Coordination Chemistry Reviews, 35 (1981) 1—39
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

1. IRON

R. DAVIS

CONTENTS

INTRODUCTION

This review covers publications cited in Volumes 90 and 91 (up to and including edition No. 20) of Chemical Abstracts and thus includes a few references from the 1978 literature. It was felt that complete Chemical Abstract coverage, rather than a restriction to primary publications appearing in 1979, would aid those wishing to make their own literature coverage to bridge the gap between the last Chemical Society Specialist Periodical Report on the Inorganic Chemistry of the Transition Elements (Vol. 6) and the present review. However, in keeping with the general content of this volume, the material for carbonyl and nitrosyl complexes has been selected with regard to its general relevance to transition metal chemistry.

1.1 CARBONYLS

A laser PE spectral study of $[Fe(CO)_5]$ has led to the following electron affinity values (eV): $Fe(CO)_4$ (2.4); $Fe(CO)_3$ (1.8); $Fe(CO)_2$ (1.22); Fe(CO) (1.26), Fe (0.164) [1].

A new method has been outlined for assigning energies to metal–metal (M–M) bonds and metal–carbon (M—C) bonds of metal carbonyls including $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. This uses the lengths and strengths of the bonds in the metal as a basis, and assumes that E(M—M) is proportional to $[d(M—M)]^{-k}$. The results indicated that M—M bonds are weaker and M—C bonds stronger than previously indicated. Moreover, the M–C bonds increase slightly in strength with nuclearity [2]. Further calculations on $[Fe_2(CO)_9]$ suggest that CO has much the same thermodynamic affinity for bridging and terminal sites, although there may be a slight preference for bridging sites [3]. Standard enthalpies of formation and bond enthalpy contributions have been reported for $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$, $[(\eta^4\text{-}C_8H_8)Fe(CO)_3]$ and $[Fe(CO)_4I_2]$ [4]. A comparison of structural, spectroscopic and electrochemical properties of $[Fe(CO)_3\{Co(CO)_3\}_2(\mu_3\text{-}PPh)]$ and $[\{Co(CO_3\}_3\text{-}(\mu_3\text{-}PPh)]$ show that the LUMO of the former and the HOMO of the latter are both M—M bonding in character [5]. XPES measurements on $[Fe(CO)_5]$ and $[H_2Fe(CO)_4]$ lead to the conclusion that the hydrogen atoms have a negative charge of —0.3 (cf. —0.8 in $[HMn(CO)_5]$ and —0.75 in $[HCo(CO)_4]$) [6].

$[Fe(CO)_4L]$ $\{L = (3,5\text{-}MeC_6H_3O)_3P\}$ reacts with $K[HB(OCHMe_2)_3]$ to yield the formyl anion complex $[Fe(CO)_3L(CHO)]^-$; such formyl species can act as hydride donors to ketones, alkyl halides and metal carbonyls [7]. $[Fe_3(CO)_{11}]^{2-}$ and $[HFe_3(CO)_{11}]^-$ react with electrophiles, R^+ (R = H, Me, Et or MeCO), giving $[Fe_3(CO)_{10}(COR)]^-$ and $[HFe_3(CO)_{10}(COR)]$, respectively [8]. The stable metallocarboxylic acid, $[(cp)(PPh_3)(CO)Fe(CO_2H)]$ has been isolated; in solvents of low dielectric constant it exists as $FeCO_2H$, but in those of high dielectric constant it exists as $FeCO^+OH^-$. $[(cp)(PPh_3)_2\text{-}FeCO_2H]$ exists only in the acylium hydroxide form [9]. $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ catalyse the high temperature conversion of CO_2, H_2 and ROH to HCO_2R [10]. The reaction of $[Fe(CO)_5]$ and $[^{18}OH]^-$, yielding $[HFe(CO)_4]^-$, has been studied and ^{18}O exchange is barely discernible. Thus the rate of decomposition of the intermediate, $[Fe(CO)_4(COOH)]^-$, to $[Fe(CO)_4H]^-$ and CO_2 is rapid relative to reversible loss of $[OH]^-$ with concomitant ^{18}O exchange. Thus, the propensity of $[Fe(CO)_5]$ to proceed to $[HFe(CO)_4]^-$, rather than undergoing exchange under the conditions of the water gas shift reaction, has been demonstrated and this suggested radical elimination of dihydrogen may be the rate-determining step in dihydrogen production [11]. $Li[R_3BH]$ (R = Et or MeEtCH) effects a quantitative homogeneous room temperature synthesis of $[(cp)Fe(CO)_2]^-$ from the dimer [12].

$[(cp)_2Fe_2(CO)_4]$ reacts photochemically with PR_3 (R = Ph or $OCHMe_2$) to yield only $[(cp)_2Fe(CO)_3L]$. At low temperature, an intermediate in this reaction can be trapped which has an infrared absorption at 1720 cm^{-1}, but no $\sigma \rightarrow \sigma^*$ absorption of an Fe—Fe bond in its electronic spectrum. It has been suggested that this is $[(cp)(OC)_2Fe(\mu\text{-}CO)Fe(CO)(PR_3)(cp)]$, containing an unsupported bridging carbonyl group [13]. $[(cp)_2Fe_2(CO)_2(CNBu)_2]$ exists, in solution, as a mixture of the $(\mu\text{-}CO)_2$ and $(\mu\text{-}CO)(\mu\text{-}CNBu)$ forms. NMR studies indicate that the interconversion between these, by the Adams—Cotton mechanism, proceeds by two different pathways with significantly different E_a values [14]. A study of $[(\eta\text{-dienyl})FeCo(CO)_5L]$ (η-dienyl = cp, Mecp or C_9H_7; L = phosphine, phosphite or arsine) shows some to have CO-bridged isomers in the solid state, while others are non-bridged. In solution, many exist as equilibrium mixtures with one non-bridged and at least two, perhaps four, bridged tautomers. The non-bridged form is favoured at higher temperatures, with bulkier L ligands, along the series $C_9H_7 >> Mecp > cp$ [15]. $[(cp)_2Fe_2(CO)_3(PPh_3)]$ can be obtained by thermal substitution of $[(cp)_2Fe_2(CO)_4]$, as well as by photolysis. It is unstable in solution in the absence of added triphenylphosphine, decomposing completely in one hour at 80°C to $[(cp)_2Fe_2(CO)_4]$ and $[(cp)Fe(CO)]_4$ and this represents an improved synthesis of the tetramer [16].

Alkylation of $[(cp)Fe(CO)(CN)(CNR)]$ (R = Me, Et or Me_2CH) with R'I ($R' \neq R$) yields $[(cp)Fe(CO)(CNR')(CNR)I]$ [17].

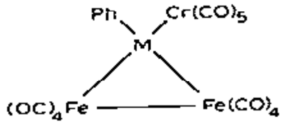
$[(cp)_2NbH_3]$ reacts with $[Fe(CO)_5]$ to form $[(cp)_2Nb(\mu\text{-}H)Fe(CO)_4]$, an X-ray structural study of which shows the iron atom to have nearly regular trigonalbipyramidal geometry (neglecting the bridging hydrogen atom) with Nb in an axial position. NMR studies suggest a different structure in solution [18]. $[(cp)_2Mo_2(CO)_4]$ reacts with $Na_2[Fe(CO)_4]$ to yield $[\{(cp)(OC)_2Mo\}_2\{\mu\text{-}Fe(CO)_4\}]$ containing a formal Mo═Mo double bond [19]. Treatment of *cis*-$[PtCl_2L_2]$ (L = RNC) with $[Fe(CO)_3(NO)]^-$ (represented by M^-) gives *trans*-$[PtL_2M_2]$ [20]. Attempted oxidation of $[Fe_2(CO)_6\{CHC(R)R'\}(PPh_2)]$ with AgX led to $[Fe_2(CO)_6\{CHC(R)R'\}(PPh_2)Ag]X$ (R = Ph; R' = NHMe, NHEt, NEt_2 or NPr_2; X = ClO_4 or PF_6). A structural study of the perchlorate showed the silver atom to bridge the iron atoms (Fe—Ag = 2.685, 2.703 Å) [21].

$[Fe(CO)_5]$ reacts with Zn(II) in the presence of amines to form $[(NH_3)_3ZnFe(CO)_4]$ and $[LZnFe(CO)_4]$ (L = en, Meen, Me_2en, dien, trien or 1,3-diaminopropane). The NH_3, dien and trien compounds are thought to be monomeric, containing trigonalbipyramidal iron, whilst the others are polymeric with octahedral iron coordination [22]. Treatment of $[(ClHg)_2Fe(CO)_4]$ with powdered zinc yields $[(ClZn)_2Fe(CO)_4]$, which reacts with R_3SnCl (R = Ph or Bu) to give *cis*-$[(R_3Sn)_2Fe(CO)_4]$ and with $[Bu_2SnCl_2]$ to give $[(\mu\text{-}Bu_2Sn)_2\{Fe(CO)_4\}_2]$ [23]. $[Fe(CO)_5]$ also reacts with [HgRCl] $\{R = CH_n(SiMe_3)_{3-n}$ (n = 0 or 2)$\}$ to give *cis*-$[Fe(CO)_4(HgR)_2]$ [24]. Reaction of $[(cp)Fe(CO)_2]^-$ with $[Ph_3Al]$ in thf gives $[(cp)Fe(CO)_2(AlPh_3)]$, an X-ray study of which shows that it contains an essentially single Fe—Al bond, of length 2.510 Å [25].

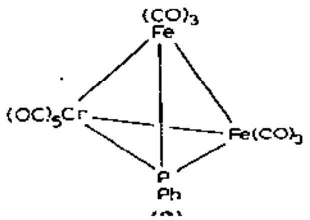
$[\{(cp)Fe(CO)_2\}_2SiHR]$ (R = Me or Cl) is obtained from $[(cp)Fe(CO)_2$-$SiHRCl]$ and $Na[Fe(cp)(CO)_2]$. Treatment of the di-iron compound with CCl_4 gives $[\{(cp)Fe(CO)_2\}_2SiClR]$ which is converted, with $Ag[BF_4]$, to $[\{(cp)Fe(CO)_2\}_2SiFR']$ (R′ = Me or F) [26]. $GeBr_2$ reacts with $[(cp)Fe(CO)_2]_2$ and $[Fe_2(CO)_9]$ to yield $[\{(cp)Fe(CO)_2\}_2GeBr_2]$ and $[\{(OC)_4Fe\}_2$-$GeBr_2]$, respectively [27]. The reactions between $SnCl_2$ and $[(cp)Fe(CO)_2L]$ (L = $CH_2CH{=}CH_2$, $CH_2CMe{=}CH_2$ or $CH_2CH{=}CHMe$) have been re-examined and extended to $SnBr_2$ and $GeCl_2$. The major products are formed by insertion to give $[(cp)Fe(CO)_2MX_2L]$ but, in the presence of excess MX_2, $[(cp)Fe(CO)_2MX_3]$ is formed [28]. UV irradiation of $[Fe(CO)_4(SnCl_3)]^-$ in MeCN gives $[Fe(SnCl_3)_5]^{5-}$ [29]. Treatment of $[(Cl_3Sn)Fe(CO)_2(cp)]$ with TlM (M = $[Co(CO)_4]$ or $[Cr(CO)_3(cp)]$) gives $[Cl_2Sn\{Fe(CO)_2(cp)\}M]$ [30]. $PhN(PF_2)_2$ reacts with $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$ to yield $[\{PhN(PF_2)_2\}_2$-$Fe_2(CO)_5]$ and reaction with $[(cp)Fe(CO)_2]_2$ under photochemical conditions gives low yields of $[(cp)Fe(\mu\text{-}F_2PNPhPF_2)(\mu\text{-}NR{=}PF_2)(\mu\text{-}PF_2)Fe(cp)]$ [31]. Specific formation of $[LFe(CO)_4]$ (L = PPh_3, $P(OPh)_3$ or $P(OMe)_3$) can be achieved by the reaction of $[Fe(CO)_5]$ with L in the presence of a catalytic amount of a polynuclear iron carbonyl anion; a convenient synthetic procedure was developed in which the anion was generated in situ [32]. Treatment of $[Fe_3(CO)_{12}]$ with $(Me_3C)_3P$ (= L) in MeOH gives $[Fe(CO)_4L]$, whereas reaction in ether gives $[Fe(CO)_3L_2]$. [33]. CO does not exchange in the complex $[(LF)Fe(CO)_4]$ (LF = 1,3-dimethyl-2-fluoro-1,3,2-diazaphospholidine); however, removal of F^- from the ligand gives $[LFe(CO)_4]^+$, which undergoes rapid exchange at room temperature [34].

$[Fe_2(CO)_9]$ reacts with $[P(CF_3)H_2]$ to give $[(OC)_4Fe\{P(CF_3)H_2\}]$ which, on heating, yields $[Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2]$; this exists in two isomeric forms, and the structure of the *trans*-isomer has been determined [35]. Structural studies of $[Fe_2(CO)_6(\mu\text{-}AsMe_2)_2]$ and $[FeCr(CO)_7(\mu\text{-}AsMe_2)_2]$ show both to possess folded M_2As_2 arrangements, which have been rationalised in terms of the geometric requirement of the ligand [36]. Reaction of $[(OC)_3Fe_2$-$(\mu\text{-}PPh_2)(\mu\text{-}CHCPh{=}NR)]$ with HX yields $[\{(OC)_3Fe\}_2(\mu\text{-}PPh_2)(\mu\text{-}X)]$ (X = Cl, Br, I or RCO_2; R = H, Me, Et or CF_3) [37]. Treatment of $Li[Co_3(CO)_{10}]$ and $[Fe_2(CO)_9]$ with PPh_2Cl gives $[(OC)_3Co(\mu\text{-}PPh_2)Fe(CO)_4]$ [38]. $[(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_2(PMe_3)]$ is an active catalyst for the dimerisation of norbornadiene to binor-S [39].

Reaction of $[(OC)_5CrMPhX_2]$ (X = Cl or Br; M = P, As or Sb) with $[Fe_2(CO)_9]$ gives (1), and the structure of phosphide has been reported. Irra-

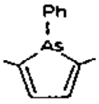


(1) (M = P, As or Sb)

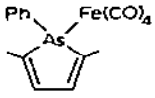


diation of (1) gives (2) [40]. [$PhPCo_2Fe(CO)_9$] and the chiral complex [$PhPFeMoCo(cp)(CO)_8$] have also been prepared [41].

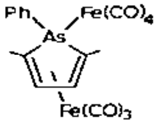
The arsole (3) reacts with [$Fe_2(CO)_9$] in benzene or with [$Fe_3(CO)_{12}$] in toluene to give a mixture of (4) and (5) whereas, with [$Fe_3(CO)_{12}$] in xylene, (4) and (6) are formed [42]. (7) and [$(cp)Fe(CO)_2I$] give (8), which on heating in xylene gives (9) and (10) [43]. Other phosphole, arsole and stibole (L) complexes [$(cp)Fe(CO)_2L$] have also been isolated [44].



