer data have also been obtained for $Fe_2F_5.7H_2O$ and have been interpreted in terms of the presence of two Fe^{3+} ions [88]. A structural study of $NaFeF_4$ shows it to adopt a similar structure to that of $NaCrF_4$ and to contain *cis*- and *trans*-linked $\{FeF_6\}$ octahedra which produce puckered layers [89]. The compound alleged to be $[pyH]_2[FeCl_5]$ could not be prepared in aqueous solution, but is obtained by treating anhydrous $FeCl_3$ in absolute alcohol with pyridine and HCl. It was, however, found to be the double salt, $[pyH][FeCl_4].[pyH]Cl$ [90]. The kinetics of the stepwise reversible replacement of Br^- by Cl^- on going from $[FeBr_4]^-$ to $[FeCl_4]^-$ has been studied. Evidence was presented in favour of an ion-pair, ion-pair mechanism and an associative mode of activation with the five-coordinate intermediate or transition state $[FeBr_3Cl_2]^{2-}$ showing exceptional stability [91].

Sr_2FeO_3F has been prepared and shows a K_2NiF_4-type layer structure [92]. Ten nitrogen-containing Lewis bases have been shown to give intercalation compounds with FeOCl. The guest molecules are located in Van der Waals' layers giving an expansion of the b-axis of the unit cell. The magnitude of this expansion has been used to provide information on the orientation of the guests [93].

Heating $[NH_4][FeCl_4]$ gives a complex mixture of products, but $[FeCl_3.NH_3]$ has been identified in the gas phase and its UV spectrum recorded [94]. Reaction between solid $FeCl_2$ and gaseous $[Al_2Cl_6]$ at 620-770 K leads to formation of gaseous $[FeAl_2Cl_8]$, which has D_{3h} symmetry and contains the iron(II) ion in a distorted octahedral environment [95].

2.3 CYANIDES

A structural study of $Na_3[Fe(CN)_6].2H_2O$ reveals layers formed by distorted octahedrally coordinated sodium ions are connected by regular $\{Fe(CN)_6\}$ octahedra [96]. Dehydration data, the vibrational spectra of the water molecules and crystallographic data for $Sr[Fe(CN)_5(NO)].nH_2O$ (n = 1, 2 or 4) show the presence of four distinct types of water molecules, with only one type (O-bonded to Sr^{2+}) common to all three hydrates. The other types are a non-hydrogen-bonded type (dihydrate), a molecule bound by a single hydrogen atom to the nitrogen atom of a cyanide ligand, and a set of two molecules which

are hydrogen-bonded to this previous type (tetrahydrate) [97].

$M_5[Fe(CN)_5(SO_3)]$ {M_5 = Na_5, Tl_5, Na_2Cr, NaM'_2 (M' = Co, Fe, Cu, Mn or Ni)} have been prepared [98] and a structural study of $Na_5[Fe(CN)_5(SO_3)].10^*5H_2O$ confirms *S*-coordinated sulphite ions {r(Fe-S) = 225.5 pm} which appear to exhibit no structural *trans* effect [99]. The effect of various substituents on the pyridine ligand upon the redox and spectral properties of $[Fe(CN)_5(R\text{-}py)]^{n-}$ (n = 2 or 3) have been reported and a correlation exists between the electron transfer band energy and the redox potential [100].

2.4 OXIDES, SULPHIDES AND RELATED COMPOUNDS

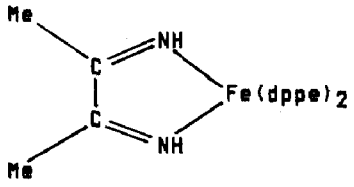
Aerial oxidation of a suspension of iron(II) hydroxide at pH 11.0 and 65 °C gives Fe_3O_4 and α-FeO(OH). When the sulphate ion concentration is low, the reaction proceeds in three stages. These are: (i) formation of iron(III) oxides and slower formation of Fe_3O_4, (ii) rapid formation of Fe_3O_4, (iii) linear formation of Fe_3O_4. At high sulphate ion concentration, formation of α-FeO(OH) is accompanied by slow formation of amorphous γ-FeO(OH) [101].

A structural study has shown $Na_3Fe_2S_4$ to consist of infinite {FeS_2} chains formed by slightly distorting edge sharing {Fe_2S_6} octahedra [102]. Na_3FeSe_3 is formed by reaction of $Na_2[CO_3]$ and iron sponge at 1000 K under dihydrogen saturated with selenium. The compound is isostructural with the sulphur analogue, the $[Fe_2Se_6]^{6-}$ anions consisting of two edge sharing octahedra [103]. The structure of Fe_3P has also been reported [104].

2.5 IRON(II)

2.5.1 Hydride complexes

Reaction of Grignard reagent with $FeCl_3$ under dihydrogen gives $FeH_6Mg_4Br_{3.5}Cl_{0.5}(thf)_8$, which contains $\{FeH_6\}^{4-}$ octahedra with magnesium ions, linked to halide ions and thf, bound to three hydride ligands on opposite octahedral faces. The r(Fe-H) distance is 169 pm [105]. When $[FeX(P_4)]^+$ (X = Br or I; P_4 = $Ph_2PC_2H_4PPhC_2H_4PPhC_2H_4PPh_2$) is treated with $[BH_4]^-$ under argon, $[FeH(P_4)]^+$ is formed, whereas reaction under dinitrogen yields $[Fe(H)(N_2)(P_4)]^+$. The latter cation, in $[FeH(N_2)(P_4)]Br.EtOH$, adopts a *trans* octahedral structure with P_4 ligand occupying the four equatorial sites [106]. The structure of *cis*-$[FeH_2\{Ph_2P(CH{=}CH)PPh_2\}_2]$ has also been reported [107]. Photolysis of $[FeH_2(dppe)_2]$ in benzene gives $[Fe(dppe)_2]$, while a similar reaction in ethanenitrile yields (*37*) [108].



(37)

2.5.2 Complexes with N-donor ligands

Some inconsistencies in earlier Mössbauer and magnetic data for $[Fe(NCS)_2(phen)_2]$ have been reinvestigated. The compound has been reprepared by the two different literature methods. These involve precipitation from methanol or extraction from propanone. The two samples differ in crystal size and quality, and these differences markedly influence the spin transition behaviour [109]. EPR and Mössbauer data have also been reported for $[Fe(NCS)_2(phen)_2]$ and $[Fe(phen)_3]Cl_2.EtOH$ doped with a 1% concentration of Mn^{2+}. The presence of the Mn^{2+} ion has no effect on the spin transition or the temperature at which it occurs. The linewidth of the EPR bands of Mn^{2+} increase dramatically near the transition temperature and remain narrow both above and below it. Broadening occurs because the lifetime, τ_{el}, of the spin-state of high-spin iron(II), which is much smaller than 3 ns at higher temperatures becomes much greater and is in the range 15 $\mu s \geq \tau_{el} \geq 3$ ns in the critical region [110]. ^1H NMR measurements in the region of the spin cross-over for these compounds are in conflict with the predictions of a "cluster" or domain theory and are in complete agreement with an Ising-type theory. This theory involves an interaction term such that the energy of the $^1A_1$ and $^5T_2$ states of a given ion depend on the spin-states of the neighbouring ions. It is assumed that this interaction term results from a change in the ligand field at a given ion caused by a change in the size of the neighbouring complex when it changes from high-spin to low-spin [111]. Changes in the XPES spectrum of $[Fe(NCS)_2(phen)_2]$ accompanying the spin cross-over have also been reported. Changes are observed in the binding energies of both metal and ligand orbitals and this yields information on the covalency changes accompanying the spin change [112]. A related study on $[Fe(NCS)_2(4,7\text{-}Me_2phen)_2]$ suggests that the methyl substituents change the magnetic transition temperature by their steric effects on the lattice parameters, not their electronic effects [113].

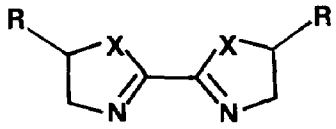
The previously reported spin triplet complexes, $[Fe(phen)_2(ox)].5H_2O$ and $[Fe(phen)_2(mal)].7H_2O$, have been shown to be $[Fe^{II}(phen)_3]_3[Fe^{III}(dianion)_3]_2.nH_2O$ [114]. The electronic ground states of iron in the highly dilute systems $[Fe_xM_{1-x}(bipy)_3]^{2+}$ and $[Fe_xM_{1-x}(phen)_3]^{2+}$ (M = Mn, Ni or Zn) have been examined by Mössbauer spectroscopy. Although the critical field potential (V_c) of the pure iron complexes, which are low-spin, is reported to be close to the cross-over point {*i.e.* $V_c = \overline{P}$ ($\overline{P}$ = mean spin-pairing energy}, the effect of metal dilution does not reduce $|V_c - \overline{P}|$ sufficiently to thermally populate the $^5T_2$ state at room temperature. $|V_c - \overline{P}|$ is estimated as $\cong$ 1200 cm^{-1} [115].

$[Fe(3,3'\text{-bipyridazine})_3]^{2+}$ has a negligible rate of dissociation in water at pH 7 and in 0.05 mol ℓ^{-1} hydroxide ion solution; at an ionic strength of 1.00 mol ℓ^{-1} ($Na[NO_3]$) and 298.5 K, the second order rate constant involving $[OH]^-$ ion attack is 3.3×10^{-5} ℓ mol^{-1} s^{-1}. Examination of kinetic and other data for a wide variety of tris(diimine) complexes of iron(II) indicates that dissociation takes place *via* attack at a ligand. The significance of the various possible intermediates has been assessed and it is suggested that the previously postulated intramolecular transfer of $[OH]^-$ from the ligand to the metal with associated M-N bond fission is important [116]. INDO-MO calculations for $[FeL(CN)_4]^{2-}$ and $[Fe(LH)(CN)_4]^-$, as well as for the free ligands L (L = py_2, phen, bipy, bipyrimidinyl, bipyrazine or bipyridazine) show the residual charge on the carbon atoms of the ring correlate well with the observed differences in the nucleophilicities of the ligands [117]. The kinetics of aquation of $[Fe(4\text{-Mephen})_3]^{2+}$ and its reactions with $[OH]^-$, $[CN]^-$ and H_2O_2 have been reported [118]. A study has also been made of the oxidation of $[Fe\{4,7\text{-}(OH)_2\text{-phen}\}_3]^{2+}$ by dioxygen in 0.1 *M* NaOH. The reaction follows the stoicheiometry of equation (1). No free $[HO_2]^-$ is formed and a plausible

$$4[FeL_3]^{2+} + 2H_2O + O_2 \longrightarrow 4[FeL_3]^{3+} + 4OH^- \qquad (1)$$

mechanism involves bound superoxide or peroxide as intermediates. As a consequence of the redox properties of L and the low oxidation potential of $[FeL_3]^{2+}$, a four-electron transfer from one $[FeL_3]^{2+}$ to one O_2 molecule is a possibility, giving an iron(IV) species with oxidised ligands [119].

The cation, $[FeL_2]^{2+}$ (L = 2,6-bis(4-phenyl-2-pyridyl)-4-phenylpyridine) undergoes two one-electron electrochemical reductions and a one-electron oxidation. The electrochemical data has been compared with that of the corresponding terpyridine and 2,6-bis(2-pyridyl)-4-phenylpyridine complexes and it appears that the *para* phenyl groups can function both as weak electron donors and acceptors [120]. $[FeL_3]X_2$ {L = (*38*)} complexes contain the chelate



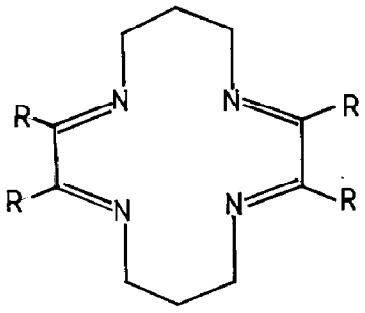
(*38a*; X = NH, R = H)
(*38b*; X = O, R = H)
(*38c*; X = O, R = Me)

ligands coordinated by the diimine group. In the case of (*38a*), the complex displays a $^5T_2 \rightleftharpoons {}^1A_1$ spin equilibrium when X = $[ClO_4]$, but not when X = $[BPh_4]$. (*38b*) and (*38c*) are both high-spin in the range 90–300 K. The cation containing (*38b*) reacts with dioxygen to produce $[Fe^{III}L_2(L\text{-}H)]^+$ in good yield, a reaction which may be reversed by acid [121].

$[Fe(ppm)_3]^{2+}$ {ppm = 2-pyridinal-2-methyl(methylamine)} undergoes a complex reaction with Ce^{4+} in H_2SO_4 solution that results in ligand oxidation. Iron(II) and iron(III) complexes are formed and partly dissociated with the consumption of ten equivalents of Ce^{4+}. The initial iron(III) product disproportionates to an iron(II) tris-complex, the ligand of which contains a formyl group and $[Fe(ppm)_3]^{2+}$. The formyl group arises by oxidation of the 2-methyl group [122].

[Fe(Pc)], and some derivatives, have been prepared by reactions of anhydrides or imides of the corresponding phthalic acid with $FeBr_2$ and urea in the presence of $Na_2[SO_4]$ or $[NH_4]_2[SO_4]$ and catalytic amounts of $[NH_4]_2[MoO_4]$ [123]. When $[Fe(CO)_5]$ is treated with phthalonitrile in dmf, [Fe(Pc)(CO)(dmf)] is formed [124]. The kinetics of the reaction of [Fe(Pc)] with CO in dmf have also been studied [125].

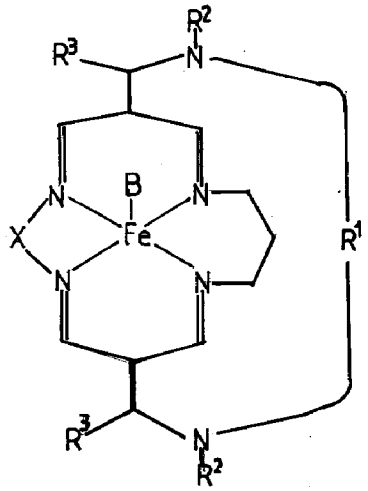
Further publications concerning the compound claimed to be $[\{Fe(Pc)\}_2(\mu\text{-}O_2)]$ (see Review for 1980 [126a; p.25]) have appeared. These include its preparation, characterisation and reaction with Lewis bases [126b]. The kinetics of electrochemical reduction of O_2 to H_2O and H_2O_2 at a rotating disk electrode coated with polymeric [Fe(Pc)] have been reported [127]. A Mössbauer study of polymeric [Fe(Pc)] indicates that the iron atoms occupy at least two different sites in the polymer [128]. A kinetic study has also been made of reaction of $[FeL(MeCN)_2]^{2+}$ {L = (*39*)} with 2-*N*-methylimidazole. The reaction proceeds by a dissociative mechanism and the rate constants for replacement of the second MeCN molecule correlate well with the predicted labilising effects of R [129]. SCF-Xα-SW calculations on $[Fe(N_2C_2H_4)_2(NCS)_2]^{n+}$ (n = 0 or 1) and $[Fe(N_2C_2H_4)_2(SCN)_2]^+$, where $N_2C_2H_4$ is a



(*39*; R = 4-MeC_6H_4 or 4-$MeOC_6H_4$)

model for α-diimine macrocyclic complexes of the type (*39*; R = H) have been reported. It is predicted that the electron removed on oxidation comes mainly from a thiocyanate 2π orbital [130].

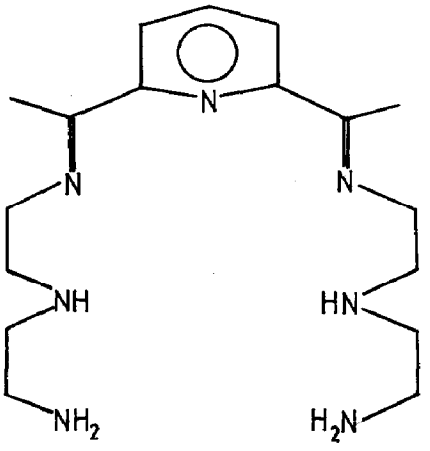
Busch and co-workers have continued their studies on totally synthetic non-porphyrin macrobicyclic complexes containing a persistent void. Thus, iron(II) complexes of the type (*40*) have been prepared, but in order to



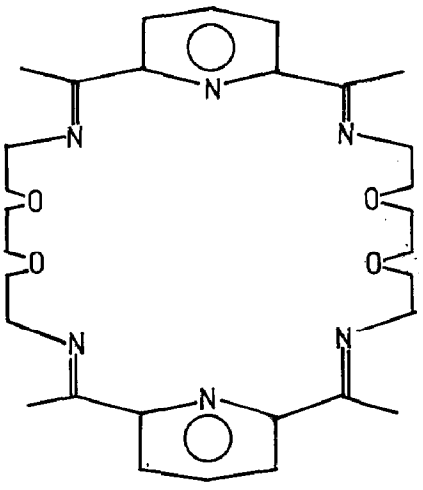
(*40*)

reversibly bind O_2 the metal ion must exhibit a redox potential that falls in a specific range. If the iron(II) ion is too easily oxidised, irreversible electron transfer occurs, giving Fe^{3+} and O_2^-. At the other extreme, there is no Fe^{2+}–O_2 interaction. The oxidation potentials of complexes of the type (*40*) are very close to those of Hb and Mb. $[Fe(L)Cl]^+$ {L = (*40*), R^1 = 3-xylyl, R^2 = R^3 = Me, X = $(CH_2)_3$} has been prepared and in non-aqueous solvents in the presence of *ca.* 1% of water, it is converted into $[Fe(L)B]^{2+}$ (B = py or 1-Meimidazole). This latter cation undergoes completely reversible oxygenation at −35 °C, but this is irreversible at room temperature. This is the most stable non-porphyrin O_2-carrying system so far reported [131].

The ligand, (*41*), forms seven-coordinate complexes of the type $[Fe(L)]X_2.nH_2O$ (X = $[ClO_4]$, n = 1; X = $[BPh_4]$, n = 0) [132]. However, the related 30-membered macrocycle (*42*) with the potential $\{N_6O_4\}$-donor set forms a low-spin complex with $\{FeN_6\}$ coordination [133].

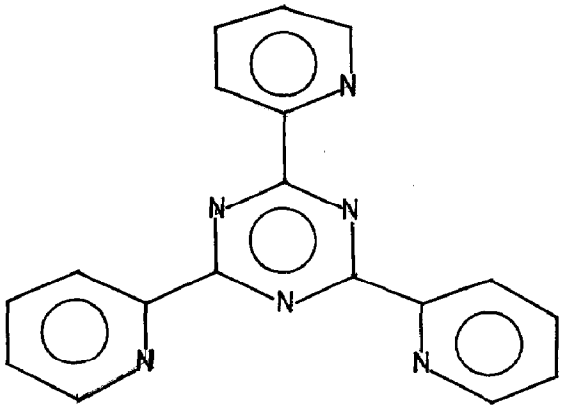


(*41*)



(*42*)

The ligand tpt, (*43*), reacts with $FeCl_2.4H_2O$ to form $[FeCl_2(tpt)].2H_2O$ which can be dehydrated at 180 °C. The anhydrous complex adopts a

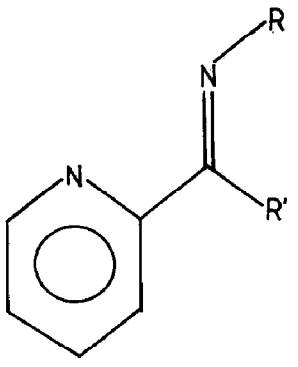


(*43*)

trigonal-bipyramidal structure with the chlorine atoms in the trigonal plane. Slow reaction of $[FeCl_2(tpt)]$ with dioxygen produces $[\{FeCl_2(tpt)\}_2O].2H_2O$ [134].