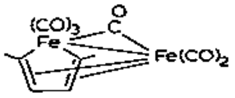
(3)



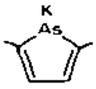
(4)



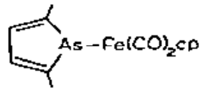
(5)



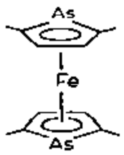
(6)



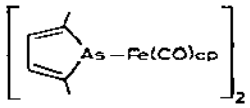
(7)



(8)



(9)



(10)

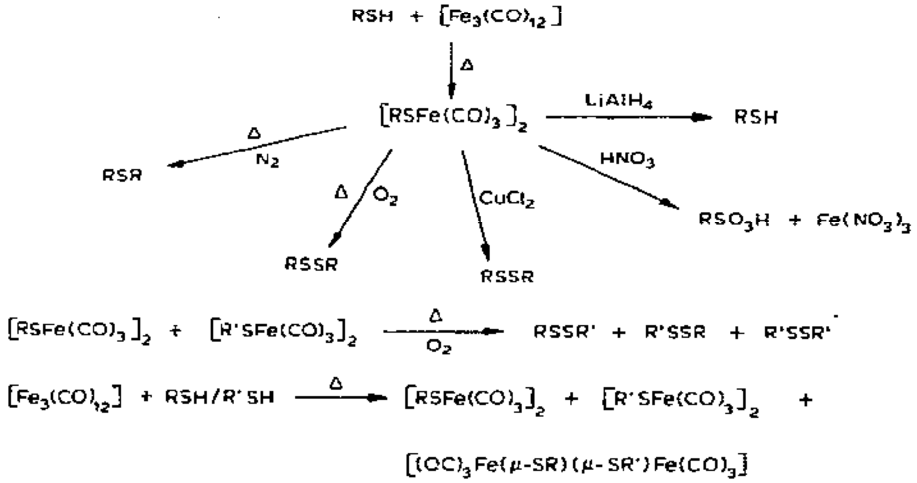
Reactions of various P-, As- and Sb-containing ligands with [$Fe_3(CO)_{12}$] under mild conditions have been investigated. [$Fe_3(CO)_{11}L$], [$Fe_3(CO)_{10}L_2$] and [$Fe_3(CO)_9\{P(OR)_3\}_3$] were formed, as well as [$Fe(CO)_4L$] and [$Fe(CO)_3L_2$]. Cluster breakdown is greatest with phosphines and least with phosphites. Only [$Fe_3(CO)_9\{P(OR)_3\}_3$] (R = Me_2CH, cych and perhaps Et, 2-MeC_6H_4 or 4-MeC_6H_4) exist solely in the non-bridged form in the solid state as well as in solution. The remainder exist as CO bridge isomers in the solid, and isomerise to a mixture of bridged and non-bridged forms in solution [45]. [$(cp)Fe(CO)(I)LFe(cp)$] {L = $(Ph_2PCH_2CH_2)_3N$ or $(Ph_2PCH_2CH_2)_3P$} have been prepared and a structural study of the former shows the {$(cp)Fe(CO)I$} unit to be *P*-bound only, whereas the {$(cp)Fe$} unit is *NP*$_2$-coordinated [46].

[$S_2Fe_2(CO)_6$] reacts with $HGeCl_3 \cdot 2\,Et_2O$ or $HMCl_3 \cdot Et_3N$ (M = Ge, Si) to give [$(Cl_2Ge)S_2Fe_2(CO)_6$] or [$M\{S_2Fe_2(CO)_6\}$], respectively. The germanium and silicon atoms are bonded to the two bridging sulphur atoms of each {$Fe_2(CO)_6S_2$} unit [47].

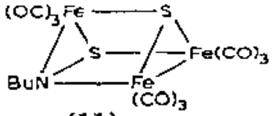
Treatment of [$Fe_2(CO)_6X_2$] (X = S or Se) with phosphine ligands (L) gives [$Fe_2(CO)_5L(X)_2$], [$Fe_2(CO)_4L_2(X)_2$] and [$Fe_3(CO)_{9-x}(S)_2$] (x = 0, 1 or 2); the proposed mechanism of the reactions implies an initial formation of [$Fe_2(CO)_6L(X)_2$] [48]. Reaction of [$Fe_2(CO)_6S_2$] with MH (M = Na or K) gives [$Fe_2(CO)_6S_2$]$^-$, which reacts with alkyl iodide to form [$Fe_2(CO)_6(SR)_2$] and with [$SnMe_2$] to form [$Fe_2(CO)_6S_2SnMe_2$], which possesses an analogous structure to the $GeCl_2$ and $SiCl_2$ adducts above. However, use of alkyl lithium compounds produces the new anions [$Fe_2(CO)_6(\mu\text{-}S)(\mu\text{-}SR)$]$^-$ [49]. Electrochemical reduction of [$Fe_2(CO)_{6-n}L_nXY$] (X = Y = SR or PR_2; X = SR, Y =

PR_2; L = PR_3) proceeds via two irreversible processes. Chemical oxidation of the complexes did not lead to the isolation of dications but to formation of $[\{Fe(PMe_2)(CO)_3\}_2Ag][NO_3]$, $[Fe(SMe)(CO)_2(PMe_3)]_2[NO_3]_2$ and $[\{Fe(SMe)(CO)_2(PMe_3)\}_2F][PF_6]$ [50]. SO_2 acts as a Lewis acid towards the Fe—Fe bond in $[(\mu\text{-}SMe)Fe(CO)_2L]_2$ (L = PMe_3 or PMe_2PH) and yields the insertion product, $[\{(\mu\text{-}SMe)Fe(CO)_2L\}_2SO_2]$ which, on treatment with dioxygen, gives the sulphate-bridged analogue [51]. $[(CH_2S_2)Fe_2(CO)_6]$ has been prepared and a structural study shows it to have a shorter iron—iron bond than is usual in such complexes [52]. $[(cp)Fe(CO)_2(SC_6H_4SMe)]$ and $[\{(cp)Fe(CO)_2\}_2S_2C_6H_4]$ have also been reported [53]. Some further reactions of $[RSFe(CO)_3]_2$ complexes are outlined in Scheme I [54].

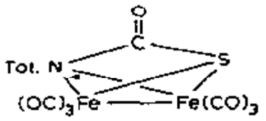
Scheme I



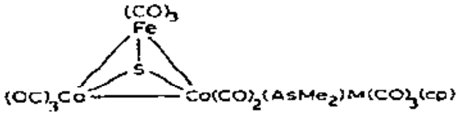
Reaction of $[Fe_2(CO)_9]$ with RN=S=NR (R = CMe_3 or 4-tolyl) leads to breakdown of the dimidosulphur ligand giving rise to **(11)** and **(12)**, respectively, the structures of which were established by X-ray crystallography [55]. XPES studies have been directed towards establishing the nature of the metal—metal bonds in $[Fe_2(CO)_6S_2]$, $[Fe_3(CO)_9S_2]$, $[Fe_2(CO)_6B_2H_6]$ and $[Fe_2(CO)_6\{SNCMe_3\}]$ [56]. **(13)** undergoes elimination of a $\{Co(CO)_4AsMe_2\}$ unit to form the chiral cluster **(14)** [57].



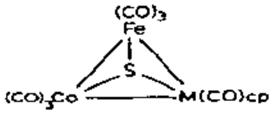
(11)



(12)



(13) (M = Cr, Mo or W)



(14) (M = Cr, Mo or W)

Treatment of $[Fe(\eta^2\text{-}CS_2)(CO)_2L_2]$ (L = PPh_3, PMe_2Ph or 3,4-dimethyl-1-phenylphosphole) with CF_3CO_2H gives $[Fe\{OC(O)CF_3\}(CO)_2L_2]$, which undergoes oxidation with $[NO][PF_6]$ to $[Fe\{OC(O)CF_3\}(NCMe)(CO)_2L_2][PF_6]$ [58]. $[(cp)Fe(CO)_2(H_2O)]^+$ reacts with $Na[S(O)_2OR]$ (R = Me or Et) to yield $[(cp)Fe(CO)_2S(O)_2OR]$, which on hydrolysis gives the strong acid $[(cp)Fe(CO)_2S(O)_2OH]$ [59].

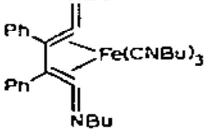
Other studies involving iron carbonyl compounds are summarised in Table 1.

1.2 NITROSYLS

Treatment of $[Fe(\eta^2\text{-}CS_2)(CO)_2(L)(L')]$ (L = L' = PPh_3 or PMe_3; L = PPh_3, L' = PMe_3 or PMe_2Ph) with $[NO][PF_6]$ yields $[Fe(CO)_2(L)(L')(NO)][PF_6]$ [60a]. $[Fe(NO)_2(dtp)_2]$ (dtp = di-isopropyl- or di-cyclohexyldithiophosphate) have been prepared and studied by EPR spectroscopy [60b]. The replacement of the carbonyl groups in $[Fe(CO)_2(NO)_2]$ by chelating ligands involves initial rate-determining unidentate coordination of the ligand, followed by rapid ring closure [61]. $[Fe(tmc)(NCMe)][BF_4]_2$ (tmc = tetramethylcyclam) reacts with NO in $MeNO_2$ or $[NO][BF_4]$ in MeCN to give the paramagnetic $[Fe(tmc)NO][BF_4]_2$ or the diamagnetic $[Fe(tmc)(NO)(OH)][BF_4]_2 \cdot MeCN$, respectively; the hydroxyl group in the latter complex appears to arise from a wet solvent. The former complex shows an $S = \frac{3}{2} \rightleftharpoons S = \frac{1}{2}$ spin equilibrium, and a structural study on the perchlorate analogue shows a distorted tetragonal pyramidal coordination, with NO in the axial position ($Fe\hat{N}O$ = 177.5°); the latter is six-coordinate with NO and OH ligands in axial positions ($Fe\hat{N}O$ = 178.3°) [62]. [Fe(*SS*)(*NN*)(NO)] complexes (*SS* = maleonitrile dithiol, *NN* = Schiff base from biacetyl and $PhNH_2$, 4-toluidine, 4-anisidine, 4-chloroaniline) have been prepared [63]. The structure of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, has been redetermined; the iron atom is displaced from the $(CN)_4$ plane by 0.183 Å towards the nitrosyl group and no significant differences were observed between Fe—C(*trans*) and Fe—C(*cis*) distances (1.918 and 1.929 Å, respectively) in contrast to other $[M(CN)_5NO]^{n-}$ ions where M—C(*trans*) is longer than M—C(*cis*). The $Fe\hat{N}O$ angle is 175.7° [64]. A study of $[^{14}CN]^-$ exchange with $[Fe(CN)_5NO]^{n-}$ (n = 1, 2 or 3) and $[Fe(CN)_5NOH]^{2-}$ has been reported [65].

1.3 IRON(0)

UV irradiation of $[Fe(CNEt)_5]$ in diethyl ether gives a 60% yield of $[Fe_2(CNEt)_9]$; $[Fe(CNCMe_3)_5]$ reacts with PhC≡CPh to give (15). The crystal



(15)

TABLE 1

Miscellaneous iron carbonyl complexes

Compound	Comments	Ref.
cis-$[\{(cp)Fe(CO)\}_2(\mu\text{-}CO)(\mu\text{-}CS)]$	X-ray structure, revealing an Fe—Fe bond length intermediate between the analogous $(\mu\text{-}CO)_2$ and $(\mu\text{-}CS)_2$ complexes	a
$[(C_5H_4R)_2Fe_2(CO)_{4-n}(CNR')_n]$	IR study of interaction with phenols	b
$[Fe_2(CO)_8\{InMn(CO)_5\}_2]$	X-ray structure, revealing a 4-membered Fe_2In_2 ring, with no Fe—Fe bond	c
$[(OC)_4Fe(GeH_2Me)_2]$	Halogenation of the germyl groups was reported	d
$[(OC)_4Fe(GeH_3)(Ge_2H_5)]$	Preparation from $[(OC)_4Fe(Ge_2H_5)_2]$	e
$[(cp)Fe(CO)_2NH_3]^+$	Reaction with R_2CO to yield a coordinated $-N{=}CR_2$ group	f
$[($*cis*-diazine$)Fe_3(CO)_9]$	Fluxional behaviour of the diazine ligand was observed	g
$[Fe(CO)_4L]\{L = PPh_2CH_2CN$ or $PPh_2(CH_2CO_2Et)\}$	Preparation described	h
$[Fe(CO)_3L_2]$ and $[Fe(CO)_4L]$ $\{L = P(NMeCH_2)_3CMe$ or $As(NMeCH_2)_3CMe\}$	Preparation described	i
$[Fe_2(CO)_7L_2]$ and $[Fe(CO)_3L_2]$ $\{L = (CMe_3NPCl)_2\}$	L chelates, bonding via both P atoms	j
$[\{(Me_2N)_3P\}_2Fe(CO)_3]$	X-ray structure, revealing a trigonal—bipyramidal structure, with axial phosphoramide ligands	k
$[(cp)Fe(CO)\{(PPh_2)_2CH_2\}][BPh_4]$	X-ray structure reported	l
$[(cp)_2Fe_2(CO)_n\{\mu\text{-}PN_3(PF_2)_2\}$ $(n = 5$ or $6)$	Prepared from $[(cp)Fe(CO)_2]^-$ and $(PF_2N)_3$ $(n = 6)$ or by decarbonylation $(n = 5)$	m
$[(cp)Fe(CO)_2\{P(CF_3)_2\}]$	Prepared from $[(cp)_2Fe_2(CO)_4]$ and $[P(CF_3)_2\{O(CH_2)_2Cl\}]$	n
$[(OC)_2(PPh_3)Mn(C_5H_4)Fe(CO)(cp)(PPh_3)]$ and $[(OC)_2(PPh_3)Mn(C_5H_4)(CO)Fe(CO)(cp)(PPh_3)]$	Preparations described	o
$[(LL')Fe_2(CO)_6]$ $\{LL' = CPh{=}CPhS$ or $C_6H_4CH_2NR$ (R = Me or Ph)$\}$	Fluxional behaviour studied	p
$[(CPh{=}CPhS)Fe_2(CO)_5]$	X-ray structure reported	p

(a) D.E. Beckman, Report 1979, IS-T-843 (Chem. Abstr., 91 (1979) 100213). (b) S. Willis and A.R. Manning, J. Chem. Res., (S), (1978) 390. (c) H. Preut and H.J. Haupt, Acta Crystallogr., B35 (1979) 2191. (d) A. Bonny and K.M. Mackay, J. Chem. Soc., Dalton Trans., (1978) 1569. (e) F.S. Wong and K.M. Mackay, Inorg. Chim. Acta, 32 (1979) L21. (f) D. Sellmann and E. Thallmair, J. Organomet. Chem., 164 (1978) 337. (g) P. Mastropasaqua, P. Lahuerta, K. Hildenbrand and H. Kisch, J. Organomet. Chem., 172 (1979) 57. (h) P. Braunstein, D. Matt, F. Mathey and D. Thavard, J. Chem. Res. (S), (1978) 232. (i) R.D. Kroshefsky, J.K. Verkode and J.R. Pipal, Phosphorus Sulphur, 6 (1979) 377. (j) L.S. Jenkins and G.R. Willey, J. Chem. Soc., Dalton Trans., (1979) 777. (k) A.H.

structures of both products have been determined [66]. Sodium-amalgam reduction of $[FeCl_2(PR_3)_x]$ (x = 2 or 3) in the presence of excess PR_3 (PR_3 = trimethylphosphine or trimethylphosphite) yields $[Fe\{P(OMe)_3\}_5]$ or $[HFe(CH_2PMe_2)(PMe_3)_3]$ [67]. Co-condensation of Me_2NPF_2 (L′) with iron atoms gives $[FeL'_5]$ and similar reaction of $MeN(PF_2)_2$ (L″) gives $[FeL''_4]$. Condensation of L′ and L″ (4 : 1) with Fe yields $[FeL'_3L'']$ [68].

1.4 IRON(II)

1.4.1 Halides

$[RPCl_3][FeCl_4]$ and $[RPCl_2Ph][FeCl_4]$ (R = Bu, amyl, C_6H_{11} or Ph_3C) have been prepared [69]. The structures of $[MeNH_3]_4[FeCl_6] \cdot H_2O$ [70], $RbFeCl_3 \cdot 2\,D_2O$ and $CsFeCl_3 \cdot 2\,D_2O$ [71] have been reported. A Mössbauer study of $Fe^{III}M^{II}F_5 \cdot 7\,H_2O$ (M = Zn, Co or Fe) and $AlFeF_5 \cdot 7\,H_2O$ shows these compounds to be isostructural, as are their corresponding dihydrates. It was suggested that the heptahydrate exhibits discrete octahedral coordination, whereas that in the dihydrate is face-shared octahedral [72]. When aqueous $FeBr_2$ is treated with MgO, dihydrogen, $MgBr_2$ and green rust, $[Fe(OH)_2]_x[FeO(OH)]_yFeOBr$ are formed [73].