The complexes, $[Fe(R_3X)_3][ClO_4]_2$, $[FeL][ClO_4]_2$ and $[FeL'_3][ClO_4]_2$ {R = 2-pyridyl, X = COH, N, P, P=O or As; L = *N*,*N*,*N'*,*N'*-tetrakis(2-pyridyl)en; L' = 2-(2'-pyridyl)imidazole} have been prepared and their electrochemical behaviour studied. Those ligands capable of d_π-p_π bonding between R and X can stabilise +1, 0 and -1 oxidation states of iron. However, L does not

stabilise low oxidation states [135].



(44)

$[FeL_3]X_2$ {L = (*44*), X = $[ClO_4]$ or [SCN]} complexes have been prepared, and it is found that their spin-states depend on R, R' and X. Thus when X = $[ClO_4]$ and R = R' = H, Me or Ph, the complexes are low-spin, but when X = [SCN] and R = R' = H or R = H, R' = Ph, intermediate spin (S = 1) behaviour is observed. When X = SCN, R = Ph, R' = H, a spin-equilibrium is established, and other combinations of R and R' with X = SCN lead to low-spin complexes [136].

A structural study of $[Fe(NCS)_2(1,2,4\text{-triazole-}N^2N^4)_2]$ shows the triazole ligand to be bridging in an octahedrally coordinated polymeric structure [137]. Other studies on complexes of *N*-donor ligands are detailed in Table 1.

2.5.3 Complexes with O- and S-donor ligands

The temperature dependence of the magnetic moment of $[Fe(acac)_2]$ can be explained using a $^5T_{2g}$ ligand field ground term. There is no magnetic interaction between the metal ions above 4 K [138].

Detailed structural studies have been reported for $Fe(RSO_3)_2$ (R = Me, CF_3 or 4-MeC_6H_4). The first of these is obtained in two forms, one with a trigonal compression, the other with a trigonal elongation. The former remains paramagnetic down to 4 K with some evidence of magnetic exchange, while the latter orders antiferromagnetically at 23 K. The other two compounds are both magnetically dilute. All three compounds show magnetic moments significantly less than 5.92 μ_B and adopt layer structures in which $\{FeO_6\}$ octahedra are bridged by $[RSO_3]^-$ ligands [139].

Thermal analysis of $FeSO_4.6H_2O$ shows a stepwise loss of water molecules. In the presence of a restricted supply of dioxygen, anhydrous $FeSO_4$ gives $Fe_2O(SO_4)_2$ with no formation of $Fe(OH)SO_4$, but in a free supply of dioxygen, $Fe(OH)SO_4$ is formed and this, in turn, decomposes to $Fe_2O(SO_4)_2$ [140]. A structural study of $Fe(HCO_2)_2.2H_2O$ shows iron(II) ions to occupy two types of

TABLE 1

Miscellaneous studies on some iron(II) complexes

Compound	Comment	Ref.
$FeL_2(NCS)_2(H_2O)_3$ (L = 4-Et-1,2,4-triazole)	preparation described	a
Complexes of (3,5-dimethyl-1-pyrazolylmethyl)amine	six-coordinate complexes described	b
$[FeL_3][picrate]_2$ (L = bipy or phen)	preparation described	c
$Fe(NSF_3)_4(AsF_6)_2$	IR shows a *trans* structure	d
Complex of *NN'''*-bis(pyridylmethylene)trien	preparation and kinetics of reaction with $[CN]^-$ described	e
$[FeL_3][InCl_4]_2$ (L = $NCCMe_2N{:}NCMe_2CN$)	shows spin equilibrium	f
Complexes of isonicotinic acid	octahedral polymers	g
Fe(dien)(phthalate)	high spin, trigonal-bipyramidal	h
$Fe(HNCSNHCSNH)_2$	polymeric	i
$[FeL_2]X_2$ (L = *cis,cis*-1,3,5-trihydroxycyclohexane; X = NO_3, $MeSO_3$ or 4-$MeC_6H_4SO_3$)	preparation described	j
$[Fe(H_2O)_2(XC_6H_4SeO_2)_2]$	chelating selenite ligands	k
Fe(3,5-dinitrosalicylate)$_2$	preparation described	l
$[Fe(Me_2NCSH)_6][ClO_4]_2$, $Fe(dmf)Br_2$	preparation described	m
$Fe(dmf)_2(S_2COEt)_2$	preparation described	n
$FeL_2(PEt_2Ph)_2$ (HL = dmgH, diphenylglyoxime, α-furildioxime)	preparation described	o
$FeL_2.4H_2O$ (HL = 2-(2-carboxyphenyliminomethyl)pyridine acid)	$\{N_2O\}$ donor ligand	p
$FeL_2(H_2O)_2$ (HL = *N*-(5-phenyl-1,3,4-thiadiaz-2-yl)acet- and benzamides)	preparation described	q
Complexes of *syn*-phenyl and *syn*-methyl-2-pyridyl-ketoxime	preparation described	r
FeLCl (HL = bis(salicylideneamino)-maleonitrile)	preparation described	s
Complexes of Schiff bases derived from furan-2-carboxaldehyde and en, dien or trien	form octahedral complexes	t
Complexes of 2'-hydroxy-3'-bromo-4-methoxy-5'-methylchalcone oxime	preparation described	u

TABLE 1 (continued)

Compound	Comment	Ref.
Complexes of thiosemicarbazones of 2-formyl- and 2-acetylthiophene	{*NS*} donor ligands giving low spin complexes	v
$[FeL_2][ClO_4]_2$ {L = RC(=NOH)CR'-(=$NCH_2CH_2NH_2$)}	octahedral {N_6} cation	w
$FeL_2(H_2O)_2$ (HL = 2-(2-hydroxy-benzylidene)amino-5-phenyl-1,3,4-oxadiazole	preparation described	x
Complexes of 1,10-phen-2,9-bis-(carbaldehydephenylhydrazone)	preparation described	y
Complexes of Schiff bases derived from sulphonamides and substituted acetophenones	preparation described	z
FeL_2X_2 (L = 2-py-N=CMeCH_2C(NR)Me)	preparation described	aa
FeL_2Cl_2 (L = *N*-carbamoylpyrazole)	{*NO*} donor ligand	bb
Complexes of *N*-phenyl-*N'*-benzo-thiazole-2-ylthiocarbamide and 2-methylbenzimidazole	preparation described	cc
FeL_2X_2 (L = thiosemicarbazones of acetone and some cyclic ketones)	preparation described	dd
Complexes of 2,3-dioxobutyran-ilide-2-oxime hydrazone and β-rescorcylaldazine	preparation described	ee
$FeL.H_2O$ (H_2L = hydrazodicarbon-imide)	polymer	ff
$FeL(en)X_2.nH_2O$ (L = $PhCONHNH_2$, salicylhydrazine, X = Cl, OAc, $\frac{1}{2}SO_4$)	preparation described	gg
$[FeL_2]^{2+}$ (L = $2NH_2NH$-1,10-phen and 2-MeNHNH-1,10-phen)	preparation described	hh
$FeL_2.2H_2O$ (HL = furfurylidene-benzoylhydrazine)	{*NO*} donor ligand	ii
$FeL_2(H_2O)_2$ (HL = 2-hydrazino benzimidazole)	preparation described	jj
FeL_2X_2 (L = hydrazidothiophosphoric acid)	preparation described	kk
FeL_2 (HL = 2-phenylamino-5-carboxy-methylthio-1,3,4-thiadiazole)	preparation described	ll

TABLE 1 (continued)

Compound	Comment	Ref.
Complexes of 4-benzoyl- and 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one	preparation described	mm
Complexes of 2-aminocyclopentene-1-dithiocarboxylic acid	preparation described	nn
$[Fe(4\text{-}Cl\text{-}2\text{-}NO\text{-}C_6H_3O)_2]$	{*OO*} chelation	oo
$[FeL_3][BF_4]_2$ (L = *N*-acetyl-pyrazole)	{*NO*} chelation	pp
Complexes of 1-amino-2-naphthol-4-sulphonic acid	preparation described	qq
$[FeL(H_2O)_4]Cl.3H_2O$ (HL = lysinemonohydrochloride)	preparation described	rr
Complex of cysteine	polymeric structure	ss

(a) G. Vos, J.A. Haasnoot and W.L. Groeneveld, *Z. Naturforsch. (Teil B)*, 36 (1981) 802. (b) F. Mani, *Cong. Naz. Chim. Inorg. (Atti)*, 12th, (1979) 105; [*Chem. Abstr.*, 95 (1981) 17270]. (c) B.D. Pandey and D.C. Rupainwar, *Trans. Met. Chem. (Weinheim, Ger.)*, 6 (1981) 249. (d) B. Buss, W. Clegg, G. Hartmann, P.G. Jones, R. Mews, M. Noltemeyer and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1981) 61. (e) J. Burgess and G.M. Burton, *Rev. Latinoam. Quim.*, 11 (1980) 107; [*Chem. Abstr.*, 94 (1982) 72236]. (f) A.P. Zuur, W.L. Driessen and P.L.A. Everstijn, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 15. (g) J.R. Allan, G.M. Baillie and N.D. Baird, *J. Coord. Chem.*, 10 (1980) 171. (h) P.R. Shukla and R. Kamul, *Acta Cience. Indica (Ser.) Chem.*, 6 (1980) 198. (i) D.G. Batyr, B.M. Baloyan, E.V. Popa and Y.Y. Kharitonov, *Koord. Khim.*, 7 (1981) 737. (j) W. Marty, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 411. (k) G. Graziosi, C. Preti and G. Tosi, *Trans. Met. Chem. (Weinheim, Ger.)*, 5 (1980) 262. (l) B.D. Heda, S.G. Kaskedikar and P.V. Khadikar, *Ind. J. Hosp. Pharm.*, 17 (1980) 39; [*Chem. Abstr.*, 94 (1981) 57307]. (m) G. Gritzner, W. Linert and V. Gutmann, *J. Inorg. Nucl. Chem.*, 43 (1981) 1193. (n) M.R. Houchin and D. Chapman, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 437. (o) K.I. Turte, V.N. Zubarev, V.N. Shafranskii, R.A. Stukan and G.A. Popovich, *Koord. Khim.*, 6 (1980) 1217. (p) F. Capitan, L.F. Capitan Vallvey and J.L. Vilchez, *J. Inorg. Nucl. Chem.*, 43 (1981) 683. (q) R.S. Srivastava, *Inorg. Chim. Acta*, 55 (1981) L71. (r) M. Mohan and B.D. Paramhans, *Gazz. Chim. Ital.*, 111 (1981) 35. (s) M. Takahashi and T. Iwamoto, *J. Inorg. Nucl. Chem.*, 43 (1981) 253. (t) P. Shukla and R. Takroo, *Ind. J. Chem.*, 20A (1981) 305. (u) N.S. Bhave and R.B. Kharat, *J. Inorg. Nucl. Chem.*, 42 (1980) 977. (v) S. Burman and D.N. Sathyanarayana, *Ind. J. Chem.*, 20A (1981) 57. (w) A.N. Singh, *Ind. J. Chem.*, 19A (1981) 1215. (x) R.S. Srivastava, *J. Inorg. Nucl. Chem.*, 42 (1980) 1526. (y) A.S. Abushameleh and H.A. Goodwin, *Aust. J. Chem.*, 33 (1980) 2171. (z) K. Lal and R.K. Shukla, *J. Ind. Chem. Soc.*, 58 (1981) 115. (aa) V.B. Rana, D.P. Singh and M.P. Teotia, *Trans. Met. Chem. (Weinheim, Ger.)*, 6 (1981) 189. (bb) J. Terheijden and W.L. Driessen, *Trans. Met. Chem. (Weinheim, Ger.)*, 5 (1980) 346. (cc) M.R. Chaurasia, S.K. Saxena and S.D. Khattri, *Ind. J. Chem.*, 19A (1981) 741. (dd) B.W. Fitzsimmons and C.A. Yong, *Inorg. Chim. Acta*, 50 (1981) 179. (ee) R.N. Kapadia, *Ind. J. Chem.*, 20A (1981) 525. (ff) D.G. Batyr, B.M. Baloyan, E.V. Popa and Y.Y. Kharitonov, *Koord. Khim.*, 7 (1981)

TABLE 1 (continued)

598. (gg) I.A. Bashkenadze, *Izv. Akad. Nauk. Gruz, SSR Ser. Khim.*, 6 (1980) 377; [*Chem. Abstr.*, 94 (1981) 218808]. (hh) A.S. Abushamleh and H.A. Goodwin, *Aust. J. Chem.*, 34 (1981) 313. (ii) D.S. Rao and M. Ganorkar, *J. Ind. Chem. Soc.*, 58 (1981) 217. (jj) G.V. Reddy and D.S. Rao, *Natl. Acad. Sci. Lett.*, 4 (1981) 13; [*Chem. Abstr.*, 95 (1981) 143325]. (kk) U. Engelhardt, B. Friedrich and I. Kirner, *Z. Naturforsch. (Teil B)*, 36 (1981) 761. (ll) R.S. Srivastava, L.D.S. Yadar, R.K. Khare and A.K. Srivastava, *Ind. J. Chem.*, 20A (1981) 516. (mm) A.K. Rana and J.R. Shah, *Ind. J. Chem.*, 20A (1981) 142, 615. (nn) S. Burman and D.N. Sathyanarayona, *Ind. J. Chem.*, 20A (1981) 53. (oo) A.T. Pilipenko, L.L. Schevchenko and T.A. Pavlova, *Izv. Vyssh. Uchebn. Zavad. Khim. Khim. Tekhnol.*, 23 (1980) 939; [*Chem. Abstr.*, 93 (1980) 214662]. (pp) W.L. Driessen and P.L.A. Everstijn, *Inorg. Chim. Acta*, 41 (1980) 179. (qq) B.D. Pandey and D.C. Rupainwar, *Ind. J. Chem.*, 20A (1981) 197. (rr) A.K. Jain, K.D. Jain and U. Sharma, *J. Ind. Chem. Soc.*, 57 (1980) 965. (ss) A. Unguireanu and M. Marc, *Rev. Roum. Chim.*, 25 (1980) 845.

octahedral sites; one has four in-plane water molecules and two axial methanoate ions, one bridging and one terminal axial- and one bridging axial methanoate ion [141].

$FeCl_2.4H_2O$ reacts with $[MS_4]^{2-}$ (M = Mo or W) to yield $[Cl_2Fe(\mu\text{-}S)_2MS_2]^{2-}$ which contain tetrahedral high-spin iron(II) centres. A structural study shows the Fe···Mo distance to be 277.5 pm, comparable to that in nitrogenase. SCCC-EH calculations show the electron density at molybdenum to be higher than that in $[MoS_4]^{2-}$ and the electron density at iron to be lower than that in $[FeCl_4]^{2-}$. The Fe→M delocalisation is much stronger in the case of molybdenum than tungsten [142]. The related anion, $[Cl_2Fe(\mu\text{-}S)_2Mo(\mu\text{-}S)_2FeCl_2]^{2-}$ has been prepared by heating $[MoS_4]^{2-}$ and MeCN [143].

Treatment of $Fe(SO_4).7H_2O$ with $[WS_4]^{2-}$ gives $[Fe(S_2WS_2)_2]^{2-}$, which undergoes electrochemical reduction to the corresponding trianion and reacts with dmf or pyridine (L) to yield $[L_2Fe(S_2WS_2)_2]^{2-}$. In the presence of an excess of L, this anion undergoes the reaction shown in equation (2) [144].

$$[L_2Fe(S_2WS_2)_2]^{2-} + (x - 2)\ L \rightleftharpoons [L_xFe(S_2WS_2)] + [WS_4]^{2-} \qquad (2)$$

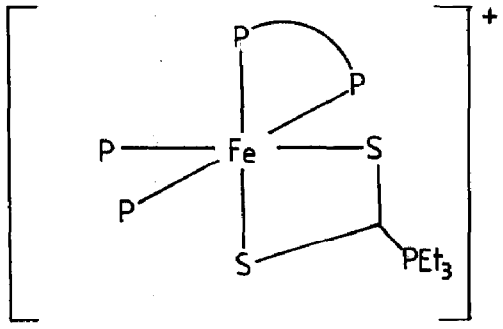
The anion $[Fe(S_2MoS_2)_2]^{3-}$ has also been obtained by reaction of $[MoS_4]^{2-}$ and $[Fe\{(C_6H_4N)CO_2\}_2]$ [145]. When $[Fe(S_2MoS_2)_2]^{3-}$ is treated with NO in dmf, $[(ON)_2Fe(S_2MoS_2)]^{2-}$ is formed. The tungsten analogue was obtained by treating $Fe(ClO_4)_2.6H_2O$ and $[WS_4]^{2-}$ in dmf with NO [146]. Other studies on complexes of *O*- and *S*-donor ligands are detailed in Table 1.

2.5.4 Complexes with P-donor ligands

The complexes, $[FeX_2L_2].L'$ (L = *cis*-$(Ph_2PCH{=}CHPPh_2)$; X = Cl, L' = Me_2CO,

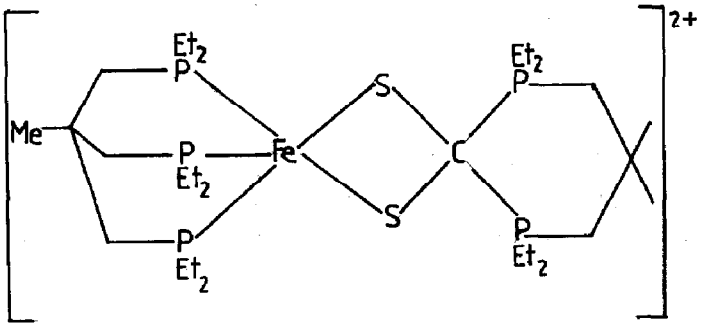
CH_2Cl_2 or $CHCl_3$; X = Br, L' = Me_2CO) show abrupt temperature induced spin transitions in the range 290-230 K between singlet and quintet ground states. A structural study of $[FeCl_2L_2].Me_2CO$ at 295 K (high-spin form) and 130 K (low-spin form) reveals a dramatic reduction in Fe-P bond lengths of *ca.* 28 pm (aver.) and only a slight reduction in Fe-Cl distances (3 pm) at the lower temperature. Comparison with solvent-free $[FeCl_2L_2]$ (high-spin at 295 K) shows that crystal packing and the presence of solvent molecules in the lattice are both factors determining the magnetic properties of these compounds. A similar structural study of $[FeCl_2\{(Ph_2PCH_2CH_2PPh_2\}_2]$ (low-spin) and its propanone solvate (high-spin) shows similar behaviour in that the Fe-Cl distances are practically identical, whereas the Fe-P distances are 266-271 pm in the high-spin form and 223-224 pm in the low-spin form [148].

Iron(II) tetrafluoroborate reacts with $Et_2PCH_2CH_2PEt_2$ and Et_3PCS_2 to form (*45*). Further reaction of (*45*) with $[BH_4]^-$ yields



(*45*)

$[Fe(Et_2PCH_2CH_2PEt_2)_2(S_2CH)]^+$ [149]. Treatment of $Fe(BF_4)_2.6H_2O$ with $MeC(CH_2PEt_2)_3$ and CS_2 gives (*46*), containing the zwitterionic $[Me_2C(CH_2PEt_2)_2CS_2]$ ligand. This is the first example of low-spin

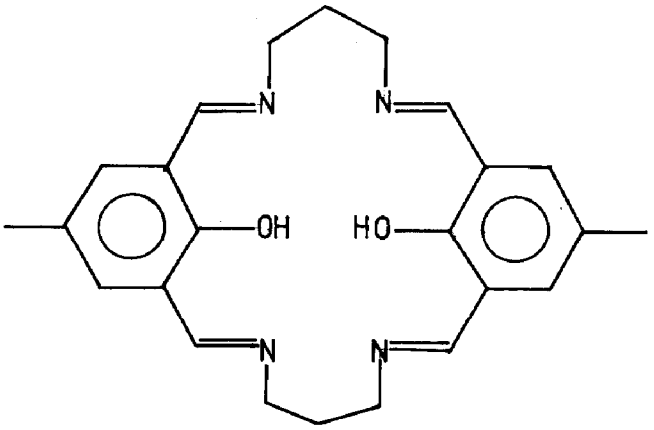


(*46*)

five-coordinate iron(II) and has distorted square-pyramidal coordination geometry [150]. Other studies on complexes with *P*-donor ligands are detailed in Table 1.