1.4.2 Cyanides

The syntheses of $M_2[Fe(CN)_6]$ (M = Co, Cu or Cd), $Cd_2Fe(CN)_4$ and $M_nZn[Fe(CN)_6]$ (M = Co, n = 1; M = Na, Cu or H, n = 2) have been reported. [74]. Diantipyrylmethane (L) and $H_n[Fe(CN)_6]$ (n = 3 or 4) form $[HL]_2H[Fe(CN)_6]$ and $[HL]_2H_2[Fe(CN)_6]\ 3\,H_2O$, whereas reaction with $H_2[Fe(CN)_5NO]$ yields $[HL]_2[Fe(CN)_5NO]$. Heating the hexacyano-complexes leads to $Fe_2[Fe(CN)_6]$, while heating the nitroprusside gives $Fe[Fe(CN)_6]$ [75]. Structural studies on $KCe[Fe(CN)_6] \cdot 4\,H_2O$ [76], $[NH_4]_4[Fe(CN)_6] \cdot 1.5\,H_2O$ [77] and $Co[Fe(CN)_6]$ [78] have been reported. The redox potential of the $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ couple has been determined in a range of non-aqueous solvents [79].

$Fe[Fe(CN)_5X] \cdot x\,H_2O$ (X = H_2O, NH_3 or CO) have been prepared and con-

---

References to Table 1 (continued)

Cowley, R.E. Davis, M. Lattman, M. McKee and K. Remadna, J. Am. Chem. Soc., 101 (1979) 5090. (l) R.B. English and M.M. De V. Steyn, Acta Crystallogr., B35 (1979) 954. (m) P.P. Greiggen and H.R. Allcock, J. Am. Chem. Soc., 101 (1979) 2492. (n) W. Clegg and S. Morton, J. Chem. Soc., Dalton Trans., (1978) 1452. (o) A.N. Nesmeyanov, E.G. Perevalova, L.I. Leont'eva and E.V. Schumilina, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2813 (Chem. Abstr., 90 (1979) 137965). (p) J.P. Hickey, J.C. Huffman and L.J. Todd, Inorg. Chim. Acta, 28 (1978) 77.

tain low spin Fe^{II}—C and high spin Fe^{III}—N centres [80]. $[Fe(CN)_5L]^{3-}$ (L = 3- or 4-cyanopyridine) have also been reported [81], as have the 3-substituted-pyridine analogues [82], and oxidation of these complexes has been studied [82,83]. $[Fe(CN)_5NO_2]^{2-}$ reacts with excess $(CH_2)_n(CH_2NH_2)_2$ (n = 1—4) (L) to form $[Fe(CN)_5HL]^{2-}$ [84]. $[Fe(CN)_5H_2O]^{3-}$ reacts with $[M(NH_3)_5L]^{2+}$ to give $Na[(NC)_5FeLM(NH_3)_5]$ (L = 4,4′-bipy or pyrazine) [85]. A mechanistic study of the oxidation of ethanol by Fenton's reagent is consistent with a radical chain mechanism involving short chains [86].

1.4.3 *N-bonded ligands*

Structural studies on $[Fe(2\text{-picoline})_6]Cl_2 \cdot EtOH$, in the high spin state at 298 and 150 K and in the low spin state at 90 K, show Fe—N distances reduce from 2.195 to 2.013 Å upon spin pairing [87]. A study has been made in an effort to discover the relationship between spin state and structure in $[Fe(2\text{-pa})_3]Cl_2 \cdot$ solvent (2-pa = 2-picolylamine). The dihydrate is low spin at room temperature and below, whereas the mono-methanolate is high spin at room temperature and becomes low spin between 100 and 200 K. The former has *fac* geometry, whereas the latter has the *mer* configuration, the difference being attributed to hydrogen bonding which occurs only in the hydrate. The mean Fe—N difference between the solvates is 0.192 Å. $[Fe(2\text{-pa})_3]X_2 \cdot S$ (X = Br, S = MeOH or EtOH; X = Cl, S = EtOH) also adopt the *mer* configuration and exhibit spin transitions [88]. A structural study on the intermediate spin complex, $[Fe(phen)_3]I_2 \cdot 2\,H_2O$ has been reported [89]. $[Fe(phen)_2(ox)] \cdot 5\,H_2O$ also shows a spin equilibrium whereas the corresponding monohydrate is high spin, as is $[Fe(phen)_2(malonate)] \cdot 2\,H_2O$ [90]. Contrary to previous studies, variable temperature Mössbauer spectra of $[Fe(2,9\text{-}Me_2phen)_2(NCS)_2]$ between 1.8 and 300 K show the complex to be high spin at all temperatures [91].

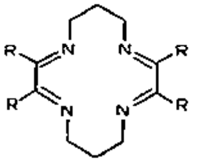
A study of the mechanism of $[OH]^-$ attack on $[Fe(phen)_3]^{2+}$ is consistent with a mechanism in which $[OH]^-$ initially attacks the 2(9)-position of the coordinated ligand, and indicates considerable C—OH ··· Fe interaction [92]. The reactions of $[OH]^-$ with $[FeL_3]^{2+}$ (L = bipy, 4,7-Me_2phen, 5-Brphen or related ligands) complexes [93], and $[Fe(2,2'\text{-bipyrimidine})_3]^{2+}$ with $[OH]^-$ $[N_3]^-$ and $[SCN]^-$ [94] have also been studied. In a similar investigation of the reaction between $[CN]^-$ and $[FeL_3]^{2+}$ (L = phen, 5-Clphen, 5-NO_2phen or bipy), $[Fe(LCN)_2L]$ was isolated and shown to be an intermediate in the substitution reaction [95]. On exposure of solid $[(6,6'\text{-dihydrazino-}2,2'\text{-bipy})FeCl_2]$ to dioxygen, quantitative transformation to a variety of iron(II) polypyridine complexes occurs, with evolution of N_2 [96].

A Mössbauer study of $[FeCl_2L_2]$ (L = 2- or 3-pyCR′=NR″; R′ = H, Me or Ph; R″ = Ph, C_6H_4Me or C_6H_4Cl) showed that the 2-pyridyl complexes changed from high spin to intermediate spin when R′ changed from H to Me or Ph, whereas changes in R″ had no effect on the spin state. The 3-pyridyl complexes are all high spin [97]. $[Fe(2,4,6\text{-tri-}(2\text{-pyridyl})\text{-}1,3,5\text{-triazine})_2]^{2+}$

undergoes two reactions with water over long periods. The first is the well known dissociative process, and the second is another example of reaction at the coordinated ligand [98].

1-Benzyl-2-phenylbenzimidazole (bpbi) and 2-coumarinylbenzimidazole (cbi) form the complexes $[FeL_2X_2]$ (L = bpbi or cbi; X = Cl, Br, I or NCS) and $[Fe(cbi)_3][ClO_4]_2$. Infrared data suggest N(3)-coordination of bpbi and N(3) and CO coordination of cbi. The perchlorate has regular octahedral coordination, whereas that of the I and NCS complexes is *pseudo*-octahedral and that of the Br and Cl complexes is distorted octahedral with bridging halide ions [99]. The high spin complexes $[Fe(HL)_2X_2] \cdot H_2O$ (HL = 2-hydroxymethylbenzimidazole; X = Cl or Br) have been reported [100].

A study has been made of the variation of half-wave oxidation potential with the properties of substituents on the ligands in the complexes $[Fe(tim)(MeCN)_2][PF_6]_2$ {tim = (**16**)}. A linear relationship with σ_p values of the substituents was established [101]. Photochemical behaviour of the complexes $[Fe(tim)(NCS)_2]$, $[Fe(tim)(imid)_2]^{2+}$ and $[Fe(tim)(MeCN)(CO)]^{2+}$ {tim = (**16**, R = Me)} has been studied by laser and flash photolysis. Rapid substitution reactions and metastable products were observed [102]. A kinetic study of axial ligand exchange in the complexes $[Fe(tim)L_2]$ and $[Fe(tim)L(MeCN)]$ {tim = (**16**, R = Me); L = imidazole or methylimidazole} has been interpreted in terms of σ and π bonding effects and the hole size of the macrocyclic ligand [103].



(**16**) (R = Pn, 4-MeC_6H_4, 4-$MeOC_6H_4$ or Me; R_4 = Me_2Pn_2)

$[(FePc)_2(O_2)]$ (PcH_2 = phthalocyanine) has been obtained from [FePc] and O_2 in dmso [104]. A similar reaction in concentrated H_2SO_4 has been studied kinetically; [FePc], presumably tetraprotonated, reversibly forms $[FePc(O_2)]$ and this is followed by formation of the unstable compound $[FePc(O_2)_2]$ [105]. XPES and EPR studies on monomeric, dimeric and polymeric forms of [FePc] have been related to the catalytic activity of the compound in the electrochemical reduction of O_2 [106].

Treatment of $[NH_4]_2[Fe(H_2O)_6][SO_4]_2$ with hydrazine hydrate in air gives $[N_2H_5][Fe(N_2H_3CO_2)_3] \cdot H_2O$ via the intermediates, $[N_2H_5]_2Fe(SO_4)_2 \cdot 3\,N_2H_4$, $[N_2H_5]_2Fe(OH)_4 \cdot (N_2H_4)_2$, $[Fe(N_2H_3CO_2)_2(N_2H_4)_2]$ and $[N_2H_5][Fe(N_2H_3CO_2)_3]$ [107]. Reaction of FeX_3 (X = Cl, Br or I) with N_2H_4, NH_2NHMe or NH_2NMe_2 (L) leads to reduction to Fe(II) and formation of polymeric FeL_2X_2 [108]. The *N*-(2-picolidene)-1-naphthylamine (L′) complex $FeL'_{1.5}(SCN)_2$ has been reported [109].

The complexes, $[Cu(imep)]^+$ and $[Cu(bidH)]^+$ (imepH = 2-(2-imidazol-4-

yl-ethylimino)methylpyridine, bidH$_2$ = 2,3-bis(2-imidazol-4-yl-ethylimino)-butane) form imidazolyl bridged complexes with [Fe(tim)(MeCN)$_2$]$^{2+}$ {tim = (**16**)} and these have been discussed in terms of the Palmer model for heme-a$_3$-Cu(β) interaction in cytochrome oxidase [110]. *Trans*-[PdX{C(NR)-CMe(NR)}L$_2$] (X = Cl or Br; R = 4-anisyl or cych; L = PPh$_3$ or PMePh$_2$) and *cis*-[PdCl{C(NR)CMe(NR)}L′] (R = 4-anisyl; L′ = dppe) from 1 : 1 adducts with FeX$_2$ which contain tetrahedrally coordinated iron [111]. FeCl$_2$ · *x* H$_2$O reacts with K$_2$[Hg(SeCN)$_4$] to form Hg(SeCN)$_4$Fe [112].

1.4.4 O-bonded ligands

Fe(SO$_3$F)$_2$ has been prepared and is thought to contain tridentate [SO$_3$F]$^-$ ligands; the octahedral derivatives [Fe(SO$_3$F)$_2$L$_n$] (L = py or en, *n* = 2; L = PPh$_3$ or 4-ClC$_6$H$_4$NH$_4$, *n* = 1) have also been isolated [113]. The complexes, [FeL$_n$X$_2$] (L = urea, thiourea, diisopropylthiourea, dimethylthiourea, 2-(1H)-tetrahydropyrimidone or 2-imidazolidinone; *n* = 3, 4 or 6, X = Cl, Br or I; *n* = 2, X = SCN) have been prepared; all are octahedral and some are polymeric. Tetrahedral [FeL$_2$X$_2$] (X = Cl, Br or I) have also been isolated [114].

Fe(β-dik)$_2$ (β-dik = acac, benzac or dibenzoylmethane) react with thiourea, phenylthiourea, MeCSNH$_2$ and PhCSNH$_2$ (L) to form [Fe(β-dik)$_2$L$_n$] (*n* = 1 or 2) [115]. [FeX$_2$LL′] and [FeX$_2$L$_2$] (X = py or substituted-py; L = dmg or α-benzildioximate; L′ = C$_6$H$_{11}$NC, CH$_3$C$_6$H$_4$NC) have also been reported [116]. The reaction of FeCl$_2$, the dioximes acac-dioxime and 1,2-diphenylethane-1,2-dionedioxime (LH), and H$_3$BO$_3$ in alcohols yield the alkoxyboron bridged encapsulated complexes, [FeL$_3$(BX)$_2$] (X = OH, OMe, OEt, OCMe$_2$H or OBu) [117]. 2,5-Dihydroxy-1,4-benzoquinone and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (L) form the iron(II) complexes [FeL(H$_2$O)$_2$]$_n$ and [FeL(pyrazine)]$_n$ [118].

There has been much interest in amine-*N*-oxide complexes and these are summarised in Table 2. Similar interest in phosphinate complexes is summarised in Table 3.

TABLE 2

Some amine-*N*-oxide complexes of iron(II)

Complexes	Ref.
[Fe(Et$_3$NO)$_2$X$_2$](X = Cl, Br or I)	119
[FeL$_4$(OClO$_3$)] [ClO$_4$] (L = 3-methylisoquinoline-*N*-oxide)	120
[FeL$_3$(ClO$_4$)$_2$] · 6 H$_2$O (L = quinoxaline-1,4-dioxide)	121
[FeL$_3$(OH$_2$)$_2$(OClO$_3$)]ClO$_4$, [(H$_2$O)$_4$LFeLFeL(OH$_2$)$_4$][ClO$_4$]$_4$ · 16 H$_2$O (L = phenazine-5,10-dioxide)	122
FeL$_2$ · 6 H$_2$O, FeL$_2$ · 0.5 H$_2$O (L = isonicotinate-*N*-oxide)	123
[FeL(LH)$_2$(OH$_2$)$_2$][ClO$_4$] 2 H$_2$O (LH = picolinic acid-*N*-oxide)	124

TABLE 3

Some phosphinate complexes of iron(II)

Complexes	Ref.
$[(O_3ClO)(H_2O)_2LFe(L)_2FeL(OH_2)_2(OClO_3)][ClO_4]_2$ {L = MePh(MeO)PO}	125
$[L_3Fe(L)_2FeL_3][ClO_4]_4$, $[Cl_2LFe(L)_2FeLCl_2]$ {L = $(4\text{-}CH_3C_6H_4O)_3PO$}	126
$[FeL_3][ClO_4]_2 \cdot H_2O$ {L = $(MeCO_2)(EtO)_2PO$}	127
$NaFeL \cdot 9\,H_2O$, $K_4FeL_2 \cdot 5\,H_2O$ (L = trimetaphosphinate)	128

1.4.5 S- and P-bonded ligands

Treatment of $[Fe(SPh)_4]^{2-}$ with $[(PhCH_2)_2S_3]$ or trithiothreitol gives $[Fe_2S_2(SPh)_4]^{2-}$ or $[Fe_2S_{12}]^{2-}$, respectively. The centrosymmetric $[Fe_2S_{12}]^{2-}$ anion consists of a rectangular Fe_2S_2 core {average r(Fe—S) = 2.192, r(Fe—Fe) = 2.701 Å}, with the remaining two coordination sites on the tetrahedral iron atoms being occupied by $[S_5]^{2-}$ ions {r(Fe—S) = 2.320} [129]. $Fe(chxn)_2$ (chxn = cyclohexylxanthate) has been prepared and Mössbauer data show it to contain two iron(II) sites, presumably in a polymeric structure. The derivatives, *trans*-$[Fe(chxn)_2L_2]$ (L = MeOH, EtOH or py), *cis*-$[Fe(chxn)_2(phen)]$ and $[Fe(chxn)_3]^-$ have also been isolated [130].

The cationic complexes $[Fe\{P(OR)_3\}_5X]^+$ have been prepared by the oxidation of $[Fe\{P(OR)_3\}_5]$ (X = H, Me or CF_3) or by addition of $P(OR)_3$ to $[Fe(thf)_2X_2]$ (X = Cl, Br or I); the latter reactions proceed under different conditions through two distinctly different isolable intermediates, both of formula $[Fe\{P(OR)_3\}_3X_2]$ [131]. $[FeLCl_2]_n$ {L = 1,3-$(Me_2PCH_2)_2C_6H_4$} and $[FeLL'Cl_2]$ (L′ = $Ph_2PCH_2CH_2PPh_2$) have been isolated; the latter is converted by sodium amalgam to [FeH(L—H)L′] [132]. *Trans*$[FeH(SiR_3)L_2]$ and *trans*-$Fe(SiR_3)_2L_2$ {R_3 = $(OEt)_3$, Cl_3 or $MeCl_2$; L = dppe} have been prepared [133]. Irradiation of $[(cp)Fe(CO)_2Br]$ and dppe in MeCN gives [cpFe(dppe)(NCMe)]Br in good yield; the MeCN molecule is easily displaced to give [(cp)Fe(dppe)X] (X = CN, SCN, SPh, I, Br, Me or H) [134].

1.4.6 Mixed donor ligands

The uridine and thymine complexes, $[FeLX_2]$ (X = Cl or Br) have been prepared; uridine binds through CO with chelation via the ribose residue and thymidine binds through the deoxyribose residue [135]. The ATP complex, $Na_2Fe(ATP) \cdot 2\,H_2O$, has been isolated and contains *pseudo*-tetrahedral coordination at the iron(II) [136]. Complexes of 1,4-di(4-methyl-3-sulphoanilino)-anthraquinone (alizarin cyanine green) and 1-amino-2-bromo-4-(2-sulpho-4-methylanilino)anthraquinone (alizarine pure blue B), FeL_2, have been isolated. The ligands are bonded via the α-amino *N* atom and the O atom of the neighbouring CO group [137a]. Iron(II) complexes of Schiff bases, derived from pyridine-2-carbaldehyde, phenyl-2-pyridylketone, 2-pyridylketone, pyridine-2,6-carbaldehyde or 2,6-diacetylpyridine and a range of amines, have been prepared and the kinetics of aquation and cyanide attack studied [137b]. Electrochemical reduction of [Fe_2(salen)$_2$O] proceeds via sequential steps to a stable Fe^{III}—Fe^{II} dimer and an unstable Fe^{II}—Fe^{II} dimer; the intermediate dimer also undergoes further dimerisation to a tetramer, which then undergoes further reduction leading to consumption of 1.5 electrons and 2 electrons per Fe_2 unit. The authors suggest that these results reflect a strong interaction between the metal centres in Fe—O—Fe that is not apparent in other physical studies [138]. [MFe(aapen)Cl] (M = Ni, Cu; aapen = Schiff base derived from 2-acetoacetylphenol and en) [139] and [CoFe(fsapn)(py)$_3$] (fsapnH_4 = *NN'*-bis(3-carboxysalicylidene)-1,2-diaminoethane) [140] have been reported. The characterisation of other iron(II) Schiff base and related complexes is summarised in Table 4 and a selection of other studies involving iron(II) complexes are cited in Table 5.

TABLE 4

Some Schiff base and related ligand complexes of iron(II)

Complex	Ref.
[FeL] (LH_2 = 2 HO-$C_6H_4CH{=}NC_6H_3$-3 OH-4 CO_2H, 4 HO-$C_6H_4CH{=}NC_6H_3$-3 OH-4 CO_2H or 3 $MeOC_6H_4CH{=}NC_6H_3$-3 OH-4 CO_2H)	141
[Fe(HL)$_2$py$_2$] (H_2L = $PhCH{=}NNHCOC_6H_4$-2 OH or $MeOC_6H_4CH{=}NNHCOC_6H_4$-2 OH)	142
[FeL_2] (LH = *N*-salicylideneaminoquanidine or *N*-salicylidenenitroaminoquanidine)	143
[FeL] (H_2L = *N*-salicylidene-5-hydrazo-1 H-tetrazole)	143
[Fe(hmpx)$_2X_2$] (hmpx = 6-methyl-pyridine-2-aldoxime; X = Cl, Br or I)	144
[FeL_2Cl]$_2$ (LH = salicylideneanisidines)	145
[$FeLX_2$] (L = $R'CMe{=}NNHCOR$; R = Ph, 2-thienyl or Me; R$'$ = 2-pyridyl; X = Cl, Br or NCS)	146
[FeL_2] (LH = $RCH{=}NC_6H_4$-2-SO_3H or $RCH{=}NCH_2CH_2SO_3H$; R = 2-furanyl)	147
[Fe(LH)$_4Cl_2$], $FeL_2 \cdot x\ H_2O$ (LH = $C_6H_4(OH)CH{=}NNH_2$)	148
[$FeLCl_2$] · 2 EtOH (L = picolinoylhydrazone)	149
[Fe(H_2L)Cl_2], [FeL(H_2O)$_2$] (H_2L = succinyldiacetonehydrazone)	150
[$FeLCl_2$] (L = 2-hydroxyl-1-naphthalidene-*N*-methyl-*S*-methyl-benzyldithiocarbazate)	151
[Fe(H_2L)Cl_2] · H_2O, [FeL(H_2O)$_2$] (LH_2 = oxalyldihydrazone)	152
[FeL]$^+$ (H_2L = 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime)	153a
Na[FeL_3] · H_2O (HL = $PhN{=}NCR{=}NOH$ (R = Me, Pr, Ph or 4-MeC_6H_4))	153b

TABLE 5

A selection of studies on some iron(II) complexes

Compound	Comments	Ref.
$[FeL_2(NCS)_2]$ (L = range of substituted phen ligands)	Magnetic study	a
$[Fe(bipy)_3]X_2$	Thermochemistry	b
$[FeL_3]^{2+}$ (L = a range of substituted bipy ligands)	Electrochemistry	c
$[Fe(bipy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$	Kinetics of $[OH]^-$, $[CN]^-$, Cl^-, Br^- or I^- attack	d
$[FeL_6]SO_4$ (L = 2-amino-5-phenyl-1,3,4-oxadiazole)	Preparation and IR spectra described	e
$[Fe(biimidazole\text{-}H)]_2$	Preparation described	f
$[Fe(C_{14}H_{24}N_4)(MeCN)_2][PF_6]_2$	X-ray structure, revealing a *pseudo*-octahedral environment for Fe(II)	g
$[FePc(4\ Mepy)_2] \cdot 0.5(4\text{-}Mepy)$	X-ray structure, revealing a *pseudo*-octahedral environment for Fe(II)	h
$[FePcL_2]$ (L = imidazole or $4\text{-}NH_2py$)	Kinetics of substitution	i
[Fe(sulphophthalocyanine)]	Photochemistry	j
[FePc]	Mössbauer study	k
$[Fe(thf)_6][SbCl_6]_2$	Preparation described	l
$FeI_2 \cdot 2$ thf	Preparation described	m
$[Fe(CF_3CO_2)_2]$	Electrochemical preparation	n
Fe(ox)	Mössbauer study	o
Fe(II)-oxalate, squarate or dihydroxybenzoquinone complexes	Magnetic study	p
$Fe(formate)_2 \cdot 2\ H_2O$	Thermal decomposition	q
$[Fe^{II}Fe^{III}O(H_3L)L]\ 3\ H_2O$ (H_4L = ascorbic acid)	Preparation described	r
Fe(II)-1,2-cyclohexanedione dioxime complexes	Preparation described	s
$Fe(II)/O_2$ reaction	Kinetic study	t
$Fe(II)/H_2O_2$ reaction	Kinetic study	u
[Fe(tetrathiafulvalene-tetrathiolate)]	Preparation described	v
$[FeHX(dppe)_2]$ and $[FeHL(dppe)]X$	Mössbauer and IR studies	w
$[Fe(9\text{-}methyladenine)X_2]$	Preparation described	x
$[Fe(1\text{-}sparteine)X_2]$	Preparation described	y
$[FeLCl_2] \cdot n\ H_2O$ (L = 2-benzoylpyridine, *n* = 2 or 6)	Preparations described	z
$[FeL_2Cl_2]$ (L = 2-carbethoxypyridine)	Preparation described	aa

TABLE 5 (continued)

Compound	Comments	Ref.
[FeL$_2$X$_2$] (L = nicotinamide or nicotinic acid)	Preparations described	bb
[FeLCl$_2$] (L = ethylenediaminetetra-acetamide)	Preparation described	cc
Fe(II)-*O*-(2-pyrroylmethyleneamino)-benzoic acid or 3-(2-pyrroylmethylene-amino)propanoic acid complexes	Preparations described	dd
Fe(II)-benzooxazole-2-thione complexes	Preparations described	ee
Fe(PhCOS)$_2$]	Preparation described	ff
Fe(II)-4-benzylamidothiosemicarbazide or 1-(α)-furyl-4-benzylamidothiosemi-carbazide complexes	Magnetic study	gg

(a) K. Madeja, W. Bochmer, T.T. Nguyen, G. Ochme, A.A. El-Saghier, A. Vertes and K. Burger, Z. Anorg. Allg. Chem., 447 (1978) 5. (b) S. Aditya and S.C. Lahiri, J. Inorg. Nucl. Chem., 40 (1978) 1069. (c) J.M. Rao, M.C. Hughes and D.J. Macero, Inorg. Chim. Acta, 35 (1979) L369. (d) G.A. Lawrence, D.R. Stranks and S. Suvachittanont, Inorg. Chem., 18 (1979) 82; S. Raman, J. Inorg. Nucl. Chem., 40 (1978) 1073. (e) N.B. Singh and J. Singh, J. Inorg. Nucl. Chem., 40 (1978) 919. (f) A.A. Abushamleh and H.A. Goodwin, Aust. J. Chem., 32 (1979) 513. (g) H.W. Smith, B.D. Sentarsiero and E.C. Lingafelter, Cryst. Struct. Commun., 8 (1979) 49. (h) F. Cariati, F. Morazzoni and M. Zocchi, J. Chem. Soc., Dalton Trans., (1978) 1018. (i) J.G. Jones and M.V. Twigg, J. Chem. Soc., Dalton Trans., (1978) 1709. (j) G. Ferraudi, Inorg. Chem., 18 (1979) 1005. (k) G. Kiss, Petrochimia, 18 (1978) 55 (Chem. Abstr., 90 (1979) 112585). (l) W.L. Driessen and M. Den Heijer, Inorg. Chim. Acta, 33 (1979) 261. (m) R. Job and R. Earl, Inorg. Nucl. Chem. Lett., 15 (1979) 81. (n) Y.A. Ol'dekop, N.A. Maier, A.A. Erdman and V.L. Shirokii, Vestsi. Akad. Navuk BSSR, Ser. Khim. Navuk, (1979) 116 (Chem. Abstr., 90 (1979) 212226). (o) F. Aramu, V. Maxia and C. Mutoni, Hyperfine Interact., 5 (1978) 399 (Chem. Abstr., 90 (1979) 31541). (p) J.T. Wrobleski and D.B. Brown, Inorg. Chem., 18 (1979) 2738. (q) Y. Masuda and S. Shishido, Thermochim. Acta, 28 (1979) 377. (r) G.T. Kurbatova, E.E. Kriss, Y.E. Alekseev and V.A. Tyumeneu, Zh. Neorg. Khim., 24 (1979) 1891. (s) K.I. Tuta, R.A. Stukan, I.I. Bulgak, D.G. Batyr and L.D. Ozol, Koord. Khim., 4 (1978) 1391. (t) I.B. Markov, Tezisy Dokl.-Konf. Molodykh Nauchn. Rab. Inst. Neorg. Khim. Akad. Nauk Latv. SSSR 6th, (1977) 38 (Chem. Abstr., 90 (1979) 29687). (u) I.A. Kulikov, V.S. Koltunov, V.I. Marchenko, A.S. Milovanova and L.K. Nikishova, Zh. Fiz. Khim., 53 (1979) 647. (v) N.M. Rivera, E.M. Engler and R.R. Schumaker, J. Chem. Soc., Chem. Comm., (1979) 184. (w) G. Mori and Y. Takashima, Chem. Lett., (1979) 425. (x) N.B. Behrens, D.M.L. Goodgame and Z. Warnke, Inorg. Chim. Acta, 31 (1978) 257. (y) J.T. Wrobleski and G.J. Long, Inorg. Chim. Acta, 30 (1978) 221. (z) M. Plytzanopoulos, G. Pneumatikakis, N. Hadjiliadis, D. Katakis and V. Papadopoulos, Chim. Chron., 8 (1979) 109. (aa) R.W. Hay and C.R. Clark, Transition Met. Chem., 4 (1979) 28. (bb) J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79. (cc) R.W. Hay, K.B. Nolan and M.M. Shuaib, Transition Met. Chem., 4 (1979) 142. (dd) N.K. Sankhla, P.K. Kanungo and R.K. Mehta, J. Indian Chem. Soc., 56 (1979) 99. (ee) C. Preti and G. Tosi, J. Coord. Chem., 8 (1978) 15. (ff) B.P. Sudha, N.S. Dixit and C.C. Patel, Indian J. Chem., 16A (1978) 856. (gg) M.C. Jain and P.C. Jain, Nat. Acad. Sci. Lett. (India), 1 (1978) 291.

1.5 IRON (III)

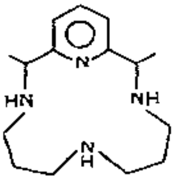
1.5.1 Halides

Amorphous FeF_3 has been prepared [154], and a structural study of $K_{0.54}(MnFe)F_3$ shows that the Mn^{2+} and Fe^{3+} ions occupy three different types of octahedral site [155]. Treatment of solid $FeCl_2$ with Br_2 at 200—600°C gives $Fe_2Br_xCl_{6-x}$ and $FeBr_yCl_{3-y}$ [156] whilst heating $FeCl_2$ in a dioxygen stream yields $FeCl_3$ and FeOCl. At temperatures above 320°C, FeOCl reacts further with O_2 to give α-Fe_2O_3 [157]. Structural studies on $[ClC(CNMe_2)_2][Fe(dmf)_6][FeCl_4]_4$ [158], $[NH_4]_2[FeCl_5(H_2O)]$ [159], $K_2[FeCl_5(H_2O)]$ [160] and $Cs_3[Fe_2Cl_9]$ [161] have been reported.

A Raman study of $FeCl_3$ intercalated into graphite shows no evidence for monomeric or dimeric $FeCl_3$: the $FeCl_3$ appears to maintain its layer structure [162].

1.5.2 N-bonded ligands

The new dibenzotetraaza[14]annulene (N_4) complex, $[Fe(N_4)(imidazole)_2]$ has been prepared [163]. The complex $[Fe(LH_4)Cl_2][BF_4]$ {LH_4 = (17)} is



(17)

an effective catalyst for the decomposition of H_2O_2 to H_2O and O_2 in aqueous solution. The complex exists primarily as the aqua-hydroxo complex and this slowly self-condenses, in the presence of air and ethanoate buffers, to a μ-oxo-dimer; the catalytically active species is the aqua-hydroxo-species, $[Fe(LH_4)(OH)(H_2O)]^{2+}$. A kinetic study is consistent with H_2O_2 decomposition by a free radical mechanism [164].

Covalent hydration has been established as an essential step in the dissociation of $[Fe(2,2':6',2''\text{-terpy})_2]^{3+}$ [165]. Fe(III) complexes of di- and tri-(2-pyridyl)amine and (4- or 5-methyl-2-pyridyl)amine constitute three complex types which can be seen as stages in the base hydrolysis of the metal ion: the first type contain the anion, $[Cl_3FeOFeCl_3]^{2-}$; the second type are $[LFeX_3]$, which are only formed by the potentially terdentate ligands; the third type, which is mostly restricted to the monopyridylamine ligands, is more complex and contains two distinct high spin iron sites [166]. *N*-(2-picolidine)-1-naphthylamine (L) forms the complexes, $[FeLX_3]\cdot H_2O$ (X = Cl or ClO_4) and $[FeL_2(SCN)_3]$ [109]. Reaction of pyrazolylphenyl (R) Grignard reagent with $FeCl_2$ yields $[FeR_3]$ [167].

Thirteen complexes of 2-hydroxymethylbenzimidazole (HL′) and 2-hydroxymethylbenzothiazole (HL″) have been isolated. $[Fe(HL)_3X_3]$ (X = Cl or Br) and $[FeL_2X]$ ($X = ClO_4$ or NO_3) are low spin octahedral complexes; $[Fe_2L_3(OH)X_2] \cdot H_2O$ (X = Cl or Br) are antiferromagnetically coupled ($S = \frac{3}{2}$) dimers with five-coordinate iron; $[Fe(HL')Cl_3] \cdot MeOH$ and $[Fe(HL')(OH)X_2] \cdot H_2O$ ($X = ClO_4$ or NO_3) are high spin complexes. $[FeL''X_2]$ (X = Cl, Br or ClO_4) have *pseudo*-tetrahedral symmetry and $[FeL''(NO_3)_2] \cdot 2\,H_2O$ contains a *pseudo*-octahedral iron(III) centre [100]. [Fe(2,2′-biimidazole-H)$_3$], $[Fe(biim)_3]$, has been prepared [168], and the iron(III) complex of dihydro-bis-(1-indazolyl)borate has been reported [169].