2.5.5 Complexes with mixed donor ligands

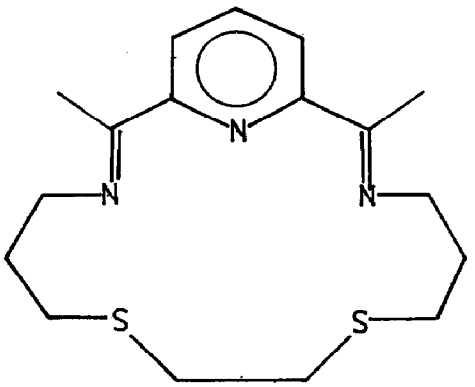
The binuclear complex $[LFe_2(imid)_4][BF_4]_2$ [L = (*47*)] contains two six-coordinate metal atoms, both sited in the equatorial ligand plane; the



(47)

Fe···Fe distance is 311.7 pm. Variable temperature magnetic data for this complex and its bis(4-methylimidazole) and bis(pyridine) analogues show all to exhibit antiferromagnetic exchange. An increase in antiferromagnetic exchange was expected for these six-coordinate complexes compared to their five-coordinate analogues as a consequence of improved orbital overlap arising from the metal ions being held in the ligand planes. This was not, however, realised possibly due to increased ligand field splitting in the six-coordinate complexes offsetting any increased antiferromagnetic interactions [151].

The quinquidentate macrocycle, (*48*), forms both high- and low-spin



(48)

complexes depending on the nature of the other ligands. Thus, $[FeLCl(MeOH)]^+$, $[FeLCl]^+$, $[FeLBr]^+$, $[FeL(NCS)_2]$ and $[FeL(MeOH)_2]^{2+}$ are all high-spin, whereas $[FeLI]^+$, $[FeL(NCS)]^+$ and $[FeL(L')]^{2+}$ (L' = MeCN, py or NH_3) are all low-spin. Structural studies on the low-spin complex, $[FeL(NCS)][BF_4]$ and the high-spin

complex, $[FeLCl(MeOH)][ClO_4]$ show that in the former the macrocycle adopts a "wrap-round" conformation occupying five of the octahedral sites, while in the latter, one sulphur atom is not coordinated and the other is only weakly bound [152].

The cytosine (L) complexes, $[FeL_2]X_2$ (X = Cl or Br) are four-coordinate with ligand bound through N(3) and O(2), whereas $[FeL_4]X_2.mH_2O$ (X = I, NO_3 or ClO_4) are six-coordinate, with water molecules hydrogen-bonded to cytosine ligands [153]. The five-coordinate purine complexes, $Fe(purH)Cl_2.2H_2O$ have also been prepared. These are probably linear oligomers with Fe–purH–Fe bridges and terminal chlorine atoms. The most likely binding sites of the purines are N(3) and N(9) [154]. Other studies on complexes with mixed donor ligands are detailed in Table 1.

2.6 IRON(III)

2.6.1 Complexes with N-donor ligands

The kinetics of the dissociation of $[Fe(5\text{-}X\text{-}phen)_3]^{3+}$ (X = Cl, Br or I) in 0–100% H_2SO_4 have been studied. There is no reaction unless water is present and these results have been interpreted in terms of covalent hydration and pseudo-base formation [155]. The structure of $[phenH][Fe(phen)Cl_4]$ has been determined [156]. $[FeL_3][ClO_4]_3$ {L = (*38a*)} is high-spin, while $[FeL_3][ClO_4]_3$ {L = (*38b*)} has a $^2T_2$ ground state and a thermally accessible $^6A_1$ excited state [121]. The structure of the octahedral complex *cis*-$[FeCl_2(2,2'\text{-biimidazole})_2]Cl.H_2O$ has been determined [157].

The thermodynamic and spectral properties of $[FeL_3]^{3+}$ {L = MeN=CRCR'=NMe; R = R' = H or Me; R = H, R' = Me; RR' = $(CH_2)_4$ or $CH_2CHMe(CH_2)_2$} in molten $AlCl_3$-[pyNEt]Br (2:1) at 25 °C have been determined. This solvent possesses the advantage over organic solvents that it is completely anhydrous and thus water-induced ligand oxidation processes do not take place. Electrochemical studies have been made and the Fe^{3+} form is found to be more stable than the Fe^{2+} form, which is the opposite behaviour to that observed in aqueous solution [158].

$[Fe(big)_2Cl_2]Cl$ {big = $H_2NC(=NH)NHC(=NH)NH_2$ and some aryl derivatives} have spin quartet (S = $^3/_2$) ground states [159]. $[FeCl_3(tpt)].1.5H_2O$ and $[\{FeCl_2(tpt)\}_2O].2H_2O$ {tpt = (*43*)} have been prepared [134]. The structure of the iron(III) μ-oxo dimer formed by the methoxy derivative of tetrabenzo-[b,f,j,n]-[1,5,9,13]-tetraazacyclohexadecine has been reported. Both ligand molecules are saddle shaped with the methoxy groups in positions *cis* to each other with respect to the planes of the ligand [160].

Other complexes of *N*-donor ligands are detailed in Table 2.

2.6.2 Complexes with O-, S- and P-donor ligands

X-ray studies on aqueous iron(III) ammonium oxalate provide evidence for the presence of distorted octahedral $[Fe(ox)_3]^{3-}$ ions [161]. Earlier EXAFS work has suggested that aqueous iron(III) solutions contain the dimer $[(H_2O)_4Fe(OH)_2Fe(OH_2)_4]^{4+}$. However, new EXAFS results are in agreement with X-ray measurements suggesting no dimers are present [162]. The rate of exchange of water between $[Fe(H_2O)_6]^{3+}$ and bulk acidic aqueous solution has been studied by ^{17}O NMR spectroscopy. The results are consistent with an associative mechanism, whereas a study of $[Fe(H_2O)_5(OH)]^{2+}$ suggest a dissociative mechanism. Solutions heated above 110 °C developed a species which exchanges water (2-15)x10^4 times faster than $[Fe(H_2O)_6]^{3+}$ and which is persistent at room temperature for months: this is an Fe(III) oligomer [163].

A study of the magnetic properties of $K_5[\{Fe_3(OH)_2\}_3(SO_4)_6O].6H_2O$ has shown that $Fe^{III}...Fe^{III}$ magnetic coupling *via* the bridging sulphate ions is small and the observed antiferromagnetism arises predominantly through the $\{Fe_3O\}^{7+}$ unit. A comparison of the antiferromagnetism in $\{Fe_3O\}^{7+}$, $\{Fe_2O\}^{4+}$ and $\{Fe_2(OH)_2\}^{4+}$ clusters shows that Fe-O bond lengths are of overriding importance, Fe-$\hat{O}$-Fe bond angles being less so [164].

The Mössbauer spectra of $[Fe^{II}Fe^{III}O(O_2CMe)_6L_3]$ (L = H_2O or py) show absorptions due to Fe^{II} and Fe^{III} sites at 17 K, but a single absorption at 300 K. This allowed an estimation of the magnitude of the thermal barrier to electron transfer [165]. $[Fe_2^{III}M^{II}O(O_2CMe)_6(py)_3].py$ (M = Mg, Mn, Co, Ni or Zn) have also been prepared and are isomorphous with the $\{Fe_2^{III}Fe^{II}\}$ complex. The magnetic properties suggest that, in these complexes also, the central *O* atom provides the main super-exchange pathway [166]. The cations $[Fe_3OL_3(H_2O)_3]^+$ (L = malonate, succinate, fumarate or phthalate) are polymeric with dicarboxylate groups bridging $\{Fe_3O\}$ clusters. These anions display both intratrimer and intertrimer spin-exchange effects. A small intertrimer exchange effect is also suggested in the corresponding ethanoate [167].

A study of the mechanism of electrochemical reduction of [Fe(β-diketonate)$_3$] complexes shows a reversible one-electron uptake which is followed, in the case of tfacac, by further reduction [168]. A comparison has been made between the electrochemistry of $[\{cis\text{-}(OC)_4Re(CH_3CO)_2\}_3Fe]$ and [Fe(acac)$_3$]. The reduction potential of the rhenium-containing complex is 0.63 V more positive than that of [Fe(acac)$_3$], reflecting the higher electronegativity of the rhenium-containing ligands [169].

A low temperature Mössbauer study of [Fe(Morphyldithiocarbamate)$_3$].CH_2Cl_2 shows an $S = {}^5/_2$ ground state at low temperature with a crystal field

TABLE 2

Miscellaneous studies on some iron(III) complexes

Compound	Comment	Ref.
$FeCl_3.S_4N_4$	preparation described	a
$[Fe(OSiMe_3)_4]^-$	preparation described	b
$Fe(OMe)_2NO_3$	preparation by treatment of $Fe(NO_3)_3.9H_2O$ with 2,2-dimethoxypropane	c
$Fe[Fe(oxalate)_3].4H_2O$	preparation and thermal decomposition described	d
Complexes of oxalate or malonate with bipy or phen	preparation described	e
FeL_3 (HL = α-iodoacetoacetanilide)	preparation described	f
Complexes of *N*-alkylacetoacetanilides	preparation described	g
FeL_3 (L = 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone)	preparation described	h
FeL_3 (L = methylphenylphosphinate)	linear polymer	i
$Fe(OH)L_2.8H_2O$ (HL = quercetin-5'-sulphonic acid)	preparation described	j
$FeL_3.2H_2O$ (HL = 2-hydroxy-3(3-methyl-2-butenyl)-1,4-naphthaquinone)	preparation described	k
$FeL(OH)$ (H_2L = 2,2'-oxydibenzoic acid)	$[FeO_6]$ coordination octahedra with bridging OH	l
Complexes of maltol	preparation described	m
$[FeL_2(H_2O)_2]^{2+}$ ($L = S_2COBu^-$)	preparation described	n
FeL_3 (HL = 4-amino-N-(5-ethyl-1,3,4-thiadiazol-2-yl)benzenesulphonamide)	preparation described	o
$Fe(HPOX)(POX)X_2$, $[Fe(HPOX)X_2]X$ (HPOX = pyridine-2-aldoxime, X = Cl, Br, I, NO_3, NCS or O_2CMe)	preparation described	p
Complexes of *syn*-phenyl-2-pyridyl ketoxime	preparation described	q
Complexes of 2'-hydroxy-3'-bromo-4-methoxy-5'-methyl chalcone oxime	preparation described	r
$[FeL[ClO_4]$ (H_2L = Schiff bases formed by *N,N'*-bis(3-aminopropyl)-piperazine and salicylaldehyde derivatives)	preparation described	s

TABLE 2 (continued)

Compound	Comment	Ref.
Complexes of substituted-1,2,4-triazoline-5-thiones	preparation described	t
$[FeCl_3L]$ (L = a range of *N,N'*-(substituted) formamidino-*N''*-(substituted) carbamides and thiocarbamides)	preparation described	u
Complexes of *N,N'-cis*-1,2- and (1R,2R)-*N,N'-trans*-1,2-cyclohexylene-bis(salicylideneamine)	preparation described	v
FeL_3 (HL = 2-amino-4-methylthiazole or 2-amino-4-phenylthiazole)	preparation described	w
$[FeClL]$ (H_2L = Schiff base formed by salicylaldehyde and alcoholamines)	preparation described	x
Complexes of 2-formyl- and 2-acetylthiophene thiosemicarbazones	preparation described	y
Complexes of 1-salicyl- and 1-phenyl-4-benzylamidothiosemicarbazone	preparation described	z
$[FeLCl)$ (H_2L = disalicylaldimino-oxamide, -malonamide or -succinamide)	preparation described	aa
FeL_3 (HL = 1-ethyl-3-phenyltriazene-1-oxide)	electrochemical study	bb
$[FeL_3][NO_3]_3$ (L = 2-py-CH_2NHSO_2Ph or 2-py$CH_2CH_2NHSO_2C_6H_4Me$-*p*)	preparation described	cc
Complexes of 2-aminocyclopentene-1-dithiocarboxylic acid	preparation described	dd

(a) U. Thewalt, *Z. Anorg. Allg. Chem.*, 476 (1981) 105. (b) E. Lagzdins, I. Pulke and A. Vaivads, *Latv. P.S.R. Zinat. Akad. Vestis. Kim. Ser.*, (1980) 540; [*Chem. Abstr.*, 94 (1981) 24215]. (c) C.E. Gomez, R. Iranzo, L.G. Lopez and F.J. Galvez, *An. Univ. Murcia Cienc. 1974-5* (Publ. 1979), 33, 169; [*Chem. Abstr.*, 93 (1980) 214996]. (d) T.K. Sanyal and N.N. Das, *J. Inorg. Nucl. Chem.*, 42 (1980) 811. (e) P. Thomas, M. Benedix and H. Hennig, *Z. Anorg. Allg. Chem.*, 468 (1980) 213. (f) N. Thankarajan and P. Sreeman, *J. Ind. Chem. Soc.*, 56 (1981) 411. (g) N. Thankarajan and P. Sreeman, *Ind. J. Chem.*, 20A (1981) 372. (h) E.C. Okafor, *Z. Naturforsch. (Teil B)*, 36B (1981) 213. (i) C.M. Mikulski, J. Unruh, R. Rabin, F.J. Iaconnianni, L.L. Pytlewski and N.M. Karayannis, *Trans. Met. Chem. (Weinheim, Ger.)*, 6 (1981) 79. (j) M. Kopacz and D. Nowak, *Zh. Neorg. Khim.*, 25 (1980) 2692. (k) S.S. Sawhney and N. Vohra, *Actas Cienc. Indica (Ser.) Chim.*, 6 (1980) 183; [*Chem. Abstr.*, 95 (1981) 34614]. (l) B.S. James and W.R. McWhinnie, *Trans. Met. Chem.*

TABLE 2 (continued)

(Weinheim, Ger.), 6 (1981) 151. (m) C. Gerard and R.P. Hugel, *J. Chem. Res. (S)*, (1980) 314. (n) M.N. Ansari, M.C. Jain and W.U. Malik, *J. Ind. Chem. Soc.*, 57 (1980) 861. (o) E.N. Zedelashvili, A. Shvelashvili and D.A. Gorgorishvili, *Zh. Neorg. Khim.*, 25 (1980) 3309. (p) M. Mohan, U. Wahid, R. Dutt and A.K. Srivastava, *Monatsh. Chem.*, 111 (1980) 1273; M. Mohan and B.D. Paramhans, *Ind. J. Chem.*, 19A (1980) 759. (q) M. Mohan and B. Das Paramhans, *Gazz. Chim. Ital.*, 111 (1981) 35. (r) N.S. Bhave and R.B. Khorat, *J. Inorg. Nucl. Chem.*, 42 (1980) 977. (s) H. Kuma and S. Yamada, *Bull. Chem. Soc. Jpn.*, 53 (1980) 3218. (t) S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Ind. J. Chem.*, 19A (1980) 703. (u) K.L. Madhok and K.P. Srivastava, *Ind. J. Chem.*, 19A (1980) 808. (v) R. Saito and Y. Kidani, *Nagoya-Shiritsu Daiguku Yakugakubu Kenkyu Nempo*, (1980) 89; [*Chem. Abstr.*, 95 (1981) 72349]. (w) S.K. Srivastava, V.P. Kudesia and K.H. Kaur, *Acta Cienc. Indica (Ser.) Chim.*, 6 (1980) 85; [*Chem. Abstr.*, 93 (1980) 230028]. (x) A. Syamal and K.S. Kale, *J. Ind. Chem. Soc.*, 58 (1981) 186. (y) S. Burman and D.N. Sathyanarayana, *Ind. J. Chem.*, 20A (1981) 57. (z) M.C. Jain, R.K. Sharma and P.C. Jain, *J. Inorg. Nucl. Chem.*, 42 (1980) 1229. (aa) K.K. Narang and U.S. Yadar, *Curr. Sci.*, 49 (1980) 852. (bb) R.N. Mukherjee and A. Chakravorty, *Ind. J. Chem.*, 20A (1981) 73. (cc) E. Uhlig and M. Doering, *Z. Chem.*, 21 (1981) 73. (dd) S. Burman and D.N. Sathyanarayana, *Ind. J. Chem.*, 20A (1981) 53.

parameter, D, of -2.85 K. This rather large value of D is attributed to the presence of a nearby excited state, probably $^2T_{2g}$ [170]. Further low temperature Mössbauer and EPR spectra of this compound show that the spin-equilibrium behaviour does not depend on particle size [171]. High-spin $[Fe(S_2CNR_2)_3]$ complexes show Fe-S stretching frequencies in the region 205-220 cm^{-1} whereas the low-spin analogues absorb between 305 and 350 cm^{-1}; intermediate spin compounds absorb in both regions [172]. The previously reported preparations of spin-crossover mixed dithiocarbamate complexes have been re-examined. In particular the reaction between $[Fe(S_2CNR_2)_3]$ and $[Fe(S_2CNR'_2)_3]$ show that the complexes are not substitutionally inert and that the product is determined by the relative stabilities and solubilities of the complexes undergoing metathesis. It was concluded that the reported preparations of $[Fe(S_2CNR_2)_2(S_2CNR'_2)]$ are in error [173].

The electrochemical reduction parameters of $[Fe(SOCNR_2)_3]$ complexes are very similar to those of dithiocarbamate analogues and trends in the two series are almost identical [174]. Magnetic and Mössbauer spectroscopic data on $[Fe(OSCNR_2)_3]$ (R = Me or Et) show the complexes to exhibit $^2T(S = \frac{1}{2}) \rightleftharpoons {}^6A(S = {}^5/_2)$ equilibria, although $[Fe(OSCNMe_2)_3]$ can be obtained in a crystalline form that remains totally high-spin down to 10 K. The analogous $[Fe(Se_2CNR_2)_3]$ complexes are essentially Mössbauer silent, probably due to selenium edge absorption or effective γ-ray scattering by selenium [175]. The electrochemical behaviour of $[Fe(S_2C_6H_4R\text{-}4)_3]$ (R = H, Me, MeO, Me_2N or Et_2N) has also been studied [176].

Treatment of $Fe(BF_4)_2.6H_2O$ with H_2S and PEt_3 gives $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$

containing an octahedral array of {Fe(PEt_3)} units with sulphide ligands triply bridging each face (μ_{eff} = 6.04 μ_B at 291 K) [177]. Other complexes with *O*-donor ligands are detailed in Table 2.