1.5.3 O-bonded ligands

X-ray scattering of concentrated aqueous solutions of $Fe_2(SO_4)_3$ shows the presence of $[Fe(H_2O)_6]^{3+}$, $[SO_4]^{2-}$ and $[Fe(H_2O)_{6-n}(OSO_3)_n]^{(3-2n)+}$ [170]. $[Fe(SO_3F)_3]$ contains bidentate SO_3F ligands [113]. Hydrolysis of $Fe(NO_3)_3$ in solution proceeds via formation of polynuclear hydroxo- and oxo-bridged complexes containing both octahedral and tetrahedral iron(III) [171]. Synthetic procedures for the preparation of $Na_3Fe_2(PO_4)_3$ [172], $FeAsO_4 \cdot 2\,H_2O$ [173] and $[Fe(O_2SeR)_3]$ (R = Me or Ph) [174] have appeared. The liquid monomeric complex $[Fe\{Al(OCMe_2H)_4\}_3]$ has been prepared and contains the bidentate ligand $[Al(OCMe_2H)_4]$ [175]. $[Fe_4(\mu\text{-}OMe)_8(O_2CMe)_4]$ has been prepared from $[Fe_4(\mu_3\text{-}O)(O_2CMe)_6(H_2O)][ClO_4]$ and MeOH and contains a chelating ethanoate group bonded to each iron atom and eight bridging methoxide groups [176]. The compounds, $[Fe^{II}Fe_2^{III}O(O_2CMe)_6 \cdot n\,L]$ (L = py, 3-picoline, $n = 4$; L = 4-picoline, $n = 3$), $[Fe_3^{III}O(O_2CMe)_6L_3]Cl$, and $[Fe_3^{III}O(O_2CMe)_6(H_2O)_3]X \cdot n\,H_2O$ (X = Cl, $n = 5$; $X = NO_3$, $n = 3$; X = O_2CMe, $n = 1$) have been prepared [177].

The complexes, $K_3[FeL_3] \cdot n\,H_2O$ (H_2L = pyrocatechol, salicylic acid or tetrachloropyrocatechol), $K_3[FeQ_2(H_2O)_2]H_2O$ (H_3Q = sulphosalicylic acid) or $K_3Na_6[FeT_3] \cdot 5\,H_2O$ (Na_2H_2T = tiron) have been prepared and react with oxalate to give $K_3[FeZ_2(ox)] \cdot n\,H_2O$ ($H_2Z = H_2L$ or H_2Q), $K_3[Fe(HQ)(ox)_2] \cdot 3\,H_2O$, $K_3[FeL(ox)_2] \cdot 3\,H_2O$, $K_3Na_4[FeT_2(ox)] \cdot 7\,H_2O$ or $K_3Na_2[FeT(ox)_2] \cdot 5\,H_2O$ [178]. The squarate complex, $[Fe(C_4O_4)(H_2O)(OH)]_2 \cdot 2\,H_2O$ has been isolated and reacts with pyridine bases to give $[Fe(C_4O_4)(py)_2(OH)]_2 \cdot 2\,H_2O$, with dmso to give $[Fe_3O(C_4O_4)_3(dmso)_3(H_2O)_3][OH]$ and with ethanolic KOH to give $[Fe(C_4O_4)(H_2O)_2]_2O$ [179]. Magnetic studies show $Na_2[Fe_2(OH)_2(H_2O)_2L_2]$ (H_4L = citric acid) to be dimeric and not monomeric as previously proposed [180a].

$[FeL_3]$ (L = acac or 3-hydroxy-2-methylpyronate) have been prepared by direct electrochemical means using an iron anode in a simple cell [180b]. The chiral β-diketones (+)-3-hydroxymethylene-, (+)-3-acetyl- and (+)-3-propionylcamphor, form tris(dik)iron(III) complexes but only one diastereoisomer was obtained [181].

Some amine-*N*-oxide complexes of iron(III) reported this year are listed in Table 6.

TABLE 6

Some amine-*N*-oxide complexes of iron(III)

Complexes	Ref.
$[FeL_6][ClO_4]_3[FeL_4(OClO_3)_2][ClO_4]$, $[FeL_3(OClO_3)(OH_2)_2][ClO_4]_2$ (L = 3-methylisoquinoline-*N*-oxide)	120
$FeL_3(ClO_4)_3 \cdot 5\,H_2O$ (L = quinoxaline-1,4-dioxide)	121, 182
$[FeL_3(OH_2)_2(OClO_3)][ClO_4]_2$, $[(O_3ClO)_x(H_2O)_yFeLFe(OH_2)_y(OClO_3)_x]$-$[ClO_4]_{6-2x}$ ($x = 1$ or 2; $y = 3$ or 4; L = phenazine-5,10-dioxide)	122
Fe(III)-8-quinolinol-*N*-oxide complexes	183

The complexes, $[(O_3ClO)(H_2O)_2LFe(\mu\text{-}L)_2FeL(H_2O)_2(OClO_3)][ClO_4]_4$ {L = MePh(MeO)PO} [125] and $[Fe\{MeCO_2(EtO)_2PO\}_3][ClO_4]_3$ [127] have been prepared. $FeCl_3$ reacts with trimetaphosphinate (L) to yield $[FeL_2]^{3-}$ [128], with Ph_3As in a 1 : 2 ratio to give $[Fe(OAsPh_3)_4Cl_2][FeCl_4]$ and in a 1 : 1.5 ratio to give $[\{FeCl_3(OAsPh_3)\}_2(\mu\text{-}OAsPh_3)]$ [184].

The semiquinone complexes $[Fe(phensq)_3] \cdot$ phenq, $[Fe(1,2\text{-}Cl_4sq)_3]$ and $[Fe(3,5\text{-}dbsq)_3]$ (phensq = 9,10-phenanthrenesemiquinone, $1,2\text{-}Cl_4sq$ = 3,4,5,6-tetrachloro-1,2-benzosemiquinone, 3,5-dbsq = 3,5-(di-*t*-butyl)-benzosemiquinone) have been prepared and a structural study on the first of these shows it to consist of weakly interacting $[Fe(phensq)_3]$ molecules and molecules of unreduced quinone [185]. $[Fe_2L_3(H_2O)_4]$ (H_2L = 2,5-dihydroxy-1,4-benzoquinone) has also been prepared [118].

1.5.4 S- and P-bonded ligands

Structural studies on $[Fe(S_2CNR_2)_3]$ (R = 2-hydroxyethyl) at 295 and 150 K show the main difference to be a decrease in Fe—S bond length from 2.390 to 2.331 Å on cooling; this is accompanied by a decrease in μ_{eff} from 4.20 to 2.40 μ_B [186]. Variable temperature magnetic data have been acquired by the NMR method for $[Fe(S_2CNR_2)_3]$ (R = Pr, Bu or CH_2Ph; R_2 = PrPh) and the assumption of a simple Boltzmann distribution between high and low spin states fits the observed behaviour [187].

EPR spectra obtained during the reaction of $[Fe(PR'_3)(S_2C_2R_2)_2]$ (R = Ph, R′ = Bu, Ph or C_2H_4Cl; R = H, R′ = OPh) with bromine indicate formation of at least three compounds; two geometrical isomers of $[Fe(PR'_3)(S_2C_2R_2)_2]^+$ and *trans*-$[Fe(PR'_3)(S_2C_2R_2)_2Br]$. With iodine, only the cation is formed [188]. $[NBu_4][Fe(1,2\text{-}C_6H_4S_2)_2]$ reacts with $N_2H_4 \cdot H_2O$ to yield $[NBu_4]_2$-$[(\mu\text{-}N_2H_4)\{Fe(1,2\text{-}C_6H_4S_2)_2\}_2]$ [189].

Ag(I) ion oxidation of [(cp)Fe(dppe)X] (X = Cl, Br, I, H, $SnMe_3$, CN or SCN) yields the corresponding cation. Similar oxidation with $[NO]^+$ gives $[cpFe(dppe)(NO)]^{2+}$ [190].

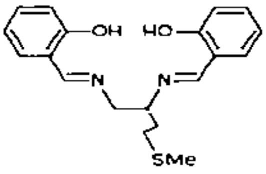
TABLE 7

Some Schiff base and related ligand complexes of iron(III)

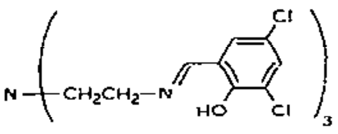
Complex	Ref.
$[FeLX]_2$ $\{LH_2 = 1,2\text{-}HOC_6H_4CR{=}NNHCOPh$ (R = H, Me, Et or Pr) or $R'CH{=}NNHCOPh$ (R′ = 2-hydroxynaphthyl); X = Cl, Br or $NO_3\}$	194
$[FeL]$ $\{LH_3$ = 4,4′-bis-(3-formyl-4-hydroxyphenylazo)biphenyl$\}$	195
$[NH_4][FeL(SO_4)_2] \cdot 4\ H_2O$ (L = ethylmalondihydrazide)	196
$[Fe\{S_2C(NH)_2Ph\}_3]$	197
$[FeL(HL)]$ (H_2L = 4-$HOC_6H_4CH{=}NC_6H_3$-3 OH-4 CO_2H or 3-$MeOC_6H_4CH{=}NC_6H_3$-3 OH-4 CO_2H)	141
$[FeL]_2[FeX_4]$, $[FeL'_2Cl] \cdot 2\ H_2O$ (HL′ = 4-phenyl-thiosemicarbazone; HL = methyl ether of HL′; X = Cl or Br)	198

1.5.5 *Mixed donor ligands*

The ligand, (18; LH_2) forms the complex $[FeL(N\text{-Meimidazole})_2][ClO_4]$ [191]. The structure of bis-(γ-salicylideneiminopropyl)aminatochloroiron(III) shows it to have octahedral $\{O_3NCl\}$ coordination [192]. The iron(III) complex of the potentially heptadentate ligand (19) has been prepared [193]. Other Schiff base and related complexes are summarised in Table 7 and other studies involving iron(III) complexes are cited in Table 8.



(18)



(19)

1.6 IRON(IV)

Treatment of $[Fe(S_2CNR_2)_3]$ (R = CMe_2H or cych) with $[BF_3]$ gives $[Fe(S_2CNR_2)_3][BF_4]$ [199]. Magnetic studies on $[Fe\{S_2C_2(CN)_2\}_2\text{-}\{S_2C{=}C(CN)_2\}_2]^{2-}$ and $[Fe\{S_2C_2(CN)_2\}_2\{S_2C{=}C(CO_2Et)_2\}_2]^{2-}$ show them to have room temperature moments corresponding to the spin-only value for 2 unpaired electrons, but below 20 K, these decrease dramatically [200]. Treatment of $[FeR_3]$ (R = pyrazolylphenyl) with ethanoic anhydride or iodine gives $[FeR_3][O_2CMe]$ and $[FeR_3]I$, respectively; the iodide reacts with LiX (X = Cl, Br or ClO_4) to yield $[FeR_3]X$ [167].

TABLE 8

A selection of studies on some iron(III) complexes

Complex	Comment	Ref.
FeOCl	Preparation of intercalation compounds with py or $PrNH_2$	a,b
$[PPh_4]_4[(NC)_5Fe(NC)Fe(CN)_4(NH_3)]$	Preparation and X-ray structure	c
trans-$[Fe(cyclam)(NCS)X]^+$	Reactivity	d
$K[Fe(PO_4)F]$	X-ray structure revealing $\{FeO_4F_2\}$ coordination	e
$[Fe(ox)_n]^{3+}$ ($n = 2$ or 3)	Photochemistry	f
Fe(III)-oxalate, squarate or dihydroxybenzoquinone complexes	Magnetic studies	g
$Na_{12}Sn_4Fe_3H_7(citrate)_9 \cdot 38\ H_2O$	Preparation described	h
$[Fe(dmso)_6]^{3+}$	Electrochemical preparation	i
$[Fe(dmf)_6][ClO_4]_3$	X-ray structure	j
$FeCl_3$-pinacol complexes	Photochemistry	k
Fe(III)-triketonates	Preparations described	l
$[Fe(RCONRO)_3]$ (R = Me or Ph), $[Fe(RCONHO)_3]$ (R = Me, Et or Ph)	Preparations described	m
Fe(III)-2,3-hydroxynaphthoic acid complexes	Preparations described	n
$[FeL_nX_3]$ (L = urea, thiourea, dimethylthiourea, 2-(1 H)-tetrahydropyrimidone or 2-imidazolidine; $n = 2$, 3 or 6; X = Cl or Br)	Preparations described	o
$[NH_4]_3[FeMo_6O_{18}(OH)_6] \cdot 5\ H_2O$	Preparation described	p
$[FeLX_2]^+$ ($L = 1,2\text{-}C_6H_4(AsMe_2)_2$; X = Cl, Br or I)	Photochemistry	q
$[FeCl\{S_2CN(CMe_2H)_2\}_2] \cdot CHCl_3$	X-ray structure	r
$[Fe(Rdtc)_2X]$ (Rdtc = 4-morpholine carbodithioic acid, X = Cl, Br or NCS)	Preparations described	s
$[Fe(S_2C_2O_2)_2X]^{2-}$ (X = Cl, Br or I)	Magnetic study	t
Fe(III)-aminopolycarboxylates	Photochemical extrusion of CO_2	u
Fe(III)-2-benzoylpyridine complexes	Preparations described	v
$[FeL_3]$ (LH = indole-2-CO_2H)	Preparation described	w
$[FeL_3]$ (HL = Schiff base from acetoacetanilide, aceto-aceta-p-toluidide or benzoylacetone with RNH_2)	Preparations described	x
$[FeCl_3(diacetamide)_2] \cdot H_2O$	Preparation described	y
Fe(III)-monohydroxamate complexes	Kinetics of formation	z
$[FeL_3]$ 2 H_2O (L = aminoacid-dithiocarbamate)	Preparation described	aa

TABLE 8 (continued)

Complex	Comment	Ref.
$[Fe(5\text{-}AMP)(OH)] \cdot H_2O$	Preparation described	bb
$[FeLCl] \cdot H_2O$ (L = 3-hydroxycarbostyril)	Preparation described	cc
$[FeL_3] \cdot H_2O$ (HL = 3,4,5-Me_3-1-OH-pyrazole-2-oxide)	Preparation described	dd
Fe(III)-D(+)-1,2-bis(4-phenyl-1,2,4-triazoline-5-thione-3-yl-ethylene glycol)	Preparation described	ee
Fe(III)-2-aminobenzothiazole complexes	Preparations described	ff
Fe(III)-monothio-β-diketonates	Magnetic study	gg
$Na[Fe(BH_4)_3]$	Preparation described	hh
$HgFe_nCl_{n+1}L_{2n}(OH)_{2n+1}$ ($L = NH_3$, $n = 0.5$; L = en, $n = 1$, 2 or 4)	Preparations described	ii
$Fe(BiOCl)X_3$ (X = OH or Cl)	Preparations described	jj