2.6.3 Complexes with mixed donor ligands

The complexes [Fe(5-MeO-Salmeen)$_2$][PF_6], [Fe(3-MeO-Salmeen)$_2$][PF_6] and [Fe(5-NO_2-Salmeen)$_2$][PF_6] (SalmeenH = Schiff base formed between salicylaldehyde and *N*-methylethylenediamine) have been prepared. The first of these is high-spin, and the other two are low-spin. All three possess the same general structure with a distorted octahedral {N_2O_4} donor set. However, there are fine differences in the structures. Thus, the high-spin complex has Fe–L bond lengths *ca.* 12 pm longer than those of the low-spin species, but the difference is not uniform, the Fe–N bonds varying more than the Fe–O bonds [178]. The spin-crossover behaviour of [Fe(X-SalEen)$_2$]Y (X-SalEenH = Schiff base formed from a substituted salicylaldehyde and *N*-ethyl-en) has been examined. Several complexes exhibit a gradual, but complete, crossover in the solid state and some show an incomplete transition with a plateau in the μ_{eff} *versus* temperature curve. However, [Fe(3-MeO-SalEen)$_2$][PF_6] shows a sudden crossover within a 2° range at 159 K. A sensitivity of physical properties to the exact method of preparation was noted. The role of nucleation and the growth mechanism in determining the spin-crossover behaviour was studied. Thus grinding samples of the 3-MeO complex leads to an incomplete spin-transition and the transition becomes more gradual. These effects are generally observed in these complexes, and are most likely due to defects caused by grinding [179]. The same group have examined other iron(III) complexes exhibiting unusual solid state properties. In many cases a Boltzmann distribution over electronic states is not seen. Mechanical grinding of compounds which normally show complete transitions leads to them displaying incomplete transitions and a certain percentage of molecules remain high-spin, even at very low temperatures. Grinding also makes the transitions more gradual. Doping iron(III) complexes has a similar effect. It appears that these effects can be explained by nucleation and growth mechanisms of the phase transitions in the solids [180]. Structural studies have been performed on both high- and low-spin forms of Cs[Fe(tsa)$_2$] (tsaH = salicylaldehydethio semicarbazone). Both contain a distorted octahedral {$S_2O_2N_2$} array and there is little difference between the two structures [181].

[Fe(dithiosalen)] (μ_{eff} = 1.90 μ_B at 295 K) reacts with O_2 in pyridine to give [{Fe(dithiosalen)}$_2$O], which arises *via* formation of a peroxo-bridged species. The μ-oxo dimer is unusual in displaying an $S = \frac{1}{2}$ spin state with weak antiferromagnetic coupling [182].

The purple intermediate formed in the reactions between $[Fe^{II}(edta)]^{2-}$ and $[O_2]^-$, and $[Fe^{III}(edta)]^-$ and H_2O_2, has been examined by resonance Raman spectroscopy and found to be $[Fe^{III}(edta)O_2]^-$, containing a peroxide ion [183].

The kinetics of the reaction of pyridoxal (pl) and pyridoxamine (pm) with Fe^{3+} at pH = 3.0 have been studied and two reactions were observed, one being 3 to 4 times faster than the other. The ternary complex, $[Fe(pm)(pl)]^+$ is formed rapidly prior to slow formation of an iron(III) Schiff-base complex [184]. Other complexes with mixed donor ligands are detailed in Table 2.

2.7 IRON(IV)

Several complexes of the type $[Fe(Se_2CNR_2)_3][BF_4]$ have been prepared and their magnetic moments of *ca.* 3.2 μ_B suggest pseudooctahedral low-spin cations [185].

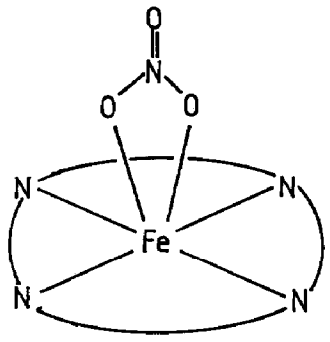
2.8 INORGANIC BIOCHEMISTRY OF IRON

This section is subdivided into the same sections used in last year's report [126a]. Again, all studies on porphyrin complexes are included in this section. One general publication of considerable relevance to the area is the *A.C.S. Advances in Chemistry Series*, No. 191 (1980) describing Biomimetic Chemistry and readers are referred to the several interesting articles in this book.

2.8.1 Complexes and enzymes containing iron porphyrins

An X-ray structural study of [Mb(O_2)] at 1.6 Å resolution has been reported. This work, performed at -12 °C, gives atomic positions to an accuracy of 10 pm. The iron atom is 22(3) pm out of the $\{N_4\}$ plane, 25 pm closer to the plane than that in [Mb]. The Fe–O distance is 183 pm and the Fe–$\hat{O}$–O angle is 115°. The Fe–N (porphyrin) average distance is 195(6) pm and the Fe–N (axial histadine) length is 207(6) pm. The movements on oxygenation are similar to those in the T–R state transition in [Hb], but smaller in magnitude [186].

When $[\{Fe(TPP)\}_2O]$ is treated with HF, high-spin [FeF(TPP)] is formed. The Fe–F distance of 179.2 pm is significantly shorter than those normally observed [187]. Similar reaction of the μ-oxo dimer with the appropriate acid leads to $[Fe(NO_3)(TPP)]$, $[\{Fe(TPP)\}_2(SO_4)]$ and $[Fe(SO_3R)(TPP)]$ (R = Ph or 4-MeC_6H_4). The nitrate complex has the structure (*49*) and this is the first example of a bidentate axial ligand. The sulphate ion acts as a bridging



(49)

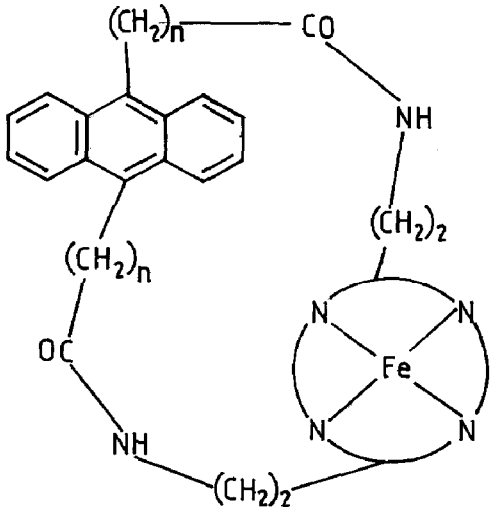
ligand [188]. Single crystal magnetic anisotropy measurements in the 80-300 K range for [FeX(TPP)] give an ordering of the zero field splitting parameter (D_x) of $D_{NCS} < D_{Cl} < D_{Br} < D_I$ [189]. ^{13}C NMR spectroscopy was used to calculate π-electron spin density distributions in the porphyrin ring of [FeCl(TPP)] [190].

The compounds, [Fe^{II}(alkyl)(Por)] have been obtained by reaction of electrogenerated iron(I) porphyrin complexes with RX. These undergo reversible electrochemical oxidation to iron(III) alkyl complexes, which are low-spin and further to transient iron(IV) alkyl species [191]. Reduction of [Fe(TPP)(CX)] (X = S or $C(C_6H_4Cl\text{-}4)_2$) gives $[Fe(TPP)(CX)]^-$ which undergoes disproportionation to [Fe(TPP)(CX)] and $[Fe(TPP)(CX)]^{2-}$. Treatment of the dianions with acid gives the carbene complexes $[Fe(TPP)(CHX)]^-$ [192]. Reaction between [Fe(TPP)] and CI_4 gives diamagnetic [(TPP)Fe-C-Fe(TPP)]. Treatment of the carbide dimer with $FeCl_3$ gives [FeCl(TPP)] and with Br_2, CBr_4 and [FeBr(TPP)] are obtained. Thus the complete series, $[\{Fe(TPP)\}_2X]$ (X = C, N, O) is now known [193].

The formation of {hemoprotein-NO} complexes by reactions of Hb, metHb, Mb, metMb, HPO and cytochrome C with cobalt-containing nitrosyl complexes has been reported. Complete stoicheiometric NO transfer occurs from Co(NO)(dmg)$_2$.MeOH and $[CoCl(NO)(en)_2][ClO_4]$ to Hb and Mb, but not to the other hemoproteins. However, $[Co(NH_3)_5(NO)]Cl_2$ transferred NO to all the hemoproteins except cytochrome C. Identical results were obtained with NO gas. Kinetic results indicate the dmg and en complexes effect direct NO transfer, while the amine complex undergoes initial decomposition to liberate NO, which reacts rapidly with the heme [194]. EPR spectroscopy suggests that [Fe(NO)(5-NO_2-OEP)] is undergoing dimerisation at 9 K, and this has led to an interpretation of the hitherto unexplained spectrum of NO-bound Hb which has been treated with salicylate [195].

The structure of [Fe(CO)(deuteropor)(thf)] has been determined. The thf acts as a very weak ligand and this leads to strengthening of the Fe–CO bond {r(Fe–C) = 170.6, r(C–O) = 212.7 pm}. The iron atom is 10 pm out of the $\{N_4\}$ plane towards the CO group. On the basis of these results, it is suggested that the different ν_{CO} values observed in [Mb(CO)] may result from modulation of the iron-histadine binding *trans* to CO [196]. ΔH and ΔS values have been determined for reversible binding of O_2 and CO to chelated protohemes having an axial imidazole ligand which is covalently attached to the porphyrin ligand. Values similar to those of high affinity hemoproteins such as isolated Hb chains and R-state Hb show that such compounds accurately mimic the natural systems [197]. This chelated protoheme has been compared with two analogues in which the two vinyl groups are replaced by either two electron-donating ethyl groups or two electron-withdrawing ethanoyl groups. In this series, neither kinetic nor equilibrium constant data for CO binding varies appreciably, but the O_2 dissociation rate varies along the series C_2H_5 < $CH{=}CH_2$ < CH_3CO. This reflects the non-polar nature of the Fe–CO bond and the polar nature of the $Fe^{\delta+}$–$O_2{}^{\delta-}$ bond [198].

The active sites of heme proteins are closely surrounded by protein side chains, which provide steric hindrance for entering ligands. It was thought that such proteins reduce the CO:O_2 binding ratio to iron by distal side steric effects. However, use of the cyclophane hemes, (*50*), has led to the



(*50*)

conclusion that this ratio is unaffected by such distal side steric effects [199]. Others have shown that distal steric hindrance can effect ligand binding, but that this effect is manifested only in the ligand association rates and has almost no effect on the "off" rates [200]. A pocket porphyrin

complex has been prepared and this mimics the reduced CO affinity of natural systems, without significantly changing the O_2 affinity, much better than do the picket-fence porphyrins. In natural systems the CO ligand is forced to tilt due to interactions with the distal residues and this is achieved in the pocket porphyrin, compared to the linear CO bonding in previous models. The reaction path employed is shown in Scheme 3 [201].

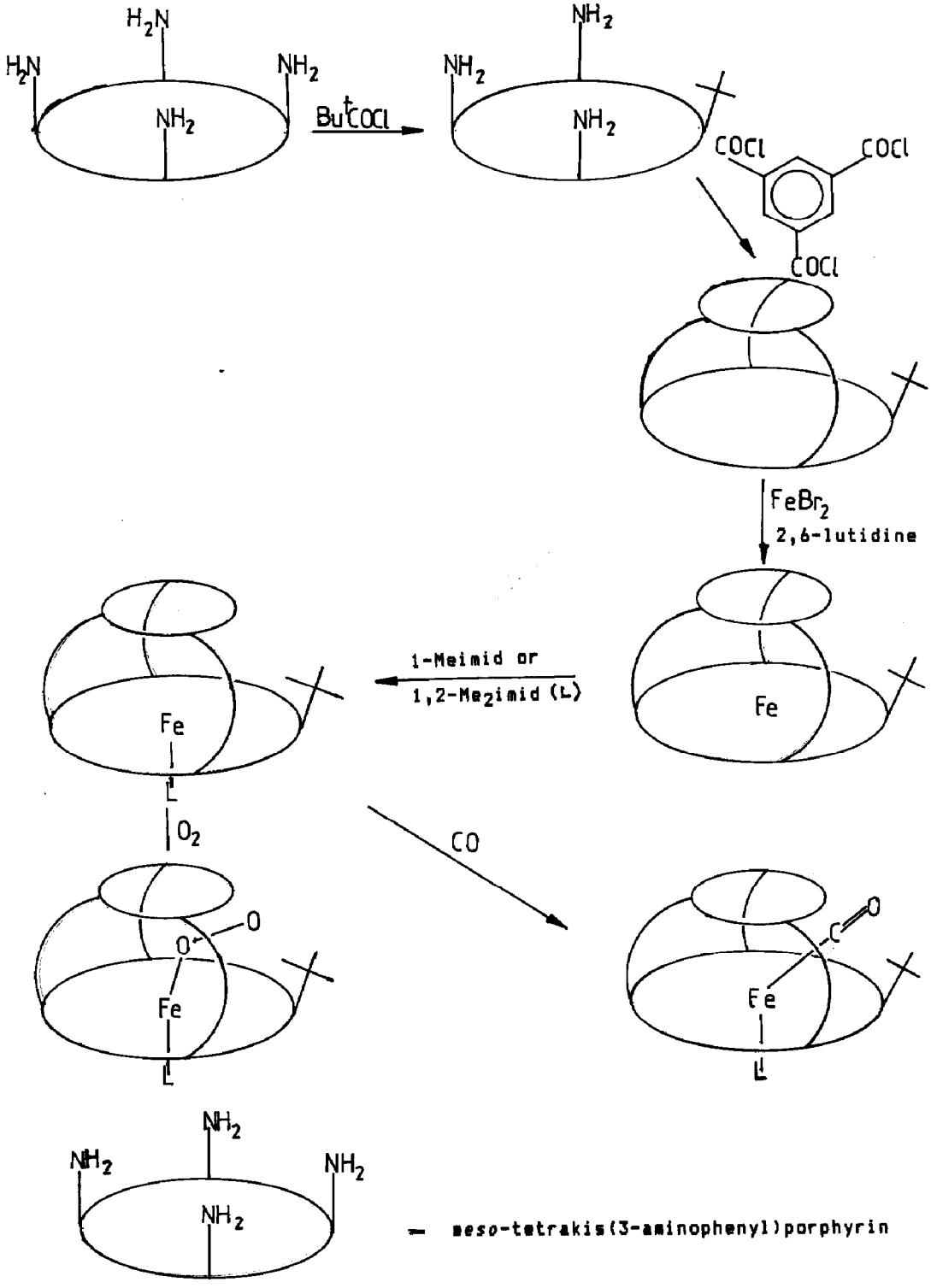
Face-to-face porphyrin dimers have been prepared as a part of a study of the design of binuclear multi-electron redox catalysts for the direct four-electron electrochemical reduction of O_2 to H_2O [202]. Two new basket-handle porphyrin-iron(II) complexes have also been prepared. One contains double face protection and the other double face protection and an axial imidazole. Both reversibly bind O_2 and CO [203].

Macroporous imidazole-containing polymers react with iron(III) porphyrin complexes to give polymeric axially ligated complexes. These can be reduced by dithionite to iron(II) species [204]. Water soluble poly-(1-vinyl-2-methylimidazole)-heme complexes have also been prepared and these bind O_2 and CO. The lifetime of the O_2 adduct is *ca.* 25 min for a polymer of molecular weight $\geqslant 3 \times 10^4$ [205].

The water soluble compound, α,β,γ,δ-tetrakis(1-(2-hydroxyethyl)pyrimium-4-yl)-porphine has been prepared and the catalytic properties of the iron complex in reducing O_2 to H_2O studied [206]. The behaviour of the iron(III) tetrakis-(*N*-methyl-4-pyridyl)porphyrin cation in aqueous solution has also been studied. Four major species are present, and these are a five-coordinate monomer, a monohydroxyl monomer, a dihydroxyl monomer and a bridged dimer. Optically coupled electrochemistry shows all the iron(III) species to be reduced to mono-aqua-iron(II) porphyrin, although a diaqua species may also be formed. These species showed superoxide dismutation activity [207].

Reduction of iron(III) in bis(histadine)hemin is accompanied by the uptake of one proton and therefore this acts as a model for the proton-coupled reduction of hemoproteins [208]. The reduction of $[Fe(Por)(CN)_2]^-$ by both $[Co(CN)_5]^{3-}$ and $[S_2O_4]^{2-}$ has been studied [209]. Electrochemical and NMR studies of $[\{LFe(TPP)\}_2N]^+$ (L = $PhNH_2$ or substituted pyridines) have been reported [210].

A study of the temperature dependence of the spin-states of aqua- and hydroxo-iron(III) heme indicates that while suitable axial ligands give rise to spin-equilibria in models, thermodynamic values for hemoproteins are determined by the interaction of the coordination centre with the protein [211]. The observed magnetic properties of unligated iron(II) porphyrins have been reproduced by calculations taking account of all possible configuration interactions and spin-orbit coupling interactions. There was good agreement



SCHEME 3. Preparation and reactivity of a pocket porphyrin complex [201].

between calculated and observed values only when it was assumed that the axial ligand field is so weak that d_{z^2} is close to d_{xy} and d_{π} [212]. The electronic structure of mono-, di- and tri-atom bridged porphyrin dimers have been examined to show how orbital symmetries and electron counts determine geometries and electronic properties [213].

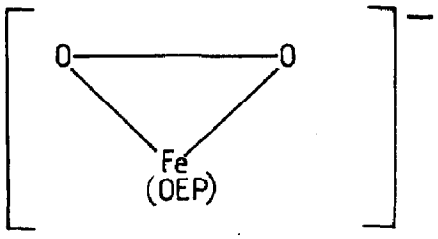
Studies on nitrosyl complexes of reduced yeast cytochrome oxidase by EPR spectroscopy has allowed the unambiguous assignment of histadine as the axial ligand in cytochrome a_3 [214]. An examination of potential iron(II) heme models for cytochrome a_3 in the O_2 reducing site of cytochrome oxidase suggests a five-coordinate high-spin iron(II) centre ligated to a heme containing an unaltered formyl group in a non-hydrogen bonded environment is a good model [215].

Reversible spin interconversion in cytochrome b_5 in the temperature range 15-83 °C has been studied. Below 45 °C, oxidised cytochrome b_5 is mainly low-spin, and this becomes high-spin above this temperature [216].

Complexes of the type [Fe(por)(R_2S)] (por = an imidazole-tailed porphyrin), [Fe(TPP)(R_2S)$_2$] and [Fe(TPP)(R_2S)$_2$]$^+$ serve as models for cytochrome c. They have been examined by X-ray crystallography and the main implications for cytochrome c are: (a) the Fe-S bond lengths in methionine ligated hemoproteins is expected to be about 233 pm and to be rather insensitive to oxidation state changes; (b) coordinate bond lengths are unlikely to contribute to Frank-Condon barriers to electron transfer; (c) the intrinsic stability of the Fe^{III}-S bond is sufficiently high that a protein conformation enforced methionine-iron contact need not be invoked [217]. An NMR study of cytochrome c' from *Rhodospirillum rubrum* suggests that ferricytochrome c' undergoes an acid to neutral change in the pH range 5-11, and that the acid form is five-coordinate and the neutral form is six-coordinate. This also suggests the sixth ligand is an acidic residue [218]. ^{1}H NMR spectra of cytochrome c oxidase reconstituted with deuterohemin IX indicates the presence of heme asymmetry which may be relevant to the function of this protein which catalyses the oxidation of ferrocytochrome c by H_2O_2 [219].

Intensive research continues into elucidation of the mechanism of action of cytochrome P-450. It has been found that [Fe(OEP)L(O_2)] (L = solvent) undergoes reversible one-electron reduction at a potential of -0.24 V (*versus* Ag/AgCl) and that the product is identical to those from the reactions of the iron(I) complex with O_2 and the iron(II) complex with O_2^-. It is not formed from the iron(III) species and $[O_2]^{2-}$. It is formulated as high-spin $[Fe(OEP)O_2]^-$, and is believed to contain the {Fe(O_2)} unit of structure (*51*).