(a) J. Dousma, T.J. Van den Hoven and P.L. De Bruyn, J. Inorg. Nucl. Chem., 40 (1978) 1089. (b) S. Kikkawa, F. Kanamaru and M. Koizumi, Bull. Chem. Soc. Jpn., 52 (1979) 963. (c) P. Roden, A. Ludi, G. Chapius, K.J. Schenk, D. Schwarzenbach and K.O. Hodgson, Inorg. Chim. Acta, 34 (1979) 113. (d) C.K. Poon and A.W.M. To, Inorg. Chem., 18 (1979) 1277. (e) E.N. Matvienko, O.V. Yakubovich, M.A. Sinovov and N.V. Belov, Dokl. Akad. Nauk SSSR, 246 (1979) 875. (f) H. Sato and T. Tominaga, Bull. Chem. Soc. Jpn., 52 (1979) 1402. (g) J.T. Wrobleski and D.B. Brown, Inorg. Chem., 18 (1979) 2738. (h) B. Binder, J. Inorg. Nucl. Chem., 41 (1979) 257. (i) J.J. Habeeb, F.F. Said and D.G. Tuck, Inorg. Nucl. Chem. Lett., 15 (1979) 113. (j) E.M. Holt, N.W. Alcock, R.H. Summer and R.O. Asplund, Cryst. Struct. Commun., 8 (1979) 255. (k) J. Sima and E. Horvath, Inorg. Chim. Acta, 31 (1978) L460. (l) L.L. Borer and W. Vanderbout, Inorg. Chem., 18 (1979) 526. (m) D.A. Brown, D. McKeith and W.K. Glass, Inorg. Chim. Acta, 35 (1979) 5. (n) A.N. Gurbanov, Azerb. Khim. Zh., (1978) 111 (Chem. Abstr., 90 (1979) 44540). (o) U. Russo, S. Calogero, N. Burriesci and M. Petrera, J. Inorg. Nucl. Chem., 41 (1979) 25. (p) B.N. Ivanov-Emin and Q.S. Olguin, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Technol., 21 (1978) 1721 (Chem. Abstr., 90 (1979) 131995). (q) J.I. Zink, P.H. Lin and B. Anfield, Inorg. Chem., 18 (1979) 1013. (r) S. Mitra, B.N. Figgis, C.L. Raston, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1979) 753. (s) S. Wajda, I. Grzybowska and K. Drabent, Pol. J. Chem., 52 (1978) 1877. (t) D. Niarchos, A. Kostikas, A. Sinopoulos, D. Coucouvanis, D. Piltingsrud and R.E. Coffman, J. Chem. Phys., 69 (1978) 4411. (u) A.L. Poznyak and S.I. Arzhankov, Dokl. Akad. Nauk SSSR, 23 (1979) 353 (Chem. Abstr., 91 (1979) 66180). (v) M. Plytzanopoulos, G. Pneumatikakis, N. Hadjiliadis, D. Katakis and V. Papadopoulos, Chem. Chron., 8 (1979) 109. (w) A.K. Singh, D. Prakash and S.K. Srivastava, J. Indian Chem. Soc., 55 (1978) 861. (x) A. Sreckantan and C.C. Patel, Proc. Indian Acad. Sci., 87A (1978) 455. (y) Y.Y. Kharitonov, G.V. Tsintsadze, A.Y. Tsivadze and E.I. Tabidze, Koord. Khim., 4 (1978) 1609. (z) N. Kujundzic and M. Pribanic, J. Inorg. Nucl. Chem., 40 (1978) 729. (aa) S. Wajda and K. Drabent, Pol. J. Chem., 53 (1979) 973. (bb) D.M.L. Goodgame and Z. Warnke, Pol. J. Chem., 52 (1978) 2075. (cc) F.I.M. Taha, M.N. Moussa, A.M. Shallaby and M.M. El Defraway, Egypt J. Chem., 19 (1976, Publ. 1978) 393. (dd) D.X. West and M.A. Venek, J. Inorg. Nucl. Chem., 40 (1978) 1027. (ee) V.J. Ram, L. Mishra and H.N. Pandey, Transition Met. Chem., 4 (1979) 237. (ff) M.J.M. Campbell, R. Grzeskowiak and G.S. Juneja, J. Inorg. Nucl. Chem., 40 (1978) 1247.

1.7 OXIDES, SULPHIDES AND PHOSPHIDES

$K_2[FeO_4]$ is easily prepared and is a selective oxidising agent for benzyl alcohols [201]. Reaction of LiCl with Fe_2O_3 at 450—750°C yields $LiFeO_2$ and $Li_{0.5}Fe_{2.5}O_4$ [202]; the latter is also obtained by heating together $[Fe_3(HCOO)_6(OH)_2][HCO_2] \cdot 4\ H_2O$ and $[HCOO]Li \cdot H_2O$ [203]. Heating $BaCO_3$ and Fe_2O_3 at 1473 K in a BaO-B_2O_3 flux gives $Ba_2Fe_6O_{11}$, which has iron in both tetrahedral and octahedral sites [204]. Heating iron with TiO_2 in 10 M NaOH produces $CaFe_2O_4$ [205]. Similar compounds, MFe_2O_4 (M = Co, Ni, Zn, Mg or Mn), have been prepared from $K_2[MCl_4]$ and $NaFeO_2$ [206]. At 400°C, β-FeO(OH) and MoO_3 form $Fe_2[MoO_4]_3$ [207]. $FeSb_2O_4$ has been prepared and has a structure similar to that of natural schafarzikite [208]. The synthesis of $GaFeO_3$ [209] and Mössbauer spectral studies of $CaBaFe_4O_8$ [210] and $FeCoCrO_4$ [211] have also been reported. The standard heat of formation of FeO(OH) has been determined as -535 ± 10.5 kJ mol^{-1} [212].

Room temperature reaction of highly dispersed iron(III) hydroxide and NaSH at pH 9 produces sodium thioferrite(III) [213]. The intense emerald green solutions formed by reactions of iron salts with alkali metal sulphides at pH 11—13 contain colloidal $MFeS_2$ (M = Li, Na or K). Solid $NaFeS_2$ and $KFeS_2$ have been isolated and have structures different from other $MFeS_2$ compounds [214]. $Ba_3(Fe^{IV}_{1-x}Si_x)S_5$ ($x = 0.8$) has been reported [215]. $Cu_2FeSn_3S_8$ has a disordered spinel structure with copper in tetrahedral sites and the octahedral sites occupied by randomly distributed iron(II) and tin(IV) ions [216]. Mössbauer spectra of Fe_xS ($x = 0.996$ or 0.93) have been reported [217].

Two groups have reported syntheses of FeP_4, containing low spin Fe(II). It has a structure very similar to that of other MP_4 (M = Cr or Mn) compounds, with iron in octahedral sites [218].

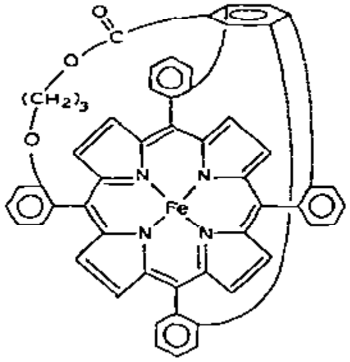
1.8 INORGANIC BIOCHEMISTRY OF IRON

Work in this area has undergone enormous growth in recent years, but the coverage given here is aimed towards those studies that illuminate the role or environment of the metal in natural systems, as well as work on model compounds.

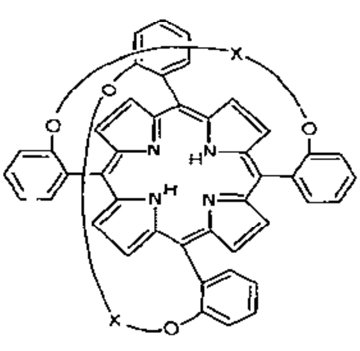
References to Table 8 (continued)

(gg) J. Akashi, K. Endo and H. Sano, J. Phys. Colloq., (1979) 405 (Chem. Abstr., 90 (1979) 196745). (hh) V. Makhaev, A.P. Borisov, N.G. Mozgina and G.N. Boika, Izv. Akad. Nauk SSSR Neorg. Mater., 14 (1978) 1726. (ii) M. Brezeanu and M. Dinculescu, Rev. Roum. Chim., 23 (1978) 699 (Chem. Abstr., 90 (1979) 161374). (jj) M. Brezeanu and M. Dinculescu, Rev. Roum. Chim., 23 (1978) 1389, 1533 (Chem. Abstr., 90 (1979) 114210; 91 (1979) 48657).

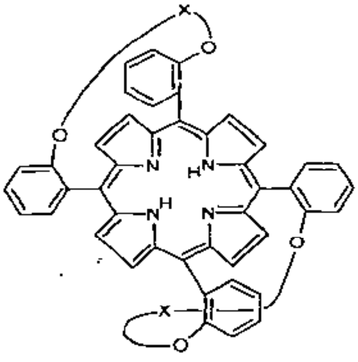
A convenient synthesis of [Fe(PPIXDME)] from haemin has been reported [219]. MO calculations performed in a search for the cause of the displacement of iron from the N_4 plane in Hb has led to the suggestion that five coordinate Fe(II) in deoxy-Hb could undergo a pseudo-Jahn-Teller distortion and that addition of O_2 would remove this. Thus, the iron atom would move into the haem plane, pulling with it the fifth ligand, and thereby triggering off the conformational changes [220]. The homologous *cap*-porphyrin complex **(20)** has been prepared and forms a five-coordinate adduct with 1-methylimidazole which, in turn, is capable of weakly binding a second imidazole molecule. Both imidazole complexes reversibly bind O_2 [221]. Similar basket-handle porphyrins have been isolated **(21, 22, 23)** and the stability of their iron(II) derivatives towards oxidation has been studied [222]. Iron porphyrin complexes have been linked to polystyrene using copolymers of styrene, 4-aminostyrene or divinylbenzene; in the solid state, reversible O_2 binding is only observed for the most highly cross-linked polymers [223]. The oxygen affinities of picket-fence porphyrins are similar to that of Mb; in solution, the lower oxygen affinities of the picket-fence



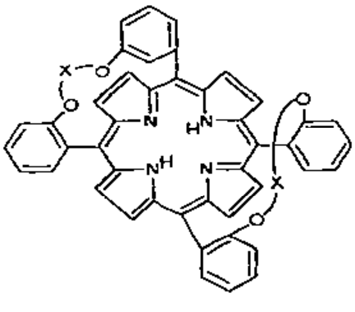
(20)



(21)



(22)



(23)

porphyrins arise as a consequence of sterically constrained axial bases and thus models the T form of Hb [224]. The heats of binding of O_2 onto isolated subunits of human Hb are different. Comparison with dimers and tetramers shows that the same intrinsic enthalpy per haem site is obtained, independent of the degree of aggregation [225]. It has been suggested that the reaction of $[O_2]^-$ with iron(II) porphyrins leads to high-spin iron(III) with side-bonded O_2 [226].

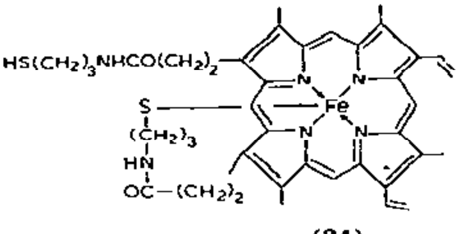
Deprotonation of the axial ligand in [Fe(PPIXDME)L] (L = H_2O, imidazole, 2-methylimidazole, PhOH, MeOH or BuOH) causes a red shift in the Soret band. The electronic spectrum of deprotonated [Fe(PPIXDME)-(2-Meimid)] is very similar to that of peroxidase and quite unlike that of Hb, suggesting that peroxidase might undergo deprotonation or strong hydrogen bonding of the proximal imidazole during catalytic action [227]. [Fe(oep)-(CS)] and [Fe(oep)(CS)L] (L = py, pip, dmf or 1-Meimid) have been prepared [228], and the structure of $[Fe(TPP)(CNBu)_2] \cdot 2$ PhMe has been determined [229].

A structural study on high spin ($S = \frac{5}{2}$) $[Fe(TPP)(OH_2)_2][ClO_4]$ shows the iron atom to be centred in the N_4 plane rather than having the out-of-plane displacement of similar complexes. The large Fe(III) ion is accommodated by radial expansion of the porphyrin core, the Fe—N distance of 2.045 Å corresponding to an increase in central hole size of ~0.055 Å, relative to low spin derivatives; this system provides a model for aquomet-Hb [230]. [Fe(TPP)I] has the metal ion 0.53 Å above the N_4 plane {r(Fe—N) = 2.054—2.076 Å} [231]. The structure of low spin $[Fe(TPP)py(N_3)]$ has also been determined [232].

Oxidation of [Fe(TPP)py(CO)] with iodine produces the radical cation $[Fe(TPP)py(CO)]^+$ [233]. EPR data on frozen solutions of high spin iron(III)-oep complexes suggests the presence of dimers [234]. The kinetics of cleavage of $[\{(TPP)Fe\}_2O]$ by imidazole to form $[Fe(TPP)(imid)_2]^+$ indicate the dimer and imidazole form a complex in a pre-equilibrium step [235]. Substituted phenoxides (L) react with $[\{Fe(PPIXDBE)\}_2O]$ to form [Fe(PPIXDBE)L], which displays spectral properties similar to those of the Met form of the α-mutant chain of Hb-M-Boston [236].

The EXAFS technique has been applied to liver microsomal (LM2) cytochrome P-450 and *Caldarcomyies fumago* chloroperoxidase. These are haemoproteins with similar spectroscopic properties which, respectively, catalyse hydroxylation and halogenation of organic substances. The nature and distances of the axial ligands are of importance in understanding their catalytic roles. The EXAFS studies of the resting state iron(III) environments shows chloroperoxidase to contain high spin, out-of-plane Fe(III) centres, whereas cytochrome P-450 contains low spin, in-plane Fe(III). The data indicate the presence of an axial sulphur ligand in both enzymes. The relevant distances are r(Fe—N(por)) = 2.05, $r(\text{Fe—C}_\alpha)$ = 3.09, and r(Fe—S) = 2.30 Å in chloroperoxidase (very similar to those in Fe(III)—PPIXDME complexes) and r(Fe—N(por)) = 2.00, $r(\text{Fe—C}_\alpha)$ = 3.07, and r(Fe—S) = 2.19

Å in cytochrome P-450 [237]. Studies on model compounds for cytochrome P-450 supported the presence of a mercaptide as the fifth ligand. When an alcohol or thiol is added to the sixth site of [Fe(PPIXDME)(4-$NO_2C_6H_4SH$)]-Cl, low spin complexes are obtained with optical EPR spectra very similar to those of cytochrome P-450. The authors conclude that a hard ligand must occupy the sixth site in the enzyme, and the significance of this to the monooxygenase mechanism has been discussed [238]. The compound, **(24)** has



(24)

been prepared and is suggested as a good model for cytochrome P-450 [239]. The oxyferryl intermediate of cytochrome P-450 has been stabilised at —30°C [240]. The activity of μ-oxo-iron porphyrin in catalysing the oxidation of cyclohexene has been studied as a function of substituents on the porphyrin rings. The results are consistent with a mechanism involving a ferryl intermediate [241]. Reaction of iron(III) porphyrins with iodosobenzene gives coloured intermediates that also mimic cytochrome P-450, again suggesting [FeO] as the active intermediate [241a].

Based on a study of the reaction of $[O_2]^-$ with tetrakis-4-(*N*-methyl)-pyridylporphyriniron(III), a mechanism has been advanced for superoxide dismutases. This complex was the most efficient studied; however, $[Fe(phen)_3]^{2+}$, $[Fe(edta)]^-$, $[Fe(edta)]^{2-}$, $[Fe(dtpa)]^{2-}$ and $[Fe(dtpa)]^{3-}$ (dtpa = diethylenetriaminepentaacetate) show some catalytic activity: $[Fe(CN)_6]^{3-}$ undergoes a stoichiometric reaction, but $[Fe(CN)_6]^{4-}$ is inactive [242]. Oxidation of some deuterated aromatics by H_2O_2-$Fe(ClO_4)_2$ showed large values of the NIH shift. A free radical mechanism for such reactions is suggested [243]. The mechanism of iron(III) catalysed decomposition of H_2O_2 has been studied and discussed in terms of the haemoprotein catalysed decomposition [244].

An EXAFS study of the active site of reduced and oxidised horse heart cytochrome-*c* suggested no conformational change in the haem region on reduction. Instead, a change in the amplitudes of some low frequency vibrations was noted. Furthermore, there is no change upon raising the pH, which results in the exchange of met-80-*S* for *N* coordination [245]. Sulphide, sulphoxide and sulphone ligands have been attached to tetraphenylporphyrins and their iron(II) binding abilities assessed in a search for simple models for cytochrome-*c* [245a]. The uncommon d^5 intermediate spin state has been found in [Fe(TPP)Y] (Y = ClO_4, BF_4, PF_6, SbF_6 or CF_3SO_3) and an X-ray study of the perchlorate salt shows the anion to be unidentate with short Fe—O bond length. The metal ion is displaced from the N_4 plane by an intermediate amount (0.3 Å) [246]. A low-temperature trapping technique has been used to study the reaction of the bacterial terminal oxidase, cytochrome-*c* with O_2 and the results are in accord with formation of an Fe(II)—O_2 link [247]. Stopped-flow circular dichroism spectroscopy has been applied to the reaction between cytochrome-*c* and iron protoporphyrins, an excellent model for the redox reaction of cytochrome-*c* with oxidases and reductases: the results were interpreted in favour of a mechanism in which either electron transport out of cytochrome-*c* is accompanied by no significant change in conformation around the active site, or any change is symmetric, so as not to induce any change in the Soret band [248]. The rôle of copper and iron in reactions of cytochrome-a_3 with O_2 has been studied and a new model advanced for cytochrome oxidase reactions [249]. Large scale preparations of the subunits of cytochrome oxidase have been reported [250]. Resonance Raman spectra of reduced cytochromes *b* and *c* and cytochrome oxidase in whole mitochondria opens up the possibility of using this technique for studying haem—haem interactions [251].

Fluorescence X-ray absorption spectra of rubredoxin and the model compound $[Fe(S_2\text{-o-xylyl})_2]$ have been obtained for both the oxidised and reduced forms. The spectra of rubredoxin and the model are very similar and both showed similar changes on reduction. The Fe—S bond lengths and strain energies were determined and any strain energy in oxidised rubredoxin is appreciably less than thermal energies, indicating that the redox potential is not regulated by strain in the Fe—S bonds [252]. The structure of a rubredoxin at 1.2 Å resolution has been reported; the Fe—S distances range from 2.24 to 2.33 Å and the S—Fe—S angles from 104° to 114° [253]. An X-ray study of the ferredoxin from *Spirulina platensis* revealed the chelating structure of the active centre. Of the six cysteinyl residues in the molecule, only four are bonded to the active centre, two to each iron atom [254]. SCF-Xα-SW m.o. calculations suggest that the antiferromagnetism of $[Fe_2S_2(SH)_4]^{2-}$ is caused by superexchange, and that the weak direct Fe—Fe bonding is concentrated in Fe—Sμ_2 orbitals [255]. $[Fe^{III}Fe^{III}S_2(SR)_4]^{2-}$ centres isolated from spinach and parsley have been reduced by dithionite to the $\{Fe^{II}Fe^{III}\}$ analogues and the kinetics of re-oxidation by a variety of Co(III) complexes have been studied. Evidence was gained for a protein-complex association and trends in the activation parameters indicate a dependence on the charge of the oxidant [256].

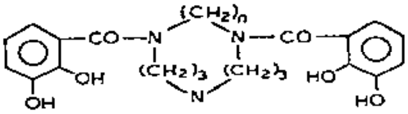
$[Fe_4S_4(SR)_4]^{2-}$ ions $\{R = (CH_2)_2OH, CMe_3$ or $Ph\}$ are synthesised conveniently and in good yields from reaction of $FeCl_3$ or $FeCl_2 \cdot 4\,H_2O$, elemental sulphur and MSR (M = Na or Li) in methanol under an inert atmosphere [257]. A structural study of $[NEt_4]_3[Fe_4S_4(SCH_2Ph)_4]$, an analogue for reduced ferredoxin, Fd_{red}, was undertaken to clarify the source of substantial differences in magnetic behaviour and Mössbauer spectra compared with the isoelectronic ion $[Fe_4S_4(SPh)_4]^{3-}$. In contrast to the $\{Fe_4S_4\}$ core of the Fd_{red} site analogue, $[Fe_4S_4(SPh)_4]^{3-}$, which is distorted from cubic to elongated D_{2d} symmetry (eight short and four long Fe—S bonds), the core of the thiobenzyl-containing anion contains six short and six long Fe—S bonds giving an idealised C_{2v} symmetry. This is the only analogue yet shown to contain a non-tetragonal core stereochemistry. However, the unconstrained core structural changes accompanying $[Fe_4S_4(SR)_4]^{2-} \rightarrow [Fe_4S_4(SR)_4]^{3-}$ are compressed $D_{2d} \rightarrow$ elongated D_{2d} not compressed $D_{2d} \rightarrow C_{2v}$ and the observed structure of the thiobenzyl anion is a result of the solid state environment [258].

A combination of extrusion and NMR techniques has been used to show that succinate hydrogenase contains two $\{Fe_2S_2\}$ centres and one $\{Fe_4S_4\}$ unit [259]. Two crystalline forms of an $\{Fe_4S_4\}_2$ protein have been obtained from *Azobacter vinelandii* [260]. The ferredoxin purified from *Clostridium perfringens* contains four iron atoms, four labile sulphur atoms and six cysteinyl residues, and acts as an electron donor for both nitrate reductase and hydrogenase [261]. Denatured *Clostridium pasteurianum*, when treated with Na_2S, $FeCl_2$ and $FeCl_3$ in 90% aqueous dmso, is converted to an $\{Fe_4S_4\}$ ferredoxin [262]. Compounds with ferredoxin cores, when irradiated with UV light, are active in water to hydrogen conversion [263]. However, $[Fe_4S_4(SR)_4]^{2-}$, bonded to an SiO_2 surface, exhibited no catalytic activity for hydrogenation or oxidation [264].

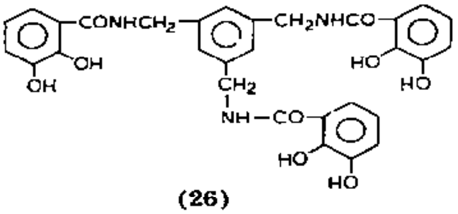
Following EXAFS studies on the molybdenum centre in nitrogenase indicating the probable presence of an $\{Fe_3MoS_4\}$ core, further model compounds have been reported. Thus, a good (60%) yield synthesis of $[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$ has been achieved; this anion undergoes total thiol exchange with $HOCH_2CH_2SH$ to form water soluble $[NEt_4]_3[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]$. The structures of both molecules have been reported and are closely similar, each containing two $\{Mo(FeSR)_3S_4\}$ cubes bridged via the molybdenum atoms by three RS ions. Electrochemical studies on the SEt complex shows the anion to undergo an irreversible one-electron oxidation and two reversible one-electron reductions. It has not yet been established whether these redox changes involve the whole dimeric assembly or whether each cubane-like cluster is oxidised or reduced independent of the other [265,266].

A kinetic study has been made of iron deposition into apoferritin [267]. There is a major difference between iron release by enterobactin and that of hydroxamate based siderophores. Release by hydroxamates has been suggested to occur by reduction of an iron(II) complex, a process that does not occur with iron(III) enterobactin. Electrochemistry of iron(III) enterobactin showed a reduction potential well below the range of physiological reducing agents and enterobactin hydrolysis is a necessary prerequisite to in vitro release of iron [268]. The stability constant of iron(III) enterobactin has been determined [269]. Rhodotorulic acid (H_2RA) is a dihydroxamic acid produced in high yields by yeast as an iron transport agent (siderophore). With iron(III) ions, the predominant complex at neutral pH is $Fe_2(RA)_3$, which involves hydroxamate linkages. Below pH 3, this dissociates to $[FeRA]^+$

[270]. Aerobactin, a dihydroxamate derivative of citric acid, is a siderophore produced from *Aerobacter aerogenes*. The iron complex, isolated as the trisodium salt, is a high-spin octahedral anion chelating to two bidentate hydroxamate groups, the central carboxylate group and a hydroxyl group of the citrate [271]. The iron(III) sequestering agents, (25) and (26), patterned on enterobactin, have been prepared. (26) removes Fe(III) from human transferrin, as well as enterobactin [272]. The amino acid sequence of haemerythrin from *Phascolopsis gouldii* has been re-investigated, and glutamic acid unambiguously confirmed and suggested as the ligating site [273]. The bleomycin-iron(II) system reacts with O_2 to produce $OH^{\cdot}$ radicals which, in turn, react with phenol and tocopherol to produce the corresponding radicals [274].



(25)



(26)

TABLE 9

Iron(II) and iron(III) complexes for which stability constant data have been reported

Complex or ligand	Ref.
Iron(II)	
$[Fe(bipy)_3]X_2$ (X = Cl, Br, I or ClO_4)	a
$FeSO_4$-1-vinyl-2-hydroxymethylimidazole and 1-vinyl-2-hydroxymethylbenzimidazole	b
2-hydroxy-1-naphthaldehyde	c
$[Fe(thiourea)_2]_2[Fe(CN)_6]$	d
Hydroxyproline hydroxamic acid	e
1-(5-chloro-2,3-dihydroxy-4-pyridylazo)-4-sulphonic acid	f
Sulphafurazole salicylaldimine	g
3-(*N*-2-furfuralideneimino)propionic acid	h
1-(2-quinolylazo)-2-acenaphthylenol or 1-(2-lepidylazo)-2-acenaphthylenol	i
Violuric acid	j
Alizarin	k
$(HSCH_2CONHCH_2)_2$	l
Diphenylthiovioluric acid	m
1,3,4-thiadiazolylo-5-thiomethanocarboxylic acid	n

TABLE 9 (continued)

Iron(III)	
Azide	o
$[Fe(phen)_3]X_3$ (X = halide or ClO_4)	p
$[Fe(phen)_2(CN)_2]X$ (X = SCN, I, Br, Cl or ClO_4)	q
$FeCl_3$-1-vinyl-2-hydroxymethylimidazole and 1-vinyl-2-hydroxymethylbenzimidazole	r
$Fe(OH)^{2+}$	s
Fe(III)-SCN-X (X = NO_3, Br, Cl, SO_4, F, glycolate, succinate, tartrate, citrate, PO_4 or ClO_4)	t
Lactic or mandelic acids	u
Glycolic, lactic, malic or benzilic acids	v
Salicylic acid	w
Phenol	x
Phosphorylserine	y
Adamantylhydroxamic acid	z
Salicylidene-2-aminophenol	aa
1-hydroxyphthalaz-4-one	bb
Tiron	cc

(a) G.I. Gromov, A.K. Pyartman and V.E. Mironov, Zh. Neorg. Khim., 23 (1978) 3376. (b) E.S. Domnina, L.V. Baikalova, L.E. Protasova, N.M. Deriglazov, N.N. Chipanina, D.D. Taryashinova, V.I. Skovobogatova and G.G. Skvortsova, Koord. Khim., 5 (1979) 14. (c) V.G. Ratolikar, J. Inorg. Nucl. Chem., 41 (1979) 250. (d) J. Hennion and J. Nicole, Bull. Soc. Chim. France, (1978) 426. (e) N. Kujundzic, Pharmazie, 33 (1978) 807 (Chem. Abstr., 90 (1979) 132040). (f) J.P. Kupta, B.S. Garg and R.P. Singh, J. Indian Chem. Soc., 56 (1979) 145. (g) K. Lal, Acta Chim. Acad. Sci. Hung., 99 (1979) 281. (h) D.C. Sehgel, C.P. Gupta and R.K. Mehta, Indian J. Chem., 16A (1978) 910. (i) I. Singh, B.S. Garg and R.P. Singh, Indian J. Chem., 17A (1979) 104. (j) N. Delannory, A. Delannoy, J. Hennion and J. Nicole, C.R. Acad. Sci., Ser. C, 287 (1978) 527. (k) K.A. Idress, M.M. Seleim and M.M. Khalil, Curr. Sci., 48 (1978) 343 (Chem. Abstr., 91 (1979) 67711). (l) S. Bateja, N.S. Chauhan, C. Bhandhari and N.C. Sogani, J. Inst. Chem., 50 (1978) 162 (Chem. Abstr., 90 (1979) 210998). (m) P. Mathur, D.P. Goel and R.P. Singh, Indian J. Chem., 16A (1978) 890. (n) E. Domagalina and S. Zareba, Chem. Anal., 23 (1978) 759 (Chem. Abstr., 90 (1979) 128321). (o) J. Belusky, Chem. Zvesti, 32 (1978) 450 (Chem. Abstr., 90 (1979) 128336). (p) G.I. Mashkova, A.K. Pyartman and V.E. Mironov, Koord. Khim., 5 (1979) 547. (q) A.K. Pyartman, G.I. Mashkova and V.E. Mironov, Koord. Khim., 5 (1979) 410. (r) R.W. Cattrall and M.Z. Ilic, J. Inorg. Nucl. Chem., 40 (1978) 1446. (s) A.V. Zotov and Z.Y. Kotova, Geokhimiya, (1979) 285 (Chem. Abstr., 90 (1979) 142769). (t) H.M. Sammour, F.A. Aly and F.M. Abdel-Gawad, Egypt J. Chem., 19 (1976, Publ. 1978) 551. (u) G. Somidevamma and P. Vani, Indian Chem. J., 14 (1979) 15. (v) E. Mentasti, Inorg. Chem., 18 (1979) 1512. (w) V.T. Novikov, V.P. Lopatinskii, L.A. Chernova, N.M. Novikova and V.L. Ivasenko, Deposited Doc. (1977) V INITI 3970-77 (Chem. Abstr., 90 (1979) 128328). (x) D.S. Veselinovic and D. Malesev, Glas. Hem. Drus. Beograd, 43 (1978) 545 (Chem. Abstr., 90 (1979) 110837). (y) J. Hegenaur, P. Saltman and G. Nace, Biochemistry, 18 (1979) 3865. (z) S.Y. Kuchmii and A.I. Yakima, Ukr. Khim. Zr., 45 (1979) 488 (Chem. Abstr., 91 (1979) 79659). (aa) C.L. Sharma, A.K. Sing and S.P. Pandey, J. Indian Chem. Soc., 56 (1979) 28. (bb) R.C. Jha, R. Thakur, I.B. Sukla and L. Singh, J. Indian Chem. Soc., 56 (1979) 426. (cc) E. Krezeszowska and Z. Jablonski, Pr. Nauk Politech. Szczecin, 90 (1978) 57 (Chem. Abstr., 91 (1979) 45155).

1.9 STABILITY CONSTANTS

Complexes and ligands for which stability constants have been measured are listed in Table 9.

1.10 REVIEWS

During the past year the following reviews relevant to the chemistry of iron have been published:

Carbonyls. F.S. Wagner, in Kirk—Othmer Encycl. Chem. Technol., 3rd edn., Vol. 4, Wiley, New York, 1978, p. 794.

Binuclear iron carbonyl complexes with N-containing ligands. A.N. Nesmeyanov, M.I. Rybinskaya and L.V. Rybin, Usp. Khim., 48 (1979) 393.

Thermochemistry of metal—carbon bonds. M.A.V. Ribeiro da Silva and A.M.M.V. Reis, Rev. Port. Quim., 20 (1978) 47 (Chem. Abstr., 90 (1979) 211042).

Reactions of NO coordinated to transition metals. J.A. McCleverty, Chem. Rev., 79 (1979) 53.

Dinitrogen complexes of transition metals. F. Bottomley, in F. Bottomley (Ed.), Treatise on Dinitrogen Fixation, Wiley, New York, 1979, p. 109.

Dinitrogen fixation in solution in the presence of transition metal complexes. A.E. Shilov, in F. Bottomley (Ed.), Treatise on Dinitrogen Fixation, Wiley, New York, 1979, p. 31.

Chemistry of mixed halides. R.P. Rastogi, B.L. Dubey, M. Lakshmi and I. Das, J. Sci. Ind. Res., 37 (1978) 622.

Metal tetrathiolenes. B.K. Teo, Adv. Chem. Ser., (1979) 173.

Ligand substituent effects in transition metal photochemistry. P.C. Ford, Rev. Chem. Intermed., 2 (1979) 267.

Heme proteins and metalloproteins; redox chemistry and oxygen binding. D. Dolphin, A.W. Addison, M. Cairns, R.K. Dinello, N.P. Farrell, B.R. James, D.R. Pauson and C. Welborn, Int. J. Quantum Chem., 16 (1979) 311.

Oxidation and oxygen activation by heme proteins. C.K. Chang and D. Dolphin, Bioorg. Chem., 4 (1978) 37.

What determines the oxygen affinities of the Hb and Mb? T. Asakura and M. Sono, in F.R. Longo (Ed.), Porphyrin Chemistry Advances, 1977 (Publ. 1979), p. 189.

The oxygenation of Hb. Q.H. Gibson, Porphyrins, Vol. 5, Part C, Academic Press, New York, 1978, p. 153.

Ligand binding of gases to Hb. S.J. Gill, Stud. Mod. Thermodyn., 1 (1979) 224.

Synthetic oxygen carriers related to biological systems. R.D. Jones, D.A. Summerville and F. Basolo, Chem. Rev., 79 (1979) 139.

Redox system Fe^{II}—Fe^{III} interconversion in oxygen-carrying proteins. Z. Bradic, R. Condrad, D.R. Eaton, P.C. Harrington, E. Olivas, D.J.A. De Waal and R.G. Wilkins, Symp., Biochemical and Clinical Aspects of Hemoglobin Abnormalities, Academic Press, New York, 1977 (Publ. 1978), p. 459.