The structural unit (*51*) is believed to be that adopted by the cytochrome P-450 complex immediately after the second one-electron reduction step. When

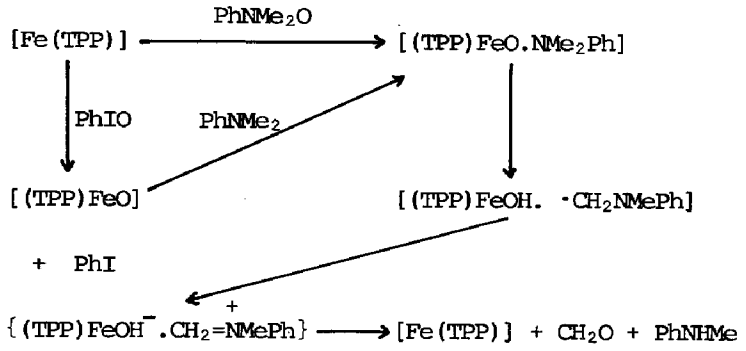


(51)

O_2 is bound in this form, it is a strong π acceptor and this leads to a weakening of the O-O bond prior to either heterolytic or homolytic cleavage which, in turn, leads to substrate hydroxylation [220]. Thermodynamic and kinetic data has been obtained for reactions of cytochrome P-450$_{cam}$ reconstituted with meso-, deutero-, dibromodeutero- and diacetyl-deuteroheme. Autoxidation of the substrate bound oxygenated species to $[O_2^{-}\text{-}Fe^{III}$ (high spin)] follows the rate law, $k[\text{p-450-}Fe^{2+}(O_2)][H^{+}]$, pH 7.00-8.50 [221]. A glutathione-hemin-pyridine mixture exhibits similar optical and EPR spectra to cytochrome P-450 in its low-spin iron(III) state. When pyridine is omitted, a high-spin iron(III) species is formed. Addition of CO to the three component mixture leads to a characteristic 450 nm absorption band. This mixture displays hydroxylation, dealkylation and aromatic methyl migration properties [222]. $[Fe(2,3,5,6\text{-}C_6F_4HS)(TPivP)]^{-}$ forms both O_2 and CO adducts and the thermal stability of the former is much higher than that of the O_2 adduct of [Fe(TPivP)]. On prolonged exposure of the thiophenolate complex to O_2, $[Fe^{III}(TPivP)(SC_6F_4H)]$ and superoxide ion is formed [223].

Iron(III) protoporphyrin IX immobilised on a polymethylmethacrylateimidazole support shows mixed function oxidase activity at a level of about 3% of that of cytochrome P-450 [224]. When peroxyacid replaces O_2 in cytochrome P-450 mediated hydroxylation reactions, the results are best accounted for by a mechanism involving homolytic cleavage of the O-O bond [225]. Reaction $PhMe_2COOH$ with cyclohexane in the presence of [FeCl(TPP)] gives cyclohexanol (40%) and cyclohexanone (20%) after 15 min. With Me_3COOH and PhIO, the yields are 20%:12% and 12%:1%, respectively. Lower efficiencies were observed with other metal porphyrin catalysts [226]. Others have observed alkane hydroxylation and alkene epoxidation activity for PhIO in the presence of catalytic amounts of iron porphyrins and invoke the intermediacy of an {FeO} species [227]. Reaction of PhIO with aromatic substrates in the presence of tetrakis(pentafluorophenyl)porphyrinatochloroiron(III) leads to phenolic products which have structures characteristic of the NIH shift reactions shown by natural cytochrome P-450 [228]. A reaction scheme for

N-dealkylation has been demonstrated (Scheme 4) and it is suggested that this is a model for cytochrome P-450 dealkylation, thereby implicating the ferryl intermediate as the dealkylating agent [229a]. The {FeO} intermediate has been stabilised at sub-zero temperatures [230].



SCHEME 4. A model for cytochrome P-450 dealkylation [229].

An acid-alkali transition and temperature dependent changes in the spin-state have been demonstrated for L-tryptophan-2,3-dioxygenase, a protoheme protein. In acid, high-spin iron(III) is present and at pH > 8, a mixture of two high-spin forms and one low-spin form is observed. The binding of a L-tryptophan is greatly facilitated by the acid-alkali transition [229b].

Three groups have shown that one-electron oxidation of [Fe(C=CAr$_2$)(Por)] leads to an [Fe(C=CAr$_2$)(Por)]$^+$ species (Ar = -C$_6$H$_4$Cl-4) which exhibits spectra very similar to those of catalyse compound I and HPO compound I, and may be considered as a carbon-containing analogue of these compounds. It has been shown that the vinylidene group has inserted into an Fe-N bond in the oxidised species and it is suggested that the natural systems may have Fe-O-N units [231]. A molecular orbital study of d^4-[FeO(Por)] complexes has shown that O-migration into an Fe-N bond is a viable reaction channel [232].

Reaction of [Fe(TMP)Cl] (TMP = tetramesitylporphyrin) with 3-ClC$_6$H$_4$CO$_3$H gives [FeO(TMP)]$^+$ containing a porphyrin radical cation, and this is also suggested as a model for HPO compound I [233]. Earlier studies on HPO compound I have shown that one oxidising equivalent exists as a porphyrin radical cation and recent ^{17}O ENDOR spectra have shown the second oxidising equivalent to be associated with an oxoferryl centre. These authors rule out the alternative Fe-OH and Fe-O-N structures [234]. Further evidence for the porphyrin π-radical cation nature of HPO compound I and catalyse compound I has been obtained from a comparison of the MCD spectra of HPO and bovine liver catalyse with those of synthetic porphyrin π-radical cations [235]. An

infrared band in the region 1270–1293 cm^{-1} is reported to be indicative of the presence of porphyrin radical cations in metalloporphyrins [236]. Oxidation potentials for [FeX(Por)] compounds have been measured in a systematic way and have been found to be insensitive to X, but to follow the expected trends for variation of substituents on the porphyrin ring. This is also consistent with oxidation of the porphyrin rather than at the metal [237]. Chemical oxidation of [FeCl(TPP)] with [phenoxathiin][$SbCl_6$] (a cation radical salt) in dry CH_2Cl_2 also leads to [FeCl(TPP)][$SbCl_6$] which contains a high-spin iron(III)-radical cation configuration, rather than iron(IV) [238].

Extended HMO calculations have been presented for HPO compound II, HPO compound I, catalyse compound I and chloroperoxidase compound I. The HPO compound II species is described in terms of an $\{Fe^{IV}O\}$ configuration and all compound I species are described as {ferryl-porphyrin π-radical cation} units. EPR data support these descriptions [239].

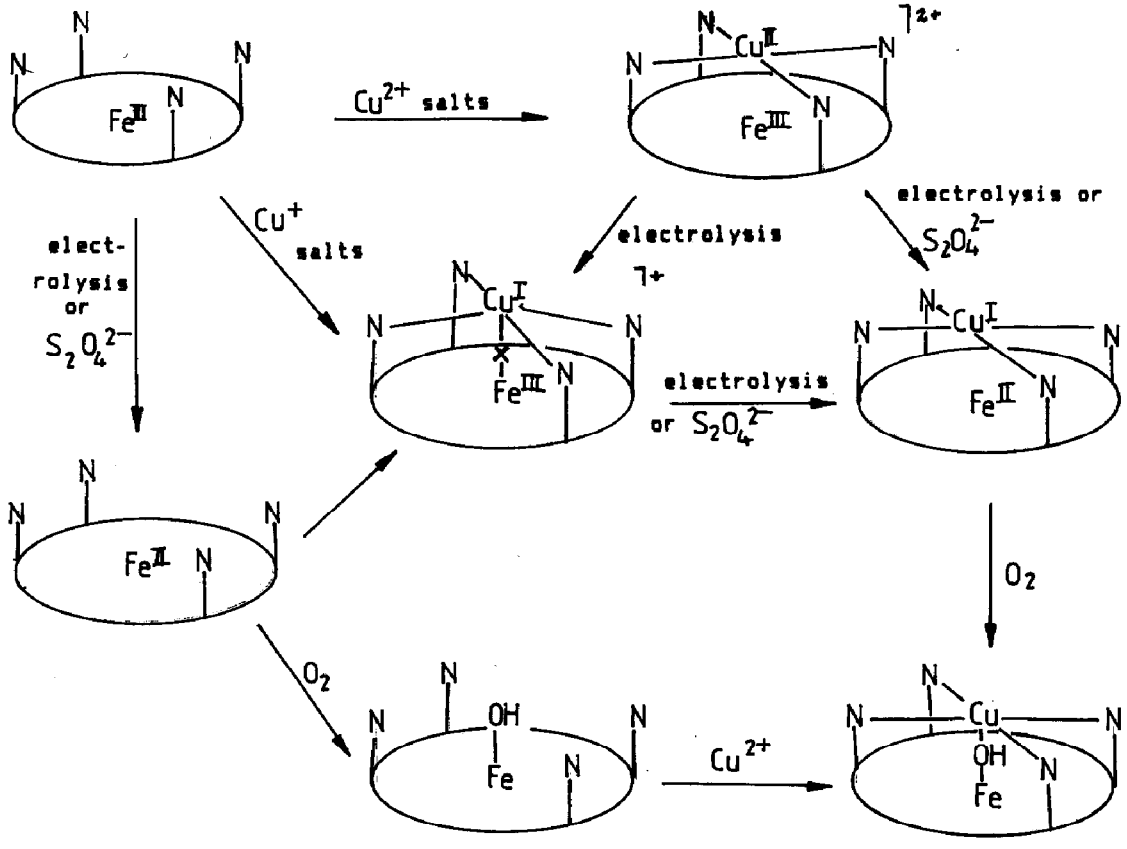
$[ClO_2]^-$ is a potential four-electron oxidant and its reaction with iron(III)-deuteroporphyrin IX complexes has been studied as a model for peroxidase behaviour. The reactions result in the formation of one or more intermediates, containing iron in oxidation states greater than 3, which play a central role in (peroxidatic) catalytic activity. At pH 6.5–7.0, the apparent molar equivalency of $[(heme)Fe^{III}]:ClO_2^-$ is *ca.* 4:1, but this ratio, as well as the rate of intermediate formation, decreases with increasing basicity. The apparent stoicheiometry at the lower pH corresponds to a one-electron oxidation of each of four [(heme)iron(III)] units to iron(IV), with $[ClO_2]^-$ being converted to chloride. This suggests an intermediate state analogous to peroxidase compound II. Heme oxidation by $[ClO]^-$ is markedly faster than that by $[ClO_2]^-$, which suggests the possibility that hypochlorite is a reactive intermediate. Absorption spectra of the intermediate are the same as those obtained by heme oxidation with peroxybenzoic acids [240].

In a study of the heme prosthetic groups in nitrite and sulphite reductases, an extensive series of iron(II) and -(III) hydroporphyrin complexes have been prepared. These include [Fe(P)L], $[Fe(P)LL']^{n+}$ (n = 0 or 1), [{Fe(P)}$_2$O] and [Fe(P)] {P = octaethylchlorin (OEC) or octaethylisobacteriochlorin (OEiBC)}. The synthetic methods for the complexes are similar to those for complexes of OEP and some of the OEiBC complexes are possible reductase analogues [241].

2.8.2 Cytochrome oxidase and Fe-Cu-containing model compounds

Studies on models for the heme centres only in cytochrome oxidase have been discussed in the previous section. Herein, consideration is given to heme-copper interactions.

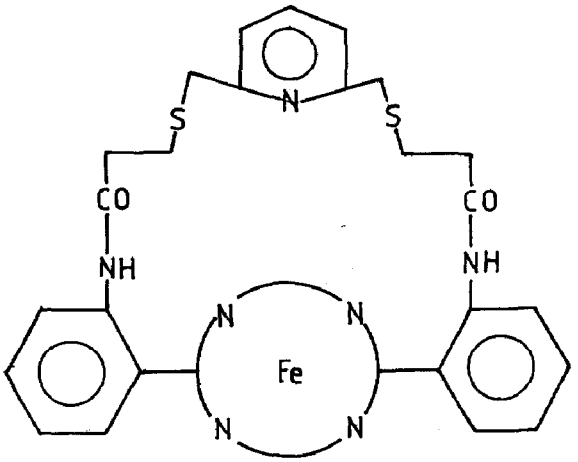
A spectroscopic study of the reaction of membrane bound mixed valence state cytochrome oxidase ($Cu_A^{2+}a^{3+}$-$Cu_B^{+}a_3^{2+}$) with oxygen suggests the formation of a Cu_B-(O_2^-)-Fe(a_3) bridge [242]. An EXAFS examination of the copper sites in cytochrome c oxidase has led to the suggestion of *S*- and *N*- (or *O*-) coordination {r(Cu-S_{av}) = 227, r(Cu-N(O)$_{av}$) = 197 pm} with 1 to 1.5 *S* atoms and 2 *N* or *O* atoms per Cu. The distribution of *S* between Cu_A and Cu_B sites is not known, although there is some evidence of two *S* atoms bound to Cu_A [243]. The reactions of iron tetrakis(2-nicotinamidophenyl)porphyrin shown in Scheme 5 have been reported [244].



SCHEME 5. Some reactions of the iron tetrakis(2-nicotinamidophenyl)porphyrin system.

The heme a_3-Cu^{2+} site is thought to be strongly antiferromagnetically coupled and the compounds [Fe(por)-X-CuN_4][ClO_4]$_2$ (X = Cl, Br or CN) in Scheme 5 show unusual temperature dependences of their magnetic moments. For X = Cl and Br, these are interpreted as equilibria between Fe^{III} ($S = {}^5/_2$) and Fe^{III} ($S = {}^3/_2$); for the cyanide, Fe^{III} ($S = \frac{1}{2}$) and Cu^{II} ($S = \frac{1}{2}$) [245].

The strapped porphyrin, (*52*), forms [Fe(por)Cl], [Fe(Por)OH], [Fe(Por)CN] and [{Fe(Por)}$_2$O], and reaction with copper(II) salts leads to products such as



(52)

[Fe(Por)-OH-Cu(NS_2)OH][ClO_4]. However, none of these show the spin-coupling between Fe and Cu observed in the natural system [246]. CuFe(fsaR)Cl.$n$$H_2O$ {H_4fsaR = *N,N'*-bis(3-carboxysalicylidene)alkanediamines} show strong antiferromagnetic coupling, the exchange integrals of *ca.* 50 cm^{-1} being the largest so far reported for Cu^{II}-Fe^{III} systems [247]. The structure of CuFe{(fsa)$_2$en}Cl.H_2O.MeOH {H_4(fsa)$_2$en = *N,N'*-bis(2-hydroxy-3-carboxybenzylidene) ethylenediamine} has been reported [248].

Addition of Cu^+ to sodium dodecylsulphate solubilised ferrihemes containing alkenic substrates gives spectral perturbations diagnostic of Cu^I-alkene π-complexes [249].

2.8.3 Rubredoxin, ferredoxin and Fe-Mo-S cluster compounds

The iron(III) complexes of Z-Cys-Ala-Ala-Cys(OMe) and Z-Ala-Cys(OMe) show CD, MCD and EPR spectra very similar to native oxidised rubredoxin. The tetrapeptide complex probably has a relatively stable chelate structure with a "hairpin turn" configuration of the ligand [250].

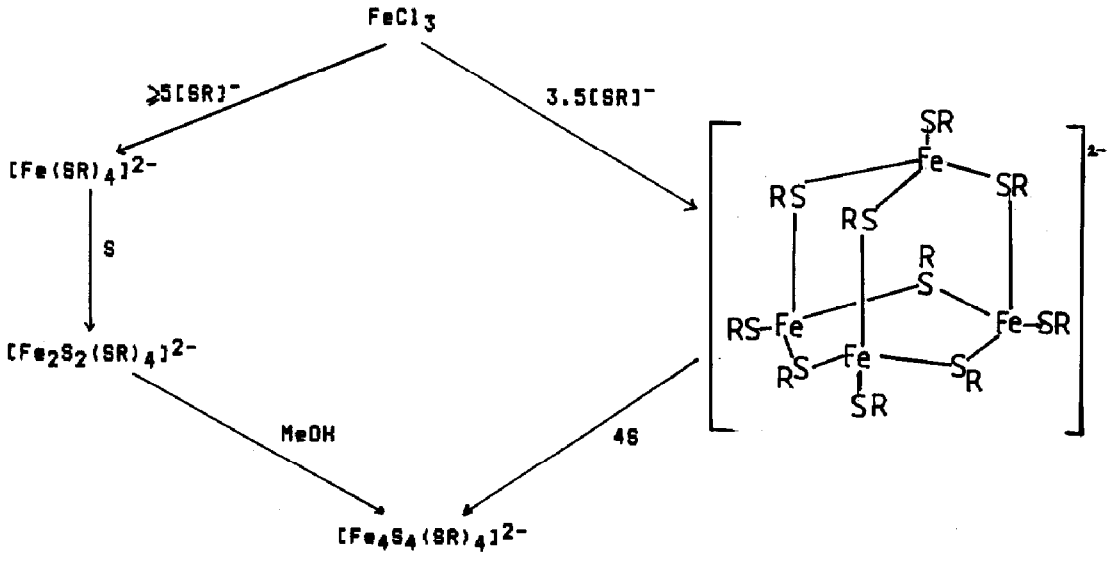
[$Fe(SPh)_4$]$^{2-}$ and [$Fe(S_2C_4O_2)_2$]$^{2-}$ have been examined as models for the active site of reduced rubredoxin. Both anions have a distorted tetrahedral structure, the distortions arising from *ortho* phenyl hydrogen-sulphur and -iron

interactions in the former, and steric constraints of the ligand in the latter. On the basis of the observed magnetic and spectroscopic data, $[Fe(SPh)_4]^{2-}$ is thought to be a good model [251].

An X-ray structural study of the [2Fe-2S] ferredoxin of *Spirulina platensis* at 2.5 Å resolution has been reported [252].

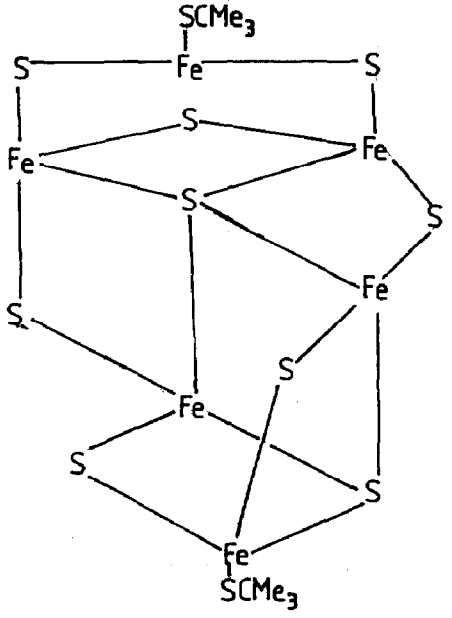
The high and low potential Fe-S centres of *Azotobacter vinelandii* have been examined by Mössbauer spectroscopy. The high potential centre is an $\{Fe_4S_4\}$ cluster, and the other is believed to contain a three iron cluster [253]. This has been confirmed by a structural study which shows the peptide chain to consist of an *N*-terminal core of residues 1 to 50 which forms {Fe-S} cluster binding sites and a *C*-terminal chain of residues 51 to 107 which wraps around the core. The $\{Fe_4S_4\}$ cluster is bound to cysteines-24, 39, 42 and 45 and the $\{Fe_3S_3\}$ unit is ligated to cysteines-8, 11, 16, 20 and 49 and to a sixth ligand which is either a glutamic acid residue or an exogenous small molecule [254]. Ferredoxin II from *Desulfovibrio gigas* is a tetrameric protein also containing an $\{Fe_3S_3\}$ cluster. Low temperature MCD spectra of both the oxidised and reduced forms have been examined. Both are paramagnetic, although only the oxidised form shows an EPR signal. The MCD spectra are consistent with ground states of $S = \frac{1}{2}$ and 2 for the oxidised and reduced forms respectively [255].

In an examination of the reaction sequence leading to $[Fe_4S_4(SR)_4]^{2-}$ anions, Holm *et al.* have found that reaction of $[PhS]^-$, $FeCl_3$ and sulphur (3.5:1:1) produces $[Fe_4(SPh)_{10}]^{2-}$ as the only identifiable intermediate. With a reactant ratio of $\geq$ 5:1:1, $[Fe(SPh)_4]^{2-}$ is formed and the reactions proceed as outlined in Scheme 6 [256]. Reaction of $FeCl_3$ with Li_2S and $LiSCMe_3$ in



SCHEME 6. Formation of $[Fe_4(SR)_{10}]^{4-}$ (R = Ph) [256].

methanol also gives $[Fe_4S_4(SCMe_3)_4]^{2-}$, but in the presence of Li[OMe], the $[Fe_6S_9(SCMe_3)_2]^{4-}$ anion is also formed. This has the structure (*53*) [257].



(53)

The structure of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ has been determined and it contains a distorted $\{Fe_4S_4\}$ cube with four approximately parallel Fe-S bonds which are shorter (223.9 pm) than the other eight (230.6 pm). Both the ^{13}C NMR spectrum of this anion and the EPR spectrum of the analogous trianion have been reported [258]. Structural characterisation of $[Fe_4S_4\{S_2C_2(CF_3)_2\}_4]^{2-}$ has also been reported. In this case, each iron atom adopts a coordination geometry that is best described as almost square pyramidal [259].

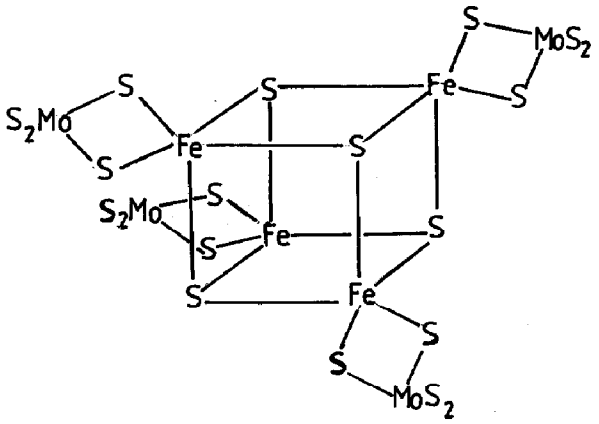
Both oxidised and reduced forms of HiPIP from *Chromatium vinosum* have been reduced by hydrated electrons formed by the pulse radiolysis of water to form super-reduced HiPIP, which has spectral characteristics close to those of $[Fe_4S_4(SR)_4]^{3-}$ [260]. The reaction of clostridial 8Fe-8S ferredoxin in its normal oxidised resting state with three inorganic oxidants has been investigated. With $[IrCl_6]^{2-}$, a fast reaction is observed which is complete in 20 s. The reactions with manganese-1,2-diaminocyclohexanetetraacetate and $[Fe(CN)_6]^{3-}$ are slower. The product is not reduced by $[S_2O_4]^{2-}$ and its UV spectrum does not resemble that of normal oxidised HiPIP. This excludes an interpretation of the results in terms of a third oxidation state of the protein [261]. The reduction of [MnCl(TPP)] by $[Fe_4S_4(SPr)_4]$ has also been studied [262]. An examination of the interaction of two HiPIP moieties with mitochondrial cytochrome c sounds a note of caution on the examination of some model systems. On the basis of kinetics, it appears that interactions are more complex than those of non-physiological reactants. Evidently specific

sites on both the HiPIP and the cytochrome mediate electron transfer. No long-lived complexes were observed [263].

Low temperature MCD spectra of $\{Fe_4S_4\}$ clusters from both *Chromatium* and *Clostridium pasteurianum* have shown the two different oxidation levels are quite distinctive and this technique should provide a means of distinguishing between the two [264]. A spectroscopic examination has demonstrated localised oxidation states in both Fd_{red} and $[Fe_4S_4(S_2\text{-}2\text{-}xlyl)_2]^{2-}$ and thus this behaviour is not necessarily a consequence of the protein structure [265].

The binary mixtures $[Fe_2S_2(SR)_4]^{2-}/[Fe_2Se_2(SR)_4]^{2-}$, $[Fe_4S_4(SR)_4]^{2-}/[Fe_4Se_4(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{3-}/[Fe_4Se_4(SR)_4]^{3-}$ all show core sulphur-selenium exchange to give equilibrium or near equilibrium distributions $[Fe_2S_{2-n}Se_n(SR)_4]^{2-}$ and $[Fe_4S_{4-n}Se_n(SR)_4]^{x-}$ (x = 2 or 3) [266].

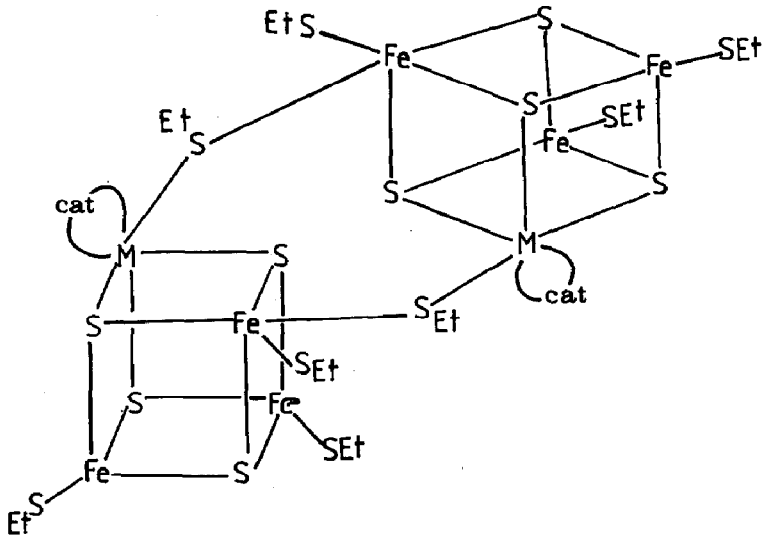
Reaction of $[MoS_4]^{2-}$ with $[Fe_4S_4(SCMe_3)_4]^{2-}$ gives (*54*). This anion undergoes a reversible one-electron reduction at 0.97 V followed by a



(*54*)

multi-electron irreversible reduction at 1.6 V. The $\{FeS_2MoS_2\}$ units of the cluster are kinetically inert to PhSH-Et_3N and when reaction does occur, it is the $\{Fe_4S_4\}$ core that is disrupted, the reaction product being $[S_2Mo(\mu\text{-}S)_2Fe(SPh)_2]^{2-}$ [267].

When $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (M = Mo or W) is treated with 3,6-Pr_2-$C_6H_2(OH)_2$ (cat) and Et_3N in MeCN, (*55*) is formed. Further reaction of this anion with p-MeC_6H_4SH yields $[MFe_3S_4(SR)_3(cat)(HSC_6H_4Me)]^{2-}$ or a related bridged species [268]. The temperature dependence of the magnetic moments of $[Fe_6M_2S_8(SPh)_6(OMe)_3]^{3-}$ (M = Mo or W) between 1.8 and 300 K in applied fields of 0.125-2.0 T suggests antiferromagnetic coupling between iron atoms in the same $\{MFe_3\}$ cube [269]. The previous report that the two one-electron reduction steps of $[Fe_6Mo_2S_8(SR)_9]^{3-}$ are reversible, while those of the tungsten analogue are irreversible has now been corrected. Reversibility is



(55)

observed for both metals [270]. Reduction of ethyne to ethene catalysed by both $[Fe_4S_4(SPh)_4]^{2-}$ and $[Fe_6Mo_2S_9(SPh)_8]^{3-}$ has been reported [271].

Other studies on simpler Fe-Mo-S systems are detailed in Section 2.5.3.

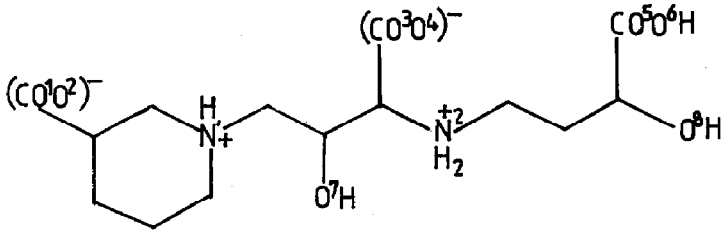
2.8.4 Iron storage and transport

A study has been made of the mechanism of iron deposition in apoferritin. The reaction involves oxidation of iron(II) catalysed by the protein with O_2 acting as the electron acceptor, followed by hydrolysis and deposition of FeO(OH) into the protein shell. It is suggested that iron(II) binds to catalytic sites situated adjacent to the peptide chains and that O_2 then bridges two iron atoms. Intramolecular electron transfer leads to $Fe^{III}-(O_2^{2-})-Fe^{III}$ units. Further iron(II) then displaces the peroxide, allowing hydrolysis of the iron(III) and migration into the shell [272].

It has been found that there is no significant iron transfer from transferrin to ferritin in the absence of reducing or chelating agents. Addition of pyrophosphate can, however, mediate this transfer and involves iron(III). An iron pyrophosphate complex has been isolated [273]. The kinetics of iron release from ferritin by catecholamides has also been studied. Mobilisation by catecholamide is very slow, but the rate increases in the presence of added ascorbic acid. The data suggest a multistep process which includes diffusion of a reductant into the ferritin core, reduction to and possible chelation of iron(II), diffusion out of the protein shell and subsequent exchange with the catecholamide [274]. An electrochemical study

of ferritin has also been published [275].

Mugineic acid (*56*), a possible phytosiderophore, is excreted from the roots of barley and appears to play an important role in iron absorption in regions of



(*56*)

iron deficiency such as alkaline soils. The high-spin iron(II) complex has a log K_{ML} value of 18.1 and is reduced by dithionite to an iron(II) complex. An X-ray crystallographic examination of the cobalt(III) analogue shows octahedral coordination with N^1, N^2, O^1 and O^5 occupying the equatorial plane and O^8 and O^3 in axial sites [276].

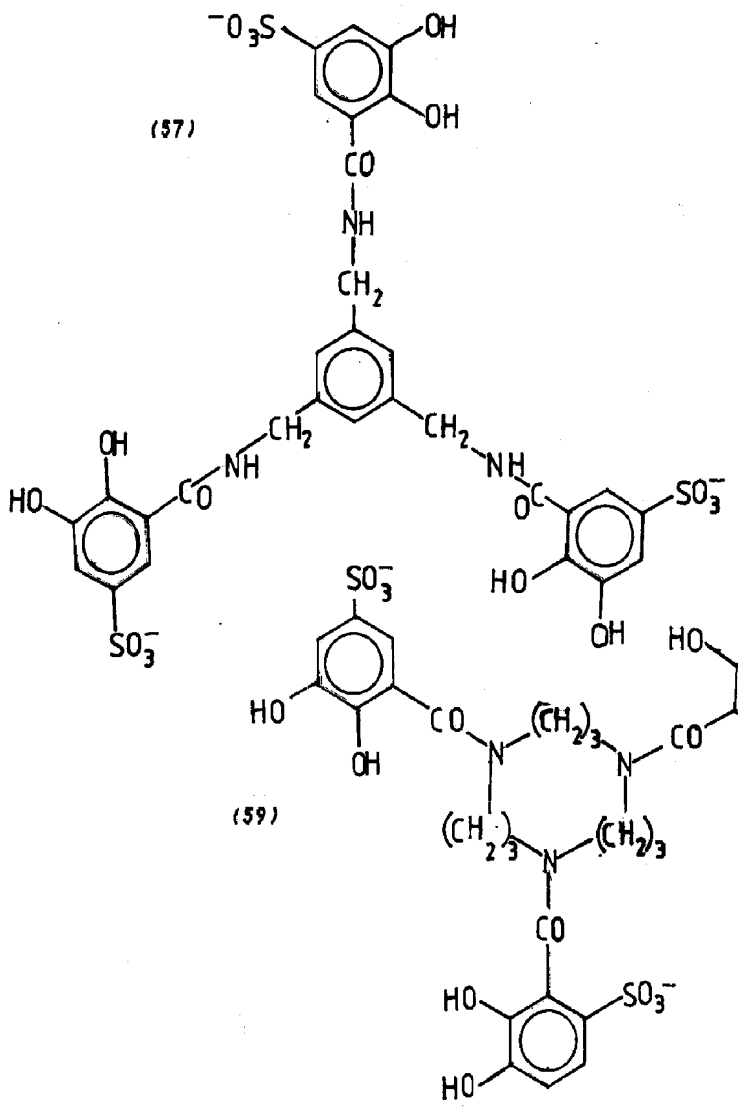
As part of a search for effective iron sequestering agents for use in cases of chronic iron overload, it has been found that the sulphonated tricatecholates, (*57*)-(*60*), form exceptionally stable iron(III) complexes (log $K \cong 40$). Protonation of these complexes results in a shift of coordination from the two phenolic groups to a mode involving one phenolic group and one amide carbonyl group, the other phenolic group being protonated [277].

The properties of enterobactin have been discussed in terms of the behaviour of $FeCl_3$ complexes of phenol, catechol, 2,3-dihydroxybenzaldehyde, 2,3-dihydroxybenzoic acid and salicylic acid [278].

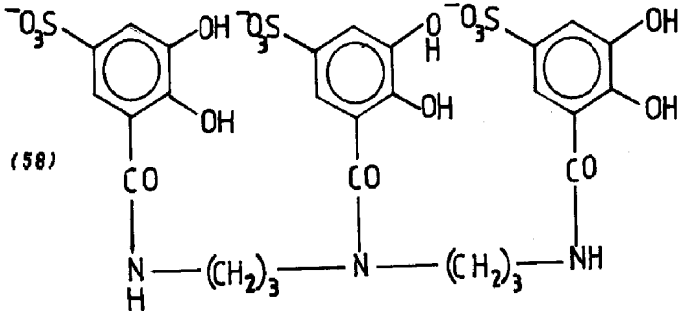
Iron exchange and removal from the two trihydroxamate siderophores, ferrioxamine B and ferrichrome A, from microbial cultures, has been examined. Exchange is extremely slow and iron removal by edta follows a two step process involving protonation of the siderophore and subsequent reaction with edta [279].

2.8.5 Miscellaneous studies

The properties of the $(semi\text{-}met)_O$ form of hemerythrin produced by one-electron oxidation of deoxyhemerythrin and the $(semi\text{-}met)_R$ form produced by one-electron reduction of methemerythrin have been described. Both forms react with F^-, Br^-, $[SCN]^-$, $[CN]^-$ and $[N_3]^-$ to give a (semi-met)-anion adduct. The rate of disproportionation of the two (semi-met) forms has been reported

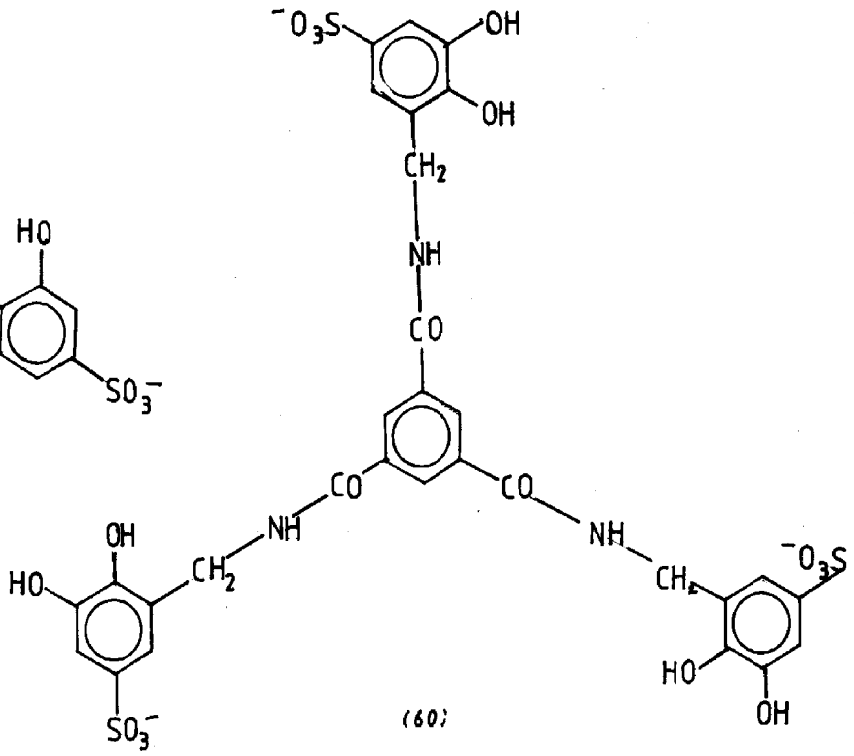


(57)



(58)

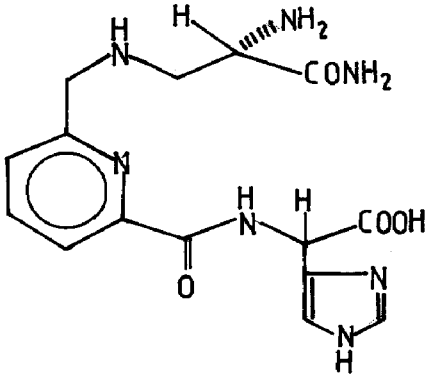
(59)



(60)

and the role of O_2, $[Fe(CN)_6]^{3-}$ and $[S_2O_4]^{2-}$ in such reactions delineated. The process was discussed in terms of the octomeric structure of the protein and it was concluded that disproportionation results from intermolecular electron transfer over distances of 28-30 Å between each binuclear iron unit [280].

Bleomycin has anti-tumour activity and is capable of breaking DNA strands. It binds iron(II) to give an oxygen-sensitive complex. Reactions of the bleomycin model, (*61*), have been studied with the aim of designing simple



(*61*)

ligands that model the action of bleomycin. Thus, a high-spin iron(II) complex has been prepared and O_2, CO and CNEt adducts of this complex can be formed. Spectra closely resemble those of [(bleomycin)Fe^{II}] and its derivatives. The CO adduct is low-spin. Spin-trapping experiments revealed the generation of hydroxyl radicals from the O_2 adduct [281].

Protocatechuate-2,3-dioxygenase and catechol-2,3-dioxygenase are high-spin iron(III)-containing enzymes which catalyse oxidative cleavage of catechols to *cis,cis*-muconic acids. It has been suggested that iron(III) is initially bound to iron(II), and this binds oxygen, but previous Mössbauer spectroscopic studies have indicated that iron(III) is present throughout, and this led to the suggestion of the formation of an iron(III)-catechol complex which activates O_2 giving a semiquinone and $[O_2]^-$ or $[HO_2]$. On this basis, it has been shown that [Fe(salen)(DBcatH)] reacts with O_2 to give [Fe(salen)(DBSQ)] (DBcatH = ditertiarybutylcatechol, DBSQ = ditertiarybutylsemiquinone). Furthermore, it is suggested that the DBcatH is not chelated, but is unidentate in contrast to resonance Raman studies on the dioxygenase [282].

REFERENCES

1 H. Brunner and H. Vogt, *Angew. Chem.*, 93 (1981) 409.
2 P.J. Krusic, *J. Am. Chem. Soc.*, 103 (1981) 2131.

3 P.J. Krusic, J.S. Filippo, B. Hutchinson, R.L. Hance and L.M. Daniels, *J. Am. Chem. Soc.*, 103 (1981) 2129.
4 B.M. Peake, P.H. Rieger, B.H. Robinson and J. Simpson, *Inorg. Chem.*, 20 (1980) 2540.
5 C. Couture, J.R. Morton, K.F. Preston and S.J. Strach, *J. Magn. Reson.*, 41 (1980) 88.
6 D. Miholova and A.A. Vlcek, *Proc. Conf. Coord. Chem. 8th*, (1980) 118; [*Chem. Abstr.*, 94 (1981) 164603]; *Inorg. Chim. Acta*, 43 (1980) 43.
7 S.W. Blanch, A.M. Bond and R. Colton, *Inorg. Chem.*, 20 (1981) 755.
8 B.M. Mattson and W.A.G. Graham, *Inorg. Chem.*, 20 (1981) 3186.
9 V.S. Kaganovich and M.I. Rybinskaya, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1980) 1653.
10 P.M. Treichel and D.A. Komar, *J. Organomet. Chem.*, 206 (1981) 77.
11 J.S. Plotkin and S.G. Shore, *Inorg. Chem.*, 20 (1981) 284.
12 D.R. Tyler and H.B. Gray, *J. Am. Chem. Soc.*, 103 (1981) 1683.
13 D.E. Fjare and W.L. Gladfelter, *Inorg. Chem.*, 20 (1981) 3533.
14 E.M. Holt, K.H. Whitmire and D.F. Shriver, *J. Organomet. Chem.*, 213 (1981) 125.
15 J.S. Bradley, G.B. Ansell, M.E. Leonowicz and E.W. Hill, *J. Am. Chem. Soc.*, 103 (1981) 4968.
16 S.J. Landon and A.L. Rheingold, *Inorg. Chim. Acta*, 47 (1981) 187.
17 R.E. Benfield, P.D. Gavens, B.F.G. Johnson, M.J. Mays, S. Aime, L. Milone and D. Osella, *J. Chem. Soc., Dalton Trans.*, (1981) 1535.
18 A.K. Baev, J.A. Connor, N.I. El-Saied and H.A. Skinner, *J. Organomet. Chem.*, 213 (1981) 151.
19 J.R. Fox, W.L. Gladfelter, T.G. Wood, J.A. Smegal, T.K. Foreman, G.L. Geoffroy, I. Tavanaiepour, V.W. Day and C.S. Day, *Inorg. Chem.*, 20 (1981) 3214; H.C. Foley and G.L. Geoffroy, *J. Am. Chem. Soc.*, 103 (1981) 7176.
20 W.L. Gladfelter, J.R. Fox, J.A. Smegal, T.G. Wood and G.L. Geoffroy, *Inorg. Chem.*, 20 (1981) 3223.
21 F. Takusagawa, A. Fumagalli, T.F. Koetzle, G.R. Steinmetz, R.P. Rosen, W.L. Gladfelter, G.L. Geoffroy, M.A. Bruck and R. Bau, *Inorg. Chem.*, 20 (1981) 3823.
22 A.A. Arduini, A.A. Bahsoun, J.A. Osborn and C. Volker, *Angew. Chem.*, 92 (1980) 1058.
23 G. Longoni and F. Morazzoni, *J. Chem. Soc., Dalton Trans.*, (1981) 1735.
24 G. Longoni, M. Manassero and M. Sansoni, *Congr. Naz. Chim. Inorg. (Atti) 12th*, (1979) 25; [*Chem. Abstr.*, 95 (1981) 143253].
25 J.W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 103 (1981) 7648.
26 D.F. Jones, U. Oehmichen, P.N. Dixneuf, T.G. Southern, J.Y. Le Marouille and D. Grandjean, *J. Organomet. Chem.*, 204 (1981) C1.
27 A.A. Pasynskii, I.L. Eremenko, B. Orazsakhatov, Y.V. Ratitin, V.M. Novotortsev, O.G. Ellert and V.T. Kalinnikov, *J. Organomet. Chem.*, 210 (1981) 385; P. Braunstein, A. Tiripicchio, M. Tiripicchio Camellini and E. Sappa, *Inorg. Chem.*, 20 (1981) 3586.
28 J. Abys and W.M. Risen, *J. Organomet. Chem.*, 204 (1981) C5.
29 A.E. Mauro and E.G. Roveri, *Ecletica Quim.*, 4 (1979) 61; [*Chem. Abstr.*, 95 (1981) 161198].
30 M. Boerner and H. Vahrenkamp, *Chem. Ber.*, 114 (1981) 1382.
31 R. Müller and H. Vahrenkamp, *Chem. Ber.*, 113 (1980) 3539.
32 R.A. Jackson, R. Kanluen and A.J. Poe, *Inorg. Chem.*, 20 (1981) 1130.
33 M.R. Churchill, C. Bueno and D.A. Young, *J. Organomet. Chem.*, 213 (1981) 139; D.A. Young, *Inorg. Chem.*, 20 (1981) 2049.
34a H. Vahrenkamp and E.J. Wucherer, *Angew. Chem.*, 93 (1981) 715.
34b D. Seyferth, R.S. Henderson, J.P. Fackler and A.M. Mazany, *J. Organomet. Chem.*, 213 (1981) C21.
35 L. Marko, *J. Organomet. Chem.*, 213 (1981) 271.
36 A.J. Blakeney, D.L. Johnson, P.W. Donovan and J.A. Gladysz, *Inorg. Chem.*, 20 (1981) 4415.
37 W. Hoenle and H.G. Von Schnering, *Z. Anorg. Allg. Chem.*, 464 (1980) 139.

38 B.A. Sosinksky, J. Shelley and R. Shong, *Inorg. Chem.*, 20 (1981) 1370.
39 N. Aktogu, S.G. Davies, J. Dubar and P. Mazerolles, *J. Organomet. Chem.*, 212 (1981) C13.
40 M. Moll, H. Behrens, P. Merbach, K. Goerting, G. Liehr and R. Boehme, *Z. Naturforsch., Teil B*, 35 (1980) 1115.
41 L.H. Staal, L.H. Polm and K. Vrieze, *Inorg. Chim. Acta*, 40 (1980) 165.
42 C.Y. Chang, C.E. Johnson, T.G. Richmond, Y.T. Chen, W.C. Trogler and F. Basolo, *Inorg. Chem.*, 20 (1981) 3167.
43 C.B. Argo and J.T. Sharp, *Tetrahedron Lett.*, 22 (1981) 353.
44 G. Gervasio, P.L. Stanghellini and R. Rossetti, *Acta Cryst., Sect. B*, 37 (1981) 1198.
45 H. Kisch, C. Krueger and A. Trautwein, *Z. Naturforsch., Teil B*, 36B (1981) 205.
46 M.O. Albers, N.J. Colville, T.V. Ashworth and E. Singleton, *J. Organomet. Chem.*, 217 (1981) 385.
47 J. Grobe and B.H. Schneider, *Z. Naturforsch., Teil B*, 36 (1981) 8.
48 J.A.S. Howell, A.J. Rowan and M.S. Snell, *J. Chem. Soc., Dalton Trans.*, (1981) 325.
49 H. Schaefer, *Z. Anorg. Allg. Chem.*, 467 (1980) 105.
50 S. Hietkamp, O. Stelzer, M. Engelhardt and G. Haegele, *Z. Anorg. Allg. Chem.*, 475 (1981) 131.
51 E. Keller and H. Vahrenkamp, *Chem. Ber.*, 114 (1981) 1124.
52 R.E. Cobbledick, W.R. Cullen, F.W.B. Einstein and M. Williams, *Inorg. Chem.*, 20 (1981) 186.
53 P.M. Treichel and L.D. Rosenheim, *Inorg. Chem.*, 20 (1981) 1539.
54 K. Fischer and H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, 475 (1981) 109.
55 A.H. Cowley, R.A. Kemp and J.W. Wilburn, *Inorg. Chem.*, 20 (1981) 4289.
56 H. Ashton, B. Brady, A.R. Manning and P.S. O'Neill, *J. Organomet. Chem.*, 192 (1980) 219.
57 H.J. Breunig, W. Fichter and T.P. Knobloch, *Z. Anorg. Allg. Chem.*, 477 (1981) 126.
58 M. Savignac, P. Cadiot and F. Mathey, *Inorg. Chim. Acta*, 45 (1980) L43.
59 P. Vierling, J.G. Riess and A. Grand, *J. Am. Chem. Soc.*, 103 (1981) 2466.
60 H. Van Dam, J.N. Louwen, A. Oskam, M. Doran and I.H. Hillier, *J. Electron Spectroscop. Relat. Phenom.*, 21 (1980) 57; [*Chem. Abstr.*, 94 (1981) 9641].
61 D. Seyferth and R.S. Henderson, *J. Organomet. Chem.*, 204 (1981) 333.
62 D. Seyferth and M.K. Gallagher, *J. Organomet. Chem.*, 218 (1981) C5.
63 D. Seyferth and R.S. Henderson, *J. Organomet. Chem.*, 219 (1981) C34.
64 A. Mueting and B.M. Mattson, *J. Inorg. Nucl. Chem.*, 43 (1981) 749.
65 D.A. Lesch and T.B. Rauchfuss, *Inorg. Chem.*, 20 (1981) 3583.
66 R.E. Cobbledick, N.S. Dance, F.W.B. Einstein, C.H.W. Jones and T. Jones, *Inorg. Chem.*, 20 (1981) 4356.
67 G. Le Borgne and R. Mathieu, *J. Organomet. Chem.*, 208 (1981) 201.
68 R.C. Pattersen, K.H. Pannell and A.J. Mayr, *Acta Cryst., Sect. B*, 36 (1980) 2434.
69 G. Nagao, K. Tanaka and T. Tanaka, *Inorg. Chim. Acta*, 42 (1980) 43.
70 H. Patin, G. Mignani, A. Benoit and M.J. McGlinchey, *J. Chem. Soc., Dalton Trans.*, (1981) 1278.
71 H. Patin, G. Mignani, A. Benoit, J.Y. Le Marouille and D. Grandjean, *Inorg. Chem.*, 20 (1981) 4351.
72 P.M. Treichel and L.D. Rosenhein, *Inorg. Chem.*, 20 (1981) 942.
73 D.J. Darenshourg, C.S. Day and M.B. Fischer, *Inorg. Chem.*, 20 (1981) 3577.
74 D. Wormsbaecher, F. Edelmann and U. Behrens, *Chem. Ber.*, 114 (1981) 153.
75 G.J. Kubas and P.J. Vergamini, *Inorg. Chem.*, 20 (1981) 2667.
76 M.H. Quick and R.J. Angelici, *Inorg. Chem.*, 20 (1981) 1123.
77 W. Petz, *J. Organomet. Chem.*, 205 (1981) 203.
78 J. Ellerman and M. Lietz, *J. Organomet. Chem.*, 213 (1981) C4.
79 P.V. Broadhurst, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Am. Chem. Soc.*, 103 (1981) 3198.
80 J.M. Bassett, G.K. Barker, M. Green, J.A.K. Howard, F.G.A. Stone and W.C. Wolsey, *J. Chem. Soc., Dalton Trans.*, (1981) 219.

81 M. Ennis, R. Kamar, A.R. Manning, J.A.S. Howell, P. Mathur, A.J. Rowan and F.S. Stephens, *J. Chem. Soc., Dalton Trans.*, (1981) 1251.
82 R. Kumar and A.R. Manning, *J. Organomet. Chem.*, 216 (1981) C61.
83 J.A.S. Howell and A.J. Rowan, *J. Chem. Soc., Dalton Trans.*, (1981) 297.
84 K.S. Suslick, P.F. Schubert and J.W. Goodale, *J. Am. Chem. Soc.*, 103 (1981) 7342.
85 P. Bowen, W. Jones, J.M. Thomas, R. Schlögl and H.P. Böhm, *J. Chem. Soc., Chem. Commun.*, (1981) 679.
86 V.I. Spitsyn, M.G. Felin, S.I. Pakhomov, A.I. Zhirov and N.A. Subbotina, *Zh. Neorg. Khim.*, 25 (1980) 3152.
87 C. Bordeleau and D.R. Wiles, *Inorg. Chim. Acta*, 41 (1980) 195.
88 B.J. Evans, *Inorg. Chem.*, 20 (1981) 504.
89 J.M. Dietrich, A. Tressaud, W. Massa and D. Babel, *J. Chem. Res. (Synop.)*, (1981) 202.
90 M.B. Millikai and B.D. James, *J. Inorg. Nucl. Chem.*, 43 (1981) 1175.
91 G.P. Algra and S. Balt, *Inorg. Chem.*, 20 (1981) 1102.
92 L. Fournes, N. Kinomura and F. Menil, *C.R. Seances Acad. Sci. Ser. C*, 291 (1980) 235.
93 R.H. Herber and Y. Maeda, *Inorg. Chem.*, 20 (1981) 1409.
94 N.W. Gregory, *Inorg. Chem.*, 20 (1981) 3667.
95 G.N. Papatheodorou, J. Meisenhelder and R. Loutfy, *J. Inorg. Nucl. Chem.*, 43 (1981) 1056.
96 T. Katila, M. Leskela, L. Niinisto, K.J. Riski and J. Valkonen, *J. Solid State Chem.*, 35 (1980) 341.
97 C.O.D. Vedova, J.H. Lesk, E.L. Varetti, P.J. Aymonino, O.E. Piro, B.E. Rivero and E.E. Castellano, *J. Mol. Struct.*, 70 (1981) 241.
98 A. Passoja and L.H.J. Lajunen, *Finn. Chem. Lett.*, (1980) 122; [*Chem. Abstr.*, 94 (1981) 24232].
99 S. Jagner, E. Ljungstroem and A. Tullberg, *Acta Cryst., Sect. B*, 36 (1980) 2213.
100 J.L. Brisset and M. Biquard, *Inorg. Chim. Acta*, 53 (1981) L125.
101 Y. Tamaura, P.V. Buduan and T. Katsura, *J. Chem. Soc., Dalton Trans.*, (1981) 1807.
102 K. Klepp and H. Boller, *Monatsh. Chem.*, 112 (1981) 83.
103 P. Mueller and W. Bronzer, *Z. Naturforsch., Teil B*, 36 (1981) 646.
104 J.O. Willerstroem and S. Rundquist, *J. Solid State Chem.*, 39 (1981) 128.
105 R. Bau, D.M. Ho and S.G. Gibbins, *J. Am. Chem. Soc.*, 103 (1981) 4960.
106 C.A. Ghilardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 205 (1981) 193.
107 E.B. Lobkovskii, M.Y. Antipin, A.P. Borisov, V.D. Makhaev, K.N. Semerenko and Y.T. Struchkov, *Koord. Khim.*, 6 (1980) 1267.
108 J. Sima, S. Sostero, A. Maldotti, O. Traverso and V. Carassati, *Proc. Conf. Coord. Chem. 8th*, (1980) 411.
109 P. Ganguli, P. Gütlich, E.W. Müller and W. Irler, *J. Chem. Soc., Dalton Trans.*, (1981) 441.
110 P.S. Rao, A. Reuveni, B.R. McGarvey, P. Ganguli and P. Gütlich, *Inorg. Chem.*, 20 (1981) 204.
111 P.S. Rao, P. Ganguli and B.R. McGarvey, *Inorg. Chem.*, 20 (1981) 3682.
112 K. Burger, C. Furlani and G. Mattiogno, *J. Electron Spectrosc. Relat. Phenom.*, 21 (1980) 249.
113 K. Burger and H. Ebel, *Inorg. Chim. Acta*, 53 (1981) L105.
114 E. König, G. Ritter and H.A. Goodwin, *Inorg. Chem.*, 20 (1981) 3677.
115 K. Bode, P. Gütlich and H. Köppen, *Inorg. Chim. Acta*, 42 (1980) 281.
116 R.D. Gillard, D.W. Knight and P.A. Williams, *Transition Met. Chem., (Weinheim, Ger.)*, 5 (1980) 321.
117 D.W. Clack, L.A.P. Kane-Maguire, D.W. Knight and P.A. Williams, *Transition Met. Chem., (Weinheim, Ger.)*, 5 (1980) 376.
118 F.M. Mikhail, P. Askalani, J. Burgess and R. Sherry, *Transition Met. Chem., (Weinheim, Ger.)*, 6 (1981) 51.
119 F.T.T. Ng and P.M. Henry, *Canad. J. Chem.*, 5 (1980) 1773.

120 J.M. Rao, D.J. Macero and M.C. Hughes, *Inorg. Chim. Acta*, 41 (1980) 221.
121 M.G. Burnett, V. McKee and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, (1981) 1492.
122 D. Soria, M.L. De Castro and H.L. Chum, *Inorg. Chim. Acta*, 42 (1980) 121.
123 V.M. Derkacheva, N.I. Bundina, N.G. Mekhryakova, T.Y. Gulina, O.L. Kaliya and E.A. Luk'yanets, *Zh. Neorg. Khim.*, 26 (1981) 1687.
124 F. Calderazzo, D. Vitali, G. Pampaloni, I. Collamati, G. Pelizzi, S. Frediani and A. Serra, *Congr. Naz. Chim. Inorg. (Atti), 12th*, (1979) 37; [*Chem. Abstr.*, 95 (1981) 17265].
125 C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi and M. Brunori, *J. Chem. Soc., Dalton Trans.*, (1981) 1120.
126a R. Davis, *Coord. Chem. Rev.*, 41 (1982) 1.
126b I. Collamati, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 69; *Cong. Naz. Chim. Inorg. (Atti), 13th*, (1980) 134 [*Chem. Abstr.*, 94 (1981) 218833]; *Cong. Naz. Chim. Inorg. (Atti), 12th*, (1979) 43 [*Chem. Abstr.*, 95 (1981) 17266].
127 H. Behret, H. Binder, G. Sandstede and G.G. Scherer, *J. Electroanal. Chem. Interfacial Electrochem.*, 117 (1981) 29.
128 J. Blomquist, L.C. Muberg, L.Y. Johansson and R. Larsson, *Inorg. Chim. Acta*, 53 (1981) L39.
129 N.N. Kildahl, T.J. Lewis and G. Anotonopoulos, *Inorg. Chem.*, 20 (1981) 3952.
130 J.G. Norman, L.M.L. Chen, C.M. Perkins and N.J. Rose, *Inorg. Chem.*, 20 (1981) 1403.
131 N. Herron and D.H. Busch, *J. Am. Chem. Soc.*, 103 (1981) 1236.
132 M.G.B. Drew, J. Nelson and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, (1981) 1685.
133 M.G.B. Drew, M. McCann and S.M. Nelson, *Inorg. Chim. Acta*, 41 (1980) 213.
134 D. Sedney, M. Kahjehnassiri and W.M. Reiff, *Inorg. Chem.*, 20 (1981) 3476.
135 R.K. Boggess, J. Hughes and C.W. Chew, *J. Inorg. Nucl. Chem.*, 43 (1981) 939.
136 H.S. Wei and C.S. Hasiao, *J. Chin. Chem. Soc. (Taipei)*, 28 (1981) 69.
137 D.W. Engelfriet and G.C. Werschoor, *Acta Cryst., Sect. B*, 37 (1981) 237.
138 N.T. Moxon and A.K. Gregson, *J. Inorg. Nucl. Chem.*, 43 (1981) 491.
139 J.S. Haynes, J.R. Sams and R.C. Thompson, *Canad. J. Chem.*, 59 (1981) 669; idem, *Chem. Phys. Lett.*, 75 (1980) 596.
140 M.S.R. Swami and T.P. Prasad, *J. Therm. Anal.*, 19 (1980) 297.
141 G. Weber, *Acta Cryst., Sect. B*, 36 (1980) 3107.
142 A. Müller, R. Josters, H.G. Tölle, A. Trautwein and E. Bill, *Inorg. Chim. Acta*, 46 (1980) L121; A. Müller, H.G. Tölle and H. Bogge, *Z. Anorg. Allg. Chem.*, 471 (1980) 115.
143 A. Müller, S. Sarkar, A.M. Dommröse and R. Filgueria, *Z. Naturforsch., Teil B*, 35 (1980) 1592.
144 P. Stremple, N.C. Baenziger and D. Coucouvanis, *J. Am. Chem. Soc.*, 103 (1981) 4601.
145 J.W. McDonald, G.D. Friesen and W.E. Newton, *Inorg. Chim. Acta*, 46 (1980) L79.
146 D. Coucouvanis, E.D. Simhon, P. Stremple and N.C. Baenziger, *Inorg. Chim. Acta*, 53 (1981) L135.
147 F. Cecconi, M. Di Varia, S. Midollini, A. Orlandi and L. Sacconi, *Inorg. Chem.*, 20 (1981) 3423.
148 M. Di Varia, S. Midollini and L. Sacconi, *Inorg. Chem.*, 20 (1981) 3430.
149 C. Bianchini, A. Meli, A. Orlandi and G. Scapacci, *J. Organomet. Chem.*, 215 (1981) C59.
150 C. Bianchini, A. Meli, A. Orlandi and L. Sacconi, *J. Organomet. Chem.*, 218 (1981) 81; *Angew. Chem.*, 92 (1980) 1055.
151 C.L. Spiro, S.L. Lambert, T.J. Smith, E.N. Dueslar, R.R. George and D.N. Hendrickson, *Inorg. Chem.*, 20 (1981) 1229.
152 C. Cairns, S.M. Nelson and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1981) 1965.
153 M. Goodgame and K.W. Johns, *Inorg. Chim. Acta*, 46 (1980) 23.

154 A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski and N.M. Karayannis, *Inorg. Chim. Acta*, 46 (1980) 235.
155 R.D. Gillard, W.S. Walters and P.A. Williams, *Transition Met. Chem. (Weinheim, Ger.)*, 6 (1981) 20.
156 M.V. Veidis, E.H. Witten, W.M. Reiff, A. Garafalo and T.F. Brennan, *Inorg. Chim. Acta*, 53 (1981) L237.
157 I.G. Dance, A.S. Abushamelah and H.A. Goodwin, *Inorg. Chim. Acta*, 43 (1980) 217.
158 H.L. Chum, D. Kiran and R.A. Osteryoung, *Inorg. Chem.*, 20 (1981) 3304.
159 S. Lahiry and V.K. Anand, *Inorg. Chem.*, 20 (1981) 2789.
160 B. Komenar and B. Kaitner, *Struct. Stud. Mol. Biol. Interest*, (1981) 123; [*Chem. Abstr.*, 95 (1981) 89299].
161 M. Magini, *Chem. Phys. Lett.*, 78 (1981) 106.
162 T.I. Morrison, G.K. Shenoy and L. Nielson, *Inorg. Chem.*, 20 (1981) 3565.
163 T.W. Swaddle and A.E. Merbach, *Inorg. Chem.*, 20 (1981) 4212; H.W. Dodgen, G. Liu and J.P. Hunt, *Inorg. Chem.*, 20 (1981) 1002.
164 J.A. Thich, B.H. Toby, D.A. Powers, J.A. Potenza and H.J. Schuger, *Inorg. Chem.*, 20 (1981) 3314.
165 C.T. Dziobkowski, J.T. Wrobleski and D.B. Brown, *Inorg. Chem.*, 20 (1981) 679.
166 A.B. Blake, A. Yavari and H. Kubicki, *J. Chem. Soc., Chem. Commun.*, (1981) 796.
167 C.T. Dziobkowski, J.T. Wrobleski and D.B. Brown, *Inorg. Chem.*, 20 (1981) 671.
168 O. Sock, P. Lemoine and M. Gross, *Electrochim. Acta*, 26 (1981) 99.
169 B.D. Beaver, L.C. Hall, C.M. Lukehart and L.D. Preston, *Inorg. Chim. Acta*, 47 (1981) 25.
170 A. Malliano and V. Papaefthimiou, *J. Chem. Phys.*, 74 (1981) 3626.
171 N.V. Duffy, T.E. Lockhart, E. Gelerinter, D. Todoroff and D.L. Uhrich, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 1.
172 B. Hutchinson, P. Neill, A. Finkelstein and J. Takemoto, *Inorg. Chem.*, 20 (1981) 2000.
173 N.V. Duffy, *Inorg. Chim. Acta*, 47 (1981) 31.
174 D.L. Perry and S.R. Cooper, *J. Inorg. Nucl. Chem.*, 42 (1980) 1356.
175 D.L. Perry, L.J. Wilson, K.R. Kunze, L. Maleki, P. Deplano and E.F. Trogu, *J. Chem. Soc., Dalton Trans.*, (1981) 1294.
176 G. Cauquis and A. Deronzier, *J. Inorg. Nucl. Chem.*, 42 (1980) 1447.
177 F. Cecconi, C.A. Ghilardi and S. Middolini, *J. Chem. Soc., Chem. Commun.*, (1981) 640.
178 P.G. Sim, E. Sin, R.H. Petty, C.L. Merrill and L.J. Wilson, *Inorg. Chem.*, 20 (1981) 1213.
179 M.S. Haddad, M.W. Lynch, W.D. Federer and D.N. Hendrickson, *Inorg. Chem.*, 20 (1981) 123; idem, ibid, 131.
180 D.N. Hendrickson, M.S. Haddad and W. Federer, *J. Coord. Chem.*, 21 (1980) 75.
181 N.A. Ryabova, V.I. Ponomarev and V. Zelentsov, *Kristallografiya*, 26 (1981) 101.
182 P.J. Marini, K.S. Murray and B.O. West, *J. Chem. Soc., Chem. Commun.*, (1981) 726.
183 R.E. Hester and E.M. Nour, *J. Raman Spectrosc.*, 11 (1981) 35.
184 M.S. El-Ezaby and A.S.I. Abu-Shady, *Inorg. Chim. Acta*, 55 (1981) 29.
185 P. Deplano and E.F. Trogu, *Congr. Naz. Chim. Inorg. (Atti)*, *13th*, (1980) 113; [*Chem. Abstr.*, 95 (1981) 17298].
186 S.E.V. Phillips, *J. Mol. Biol.*, 142 (1980) 531.
187 K. Anzai, K. Hatano, Y.J. Lee and W.R. Scheidt, *Inorg. Chem.*, 20 (1981) 2337.
188 M.A. Phillippi, N. Baenziger and H.M. Goff, *Inorg. Chem.*, 20 (1981) 3904.
189 D.V. Behere, R. Birdy and S. Mitra, *Inorg. Chem.*, 20 (1981) 2786.
190 J. Mispelter, M. Momenteau and J.M. Lhoste, *J. Chem. Soc., Dalton Trans.*, (1981) 1729.
191 D. Lexa, J. Mispelter and J.M. Saveant, *J. Am. Chem. Soc.*, 103 (1981) 6806.

192 M. Lange, J.P. Battioni, D. Mansuy, D. Lexa and J.M. Saveant, *J. Chem. Soc., Chem. Commun.*, (1981) 888.
193 D. Mansuy, J.P. Lecomte, J.C. Choltard and J.F. Bartoli, *Inorg. Chem.*, 20 (1981) 3119.
194 M.P. Doyle, F.J. Van Doornik and C.L. Funckes, *Inorg. Chim. Acta*, 46 (1980) L111.
195 H. Kon, M. Chikira and K.M. Smith, *J. Chem. Soc., Dalton Trans.*, (1981) 1726.
196 W.F. Scheidt, K.J. Haller, M. Fons, T. Mashiko and C.A. Reed, *Biochemistry*, 20 (1981) 3653.
197 T.G. Traylor and A.P. Berzinis, *Proc. Natl. Acad. Sci. U.S.A.*, 77 (1980) 3171.
198 T.G. Traylor, D.K. White, D.H. Campbell and A.P. Berzinis, *J. Am. Chem. Soc.*, 103 (1981) 4932.
199 T.G. Traylor, M.J. Mitchell, S. Tsuchiya, D.H. Campbell, D.V. Stynes and N. Koga, *J. Am. Chem. Soc.*, 103 (1981) 5234.
200 B. Ward, C.B. Wang and C.K. Chang, *J. Am. Chem. Soc.*, 103 (1981) 5236.
201 J.P. Collman, J.I. Brauman, T.J. Collins, B. Iverson and J.L. Sessler, *J. Am. Chem. Soc.*, 103 (1981) 2450.
202 J.P. Collman, A.O. Chong, G.B. Jameson, R.T. Oakley, E. Rose, E.R. Schmittou and J.A. Ibers, *J. Am. Chem. Soc.*, 103 (1981) 516.
203 M. Momenteau and B. Loock, *J. Mol. Catal.*, 7 (1980) 315.
204 M. Kühn and M. Benes, *Z. Chem.*, 20 (1980) 351.
205 H. Nishide, H. Ohno and E. Tsuchida, *Makromol. Chem. Rapid Commun.*, 2 (1981) 55.
206 N. Kobayashi, M. Fijihira, T. Osa and T. Kuwana, *Bull. Chem. Soc. Japan*, 53 (1980) 2195.
207 P.A. Forshey and T. Kuwana, *Inorg. Chem.*, 20 (1981) 693; Y. Ilan, J. Rabani, I. Fridovich and R.F. Pasternack, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 93.
208 D.A. Baldwin, V.M. Campbell, L.A. Carleo, H.M. Marques and J.M. Pratt, *J. Am. Chem. Soc.*, 103 (1981) 186.
209 P. Worthington and P. Hambright, *Inorg. Chim. Acta*, 46 (1980) 487; *J. Inorg. Nucl. Chem.*, 42 (1980) 1651.
210 K.M. Kadish, R.K. Rhodes, L.A. Bottomley and H.M. Goff, *Inorg. Chem.*, 20 (1981) 3195.
211 Y. Huang and R.J. Kassner, *J. Am. Chem. Soc.*, 103 (1981) 4927.
212 H. Kobayashi, Y. Kaizu and K. Eguchi, *Adv. Chem. Ser.*, 191 (1980) 327.
213 K. Tatsumi and R. Hoffman, *J. Am. Chem. Soc.*, 103 (1981) 3328.
214 T.H. Stevens and S.I. Chem, *J. Biol. Chem.*, 256 (1981) 1069.
215 J. Van Stellandt-Frentrup, I. Salmeen and G.T. Babcock, *J. Am. Chem. Soc.*, 103 (1981) 5981.
216 T. Sugiyama, R. Miura, T. Yamano, K. Shiga and H. Watari, *Biochem. Biophys. Res. Commun.*, 97 (1980) 22.
217 T. Mashiko, C.A. Reed, K.J. Haller, M.E. Kartner and W.R. Scheidt, *J. Am. Chem. Soc.*, 103 (1981) 5758.
218 G.N. La Mar, J.T. Jackson and R.G. Bartsch, *J. Am. Chem. Soc.*, 103 (1981) 4405.
219 J.D. Satterlee and J.E. Erlman, *J. Am. Chem. Soc.*, 103 (1981) 199.
220 C.H. Welborn, D. Dolphin and B.R. James, *J. Am. Chem. Soc.*, 103 (1981) 2869.
221 D. Dolphin, B.R. James and C.H. Welborn, *J. Mol. Catal.*, 7 (1980) 201.
222 H. Sakurai, S. Shimomura and K. Ishiza, *Biochem. Biophys. Res. Commun.*, 101 (1981) 1102.
223 M. Schappacher, L. Ricard, R. Weiss, R. Monteil-Montoya, E. Bill, U. Gonser and A. Trautwein, *J. Am. Chem. Soc.*, 103 (1981) 7646.
224 M. Kühn and P. Mohr, *Pharmazie*, 36 (1981) 383; [*Chem. Abstr.*, 95 (1981) 57146].
225 R.E. White, S.H. Sliger and M.J. Coon, *J. Biol. Chem.*, 255 (1980) 11108.
226 D. Mansuy, J.F. Bartoli, J.C. Chottard and M. Lange, *Angew. Chem.*, 92 (1980) 938.

227 J.T. Groves, W.J. Kruper, T.E. Nemo and R.S. Myers, *J. Mol. Catal.*, 7 (1980) 169.
228 C.K. Chang and F. Ebina, *J. Chem. Soc., Chem. Commun.*, (1981) 778.
229a P. Shannon and T.C. Bruice, *J. Am. Chem. Soc.*, 103 (1981) 4580.
229b R. Makino, K. Sakaguchi, T. Iizuka and Y. Ishimaru, *J. Biol. Chem.*, 255 (1980) 11883.
230 C. Bonfils, K.K. Anderson, P. Maurel and P. Debey, *J. Mol. Catal.*, 7 (1980) 229.
231 D. Mansuy, J.C. Chottard, M. Lange and J.P. Battioni, *J. Mol. Catal.*, 7 (1980) 215; B. Chevrier and R. Weiss, *J. Am. Chem. Soc.*, 103 (1981) 2899; L. Latos-Graznski, R.J. Cheng, G.N. La Mar and A. Balch, *J. Am. Chem. Soc.*, 103 (1981) 4270.
232 K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 20 (1981) 3771.
233 J.T. Groves, R.C. Haushalter, M. Nakamura, T.E. Nemo and B.J. Evans, *J. Am. Chem. Soc.*, 103 (1981) 2884.
234 J.E. Roberts, B.M. Hoffman, R. Rutter and L.P. Hager, *J. Am. Chem. Soc.*, 103 (1981) 7654.
235 W.R. Browlett and M.J. Stillmann, *Biochim. Biophys. Acta*, 660 (1981) 1.
236 E.T. Shimomura, M.A. Phillippi, H.M. Goff, W.F. Scholz and C.A. Read, *J. Am. Chem. Soc.*, 103 (1981) 6778.
237 M.A. Phillippi, E.T. Shimomura and H.M. Goff, *Inorg. Chem.*, 20 (1981) 1322.
238 P. Gans, J.C. Marchon, C.A. Reed and J.R. Regnard, *Nouv. J. Chim.*, 5 (1981) 203.
239 L.K. Hanson, C.K. Chang, M.S. Davis and J. Fajer, *J. Am. Chem. Soc.*, 103 (1981) 663.
240 H.C. Kelly, K.J. Parigi, I. Wilson, D.M. Davies, P. Jones and L.J. Roettger, *Inorg. Chem.*, 20 (1981) 1086.
241 A.M. Stolzenberg, S.H. Strauss and R.H. Holm, *J. Am. Chem. Soc.*, 103 (1981) 4763.
242 M.G. Clore and M. Denis, *Inorg. Chim. Acta*, 55 (1981) L47.
243 R.A. Scott, S.P. Cramer, R.W. Shaw, H. Beinert and H.B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, 78 (1981) 664.
244 M.J. Gunter, L.N. Mander and K.S. Murray, *J. Chem. Soc., Chem. Commun.*, (1981) 799.
245 K.J. Berry, P.E. Clark, M.J. Gunter and K.S. Murray, *Nouv. J. Chim.*, 4 (1980) 581.
246 M.J. Gunter, L.N. Mander, K.S. Murray and P.E. Clark, *J. Am. Chem. Soc.*, 103 (1981) 6784.
247 H. Okawa, W. Kanda and S. Kida, *Chem. Lett.*, (1980) 1281.
248 J. Jaud, Y. Journaux, J. Galy and O. Kahn, *Nouv. J. Chim.*, 4 (1980) 629.
249 E.A. Deardorff, P.A.G. Carr and J.K. Hurst, *J. Am. Chem. Soc.*, 103 (1981) 6611.
250 N. Ueyama, M. Nakata and A. Nakamura, *Bull. Chem. Soc. Japan*, 54 (1981) 1727.
251 D. Coucouvanis, D. Swenson, N.C. Baenziger, C. Murphy, D.G. Holah, N. Sfarnas, A. Simopoulos and A. Kostikas, *J. Am. Chem. Soc.*, 103 (1981) 3350.
252 K. Fukuyama, T. Hase, S. Matsumoto, T. Tsukihara, Y. Katsube, N. Tanaka, M. Kakudo, K. Wada and H. Matsubara, *Nature*, 286 (1980) 522.
253 H.M. Emptage, T.A. Kent, H.H. Boi, W.H. Orme-Johnson and E. Munck, *Cienc. Biol. (Coimbra)*, 5 (1980) 203; [*Chem. Abstr.*, 93 (1980) 199491].
254 D. Ghosh and W. Furey, *J. Biol. Chem.*, 256 (1981) 4185.
255 A.J. Thomson, A.E. Robinson, M.K. Johnson and J.J.G. Moura, *Biochem. Biophys. Acta*, 670 (1981) 93.
256 K.S. Hagan, J.G. Reynolds and R.H. Holm, *J. Am. Chem. Soc.*, 103 (1981) 4054.
257 G. Christou, R.H. Holm, M. Sabat and J.A. Ibers, *J. Am. Chem. Soc.*, 103 (1981) 6269.
258 G. Christou, C.D. Garner, M.G.B. Drew and R. Cammack, *J. Chem. Soc., Dalton Trans.*, (1981) 1550.

259 T.H. Lammen, J.A. Kocal, F.Y.K. Lo, M.W. Chen and L.F. Dahl, *J. Am. Chem. Soc.*, 103 (1981) 1932.
260 J. Butler, G.A. Sykes, G.W. Buxton, P.C. Harrington and R.G. Wilkins, *Biochem. J.*, 189 (1980) 641.
261 M.A. Harmer and G.A. Sykes, *Biochem. Biophys. Res. Commun.*, 101 (1981) 83.
262 P. Krausz, P. Maillard, S. Gaspard and C. Gianotti, *C.R. Seances Acad. Sci. Ser. C*, 291 (1980) 129.
263 I. Mizraki and M.A. Cusanovich, *Biochemistry*, 19 (1980) 4733.
264 M.K. Johnson, A.J. Thomson, A.E. Robinson, K.K. Rao and D.O. Hall, *Biochim. Biophys. Acta*, 667 (1981) 433.
265 P.K. Mascharak, G.C. Papaefthymiou, R.B. Frankel and R.H. Holm, *J. Am. Chem. Soc.*, 103 (1981) 6110.
266 J.G. Reynolds and R.H. Holm, *Inorg. Chem.*, 20 (1981) 1873.
267 B.A. Averill, H.C. Silvas, R.H. Tieckelmann and W.H. Orme-Johnson, *Molybdenum Chem. Biol. Significance, [Proc. Int. Symp.]*, (1979) 217; [*Chem. Abstr.*, 94 (1981) 43258]; B.A. Averill, R.H. Tieckelmann, H.C. Silvas and B.K. Teo, *Cienc. Biol. (Coimbra)*, 5 (1980) 163; [*Chem. Abstr.*, 94 (1981) 1541].
268 W.H. Armstrong and R.H. Holm, *J. Am. Chem. Soc.*, 103 (1981) 6246.
269 G. Christou, D. Collison, C.D. Garner and F.E. Mabbs, *Inorg. Nucl. Chem. Lett.*, 17 (1981) 137.
270 C.D. Garner and R.D. Millar, *J. Chem. Soc., Dalton Trans.*, (1981) 1664.
271 K. Tanaka and T. Tanaka, *Chem. Lett.*, (1981) 895.
272 R.R. Crichton, F. Roman, F. Roland, E. Paques, A. Paques and E. Vandamme, *J. Mol. Catal.*, 7 (1980) 267.
273 K. Konopka, J.C. Mareschal and R.R. Crichton, *Biochem. Biophys. Res. Commun.*, 96 (1980) 1408.
274 T.P. Tufan, V.L. Pecoraro and K.N. Raymond, *Biochem. Biophys. Res. Commun.*, 558 (1981) 420.
275 N. Imai, Y. Umezawa, Y. Arafa and S. Fujiwara, *Biochim. Biophys. Acta*, 626 (1980) 501.
276 Y. Suguira, H. Tanaka, Y. Mino, T. Ishida, N. Ota, M. Inoue, K. Notomo, H. Yoshioko and T. Takemoto, *J. Am. Chem. Soc.*, 103 (1981) 6979.
277 W.R. Harris, K.N. Raymond and F.L. Weitl, *J. Am. Chem. Soc.*, 103 (1981) 2667.
278 R.C. Hider, A.R. Mohd-Nor, J. Silver, I.E.G. Morrison and L.V.C. Rees, *J. Chem. Soc., Dalton Trans.*, (1981) 609.
279 T.P. Tufano and K.N. Raymond, *J. Am. Chem. Soc.*, 103 (1981) 6617.
280 P.C. Harrington and R.G. Wilkins, *J. Am. Chem. Soc.*, 103 (1981) 1550.
281 M. Otsuka, M. Yoshida, S. Kobayashi, M. Ohno, Y. Suguira, T. Takita and H. Umezawa, *J. Am. Chem. Soc.*, 103 (1981) 6986.
282 R.B. Lauffer, R.H. Heistand and L. Que, *J. Am. Chem. Soc.*, 103 (1981) 3947.