Molecular evolution of Hb. J. Matsuda, Kagaku To Seibutsu, 16 (1978) 433 (Chem. Abstr., 90 (1979) 1712).

Conformational change and cooperative ligand binding in Hb. J. Otsuka and T. Kunisawa, Adv. Biophys., 11 (1978) 53.

Electronic aspects of the heme. Y. Seno and J. Otsuka, Adv. Biophys., 11 (1978) 13.

Resonance Raman studies on ligand iron interactions in hemoproteins and metalloproteins. T. Kitagawa, Y. Ozaki and Y. Kyogoku, Adv. Biophys., 11 (1978) 153.

MCD approach to hemoprotein analysis. M. Hatano and T. Nozawa, Adv. Biophys., 11 (1978) 95.

Binuclear metal complexes of cofacial diporphyrins. C.K. Chang, Adv. Chem. Ser., (1979) 173.

Oxygenases and dioxygenases. M. Nozaki, Top. Curr. Chem., 78 (1979) 145.

Isolation and purification of cytochrome P-450 and the existence of multiple forms. F.P. Guengerick, Pharmacol. Ther., 6 (1979) 99.

Multiple forms of cytochrome P-450 — criteria and significance. E.F. Johnson, Rev. Biochem. Toxicol., 1 (1979) 1.

Coordination chemistry of cytochrome P-450 and iron porphyrins. D. Mansay, Biochimie, 60 (1978) 969.

Model system studies of axial ligation in the oxidised reaction state of cytochrome P-450 enzymes. R.H. Holm, S.C. Tang, S. Koch and G.C. Papaefthymiou, Adv. Exp. Med. Biol., 74 (1976) 321.

A comparison of the structures of electron transfer proteins. E.T. Adman, Biochim. Biophys. Acta, 549 (1979) 107.

Mitochondrial cytochrome c. D.L. Brautigar, S. Ferguson-Miller and E. Margohash, Methods Enzymol., 53 (1978) 128.

Structure and function in mitochondrial-type cytochromes c. M.D. Kamen and B.J. Errede, Symp., Versatility Proteins, Academic Press, New York, 1978, p. 229.

Electron transfer by cytochromes, mechanisms and problems. M.A. Cusanovich, Symp., Frontiers of Biological Energy, Academic Press, New York, 1978, p. 100.

Mechanisms of electron transfer by high potential c-type cytochromes. M.A. Cusanovich, Bioorg. Chem., 4 (1978) 117.

Cytochromes-c_2. R.E. Dickerson and T. Takano, Symp., Frontiers of Biological Energy, Academic Press, New York, 1978, p. 107.

Iron- and manganese-containing superoxide dismutases. J.M. McCord, Adv. Exp. Med. Biol., 74 (1976) 540.

The ferritin molecule — a sink and a source of iron. P.M. Harrison and S.H. Banyard, FEBS-Symp., (Transp. Proteins), 58 (1978) 259.

REFERENCES

1 P.C. Engelking and W.C. Lineberger, J. Am. Chem. Soc., 101 (1979) 5569.
2 C.E. Housecroft, K.E. Wade and B.C. Smith, J. Chem. Soc., Chem. Commun., (1978) 765.
3 C.E. Housecroft, K.E. Wade and B.C. Smith, J. Organomet. Chem., 170 (1979) C1.
4 J.A. Connor, C.P. Demain, H.A.S. Skinner and M.T. Zafarani-Moattar, J. Organomet. Chem., 170 (1979) 117.
5 H. Beurlich, T. Madach, F. Richter and H. Vahrenkamp, Angew. Chem., 91 (1979) 751.
6 H.W. Chen, W.L. Jolly, J. Kopf and T.H. Lee, J. Am. Chem. Soc., 101 (1979) 2607.
7 C.P. Casey and S.M. Neumann, Adv. Chem. Ser., 173 (1979) 131.
8 H.A. Hodali and D.F. Shriver, Inorg. Chem., 18 (1979) 1236.
9 N. Grice, S.C. Kas and R. Pettit, J. Am. Chem. Soc., 101 (1979) 1627.
10 G.O. Evans and C.J. Newell, Inorg. Chim. Acta, 31 (1978) L387.
11 D.J. Darensbourg, M.Y. Darensbourg, N. Walker, J.A. Froelich and K.L.C. Barros, Inorg. Chem., 18 (1979) 1401.
12 J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker and J.C. Selover, Inorg. Chem., 18 (1979) 553.
13 D.R. Tyler, M.A. Schmidt and H.B. Gray, J. Am. Chem. Soc., 101 (1979) 2753.
14 J.A.S. Howell and P. Mathur, J. Organomet. Chem., 174 (1979) 335.
15 D.J. Thornhill and A.R. Manning, Inorg. Chim. Acta, 33 (1979) 45.
16 A.J. White, J. Organomet. Chem., 168 (1979) 197.
17 B.V. Johnson, D.P. Sturtzel and J.E. Shade, Inorg. Chim. Acta, 32 (1979) 243.
18 K.S. Wong, W.R. Scheidt and J.A. Labinger, Inorg. Chem., 18 (1979) 136.
19 M.D. Curtis and P.J. Klingler, J. Organomet. Chem., 161 (1978) 23.
20 J.P. Barbier and P. Braunstein, J. Chem. Res. (S), (1978) 412.

21 A.J. Carty, G.N. Mott and N.J. Taylor, J. Am. Chem. Soc., 101 (1979) 3131.

22 A.E. Mauro, Edetica Quim., 3 (1978) 27 (Chem. Abstr., 90 (1979) 179331); A.E. Mauro, Y. Hase and O. Sala, J. Mol. Struct., 51 (1979) 9.

23 J.M. Burlitch and R.C. Winterton, Inorg. Chem., 18 (1979) 2309.

24 F. Glockling, V.B. Mahale and J.J. Sweeney, J. Chem. Soc., Dalton Trans., (1979) 767.

25 J.M. Burlitch, M.E. Leonowicz, R.B. Preston and R.E. Hughes, Inorg. Chem., 18 (1979) 1097.

26 W. Malisch and W. Ries, Chem. Ber., 112 (1979) 1304.

27 J.V. Scribelli and M.D. Curtis, Synth. React. Inorg. Met.-Org. Chem., 8 (1978) 399.

28 J.D. Cotton, J. Organomet. Chem., 159 (1978) 465.

29 T. Kruck, W. Theilmann and C. Sauer, Z. Naturforsch., 33B (1978) 1291.

30 H. Behrens, K. Goerting, P. Merbach and M. Moll, Z. Anorg. Allg. Chem., 454 (1979) 67.

31 R.B. King and S. Goel, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 139.

32 S.B. Butts and D.F. Shriver, J. Organomet. Chem., 169 (1979) 191.

33 H. Schumann and J. Opitz, J. Organomet. Chem., 166 (1979) 233.

34 D.W. Bennett and R.W. Parry, J. Am. Chem. Soc., 101 (1979) 753.

35 W. Clegg and S. Morton, Inorg. Chem., 18 (1979) 1189.

36 H. Vahrenkamp and E. Keller, Chem. Ber., 112 (1979) 1991.

37 G.N. Mott and A.J. Carty, Inorg. Chem., 18 (1979) 2926.

38 J.C. Burt, R. Boese and G. Schmidt, J. Chem. Soc., Dalton Trans., (1978) 1387.

39 H.J. Langenbach, E. Keller and H. Vahrenkamp, J. Organomet. Chem., 171 (1979) 259.

40 G. Huttner, G. Mohr, P. Friedrich and H.G. Schmidt, J. Organomet. Chem., 160 (1978) 59; G. Huttner, G. Mohr and P. Friedrich, Z. Naturforsch., 33B (1978) 1254.

41 J.C. Burt and G. Schmidt, J. Chem. Soc., Dalton Trans., (1978) 1385; F. Richter, H. Beurich and H. Vahrenkamp, J. Organomet. Chem., 166 (1979) C5.

42 G. Thiollet and F. Mathey, Inorg. Chim. Acta, 35 (1979) L331.

43 G. Thiollet, F. Mathey and R. Poilblanc, Inorg. Chim. Acta, 32 (1979) L67.

44 E.W. Abel and C. Towers, J. Chem. Soc., Dalton Trans., (1979) 814.

45 S.M. Grant and A.R. Manning, Inorg. Chim. Acta, 31 (1978) 41.

46 J.P. Barbier, P. Dapporto, L. Sacconi and P. Stoppioni, J. Organomet. Chem., 171 (1979) 185.

47 N.S. Nametkin, V.D. Tyurin, G.G. Aleksandrov, O.V. Kuz'min, A.I. Nekhaev, V.G. Andrianov, M. Mavlonov and Y.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1353.

48 R. Rossetti, G. Gervasio and P.L. Stanghellini, Inorg. Chim. Acta, 35 (1979) 73.

49 D. Seyferth and R.S. Henderson, J. Am. Chem. Soc., 101 (1979) 508.

50 R. Mathieu, R. Poilblanc, P. Lemoine and M. Gross, J. Organomet. Chem., 165 (1979) 243.

51 M.S. Arabi, R. Mathieu and R. Poilblanc, Inorg. Chim. Acta, 34 (1979) L207.

52 A. Shaver, P.J. Fitzpatrick, K. Steliou and I.S. Butler, J. Am. Chem. Soc., 101 (1979) 1313.

53 D. Sellmann and E. Unger, Z. Naturforsch., 33B (1978) 1438.

54 N.S. Nametkin, V.D. Tyurin and M.A. Kulina, Neftekhimiya, 18 (1978) 807 (Chem. Abstr., 90 (1979) 80137).

55 R. Meij, D.J. Stufkens, K. Vrieze, A.M.F. Brouwers, D.J. Schagen, J.J. Zwinselman, A.R. Overbeek and C.H. Stam, J. Organomet. Chem., 170 (1979) 337.

56 H. Van Dam, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 31 (1978) L377; E.L. Anderson and T.P. Fehlner, Inorg. Chem., 18 (1979) 2325.

57 F. Richter and H. Vahrenkamp, Angew. Chem., 90 (1978) 916.

58 H. Le Bozec, A. Gorgues and P. Dixneuf, J. Organomet. Chem., 174 (1979) C24.

59 C.A. Poffenberger and A. Wojcicki, J. Organomet. Chem., 165 (1979) C5.

60 (a) D. Touchard, H. Le Bozec and P. Dixneuf, Inorg. Chim. Acta, 33 (1979) L141; (b) N. Iordanov and D. Shopov, Inorg. Chim. Acta, 31 (1978) 31.

61 B.J. Plankey and J.V. Rund, Inorg. Chem., 18 (1979) 957.
62 K.D. Hodges, R.G. Wollmann, S.L. Kessel, D.N. Hendrickson, D.G. Van Derveer and E.K. Barefield, J. Am. Chem. Soc., 101 (1979) 906.
63 P. Thomas, D. Reborek, V.I. Nefedov and E.K. Zhumadilov, Z. Anorg. Allg. Chem., 448 (1979) 167.
64 F. Bottomley and P.S. White, Acta Crystallogr., B35 (1979) 2193.
65 B. Jezowska-Trzebiatowska and A. Keller, Bull. Acad. Pol. Sci., Ser. Sci. Chem., 26 (1978) 891.
66 J.M. Bassett, M. Green, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1978) 1000.
67 T.V. Harris, J.W. Rathke and E.L. Muetterties, J. Am. Chem. Soc., 100 (1978) 6966.
68 R.B. King and M. Chang, Inorg. Chem., 18 (1979) 364.
69 M.S. Saini, D.M. Puri, S.N. Dubey and D.C. Gupta, J. Indian Chem. Soc., 56 (1979) 201.
70 L.D. Arutyunyan, Y.I. Ponomarev, L.O. Atovmyan, E.A. Lavrent'eva and M.L. Khidekel, Koord. Khim., 5 (1979) 943.
71 J.A.J. Basten, Q.A.G. Van Vlimmeren and W.J.M. De Jonge, Phys. Rev., B18 (1978) 2179.
72 T.W. Balcerek, L. Cathey and D.G. Karraker, J. Inorg. Nucl. Chem., 40 (1978) 773.
73 C.F.V. Mason, M.G. Bowman and M.A. David, J. Inorg. Nucl. Chem., 40 (1978) 1739.
74 M. Cola, M.T. Ganzeli-Valentini and P.A. Borroni, J. Inorg. Nucl. Chem., 40 (1978) 1041.
75 K.N. Mikhalevich, O.I. Kuntyi and D.I. Semenishin, Koord. Khim., 4 (1978) 1695.
76 D.F. Mullica and M.O. Milligan, Inorg. Nucl. Chem. Lett., 15 (1979) 1.
77 B. Morosin, Acta Crystallogr., B34 (1978) 3730.
78 K. Fukumura and T. Kobayashi, J. Phys. Colloq., (1979) 373 (Chem. Abstr., 90 (1979) 195940).
79 S.P. Rao, S.R. Singh and S.R. Bandakavi, Proc. Indian Natl. Sci. Acad., 44A (1978) 333.
80 E. Fluck, H. Inoue, M. Nagao and S. Yanagisawa, J. Inorg. Nucl. Chem., 41 (1979) 287.
81 G. Del V. Moreno, N.E. Katz, J.A. Olabe and P.J. Aymonino, Inorg. Chim. Acta, 35 (1979) 183.
82 J.L. Brisset, M. Biquard and V.I. Limbi, C.R. Acad. Sci., Ser. C, 288 (1979) 513.
83 S. Del V. Alonso, C.O. Della Vedova, N.E. Katz, M.A. Martinez and P.J. Aymonino, J. Inorg. Nucl. Chem., 40 (1978) 2074.
84 N.E. Katz, J.A. Olabe and P.J. Aymonino, J. Inorg. Nucl. Chem., 41 (1979) 410.
85 A. Yeh, A. Haim, M. Tanner and A. Ludi, Inorg. Chim. Acta, 33 (1979) 51.
86 A.Y. Sychev, Y.I. Skurlatov, V.G. Isak and M.H. Hiem, Zh. Fiz. Khim., 52 (1978) 2936; 2938.
87 M. Mikami, M. Konno and Y. Saito, Chem. Phys. Lett., 63 (1979) 566.
88 A.M. Greenaway, C.J. O'Connor, A. Schrock and E. Sinn, Inorg. Chem., 18 (1979) 2692.
89 L. Johansson, M. Molund and O.A. Oskarsson, Inorg. Chim. Acta, 31 (1978) 117.
90 E. Koenig, R. Schnakig, G. Ritter, W. Irler, B. Kanellokopulos and B. Powietzka, Inorg. Chim. Acta, 35 (1979) 239.
91 B.W. Dockum and W.M. Reiff, Inorg. Chim. Acta, 35 (1979) 285.
92 M.J. Blandamer, J. Burgess and D.L. Roberts, J. Chem. Soc., Dalton Trans., (1978) 1086.
93 M.J. Blandamer, J. Burgess, P. Cookson, D.L. Roberts, P. Wellings, F.M. Mekhail and P. Askalani, J. Chem. Soc., Dalton Trans., (1978) 996.
94 R.D. Gillard, R.J. Lancashire and P.A. Williams, Transition Met. Chem., 4 (1979) 115.
95 J. Burgess and R.I. Haines, J. Chem. Soc., Dalton Trans., (1978) 1447.
96 J. Lewis and K.P. Wainwright, Inorg. Chim. Acta, 34 (1979) 57.

97 H.H. Wei and L.R. Leu, J. Phys. Colloq., (1979) 355 (Chem. Abstr., 90 (1979) 196744).
98 V.M.S. Gil, R.D. Gillard, P.A. Williams and R.S. Vagg, Transition Met. Chem., 4 (1979) 14.
99 P.T. Joseph, C. Pavithran, K.G.G. Warrier and C.P. Prabhakaran, Transition Met. Chem., 3 (1978) 286.
100 M.J.M. Campbell, R. Grzeskowiak and G.S. Juneja, J. Inorg. Nucl. Chem., 40 (1978) 1507.
101 R.G. Goel, P.M. Henry and P.C. Polyzon, Inorg. Chem., 18 (1979) 2148.
102 G. Ferraudi, Inorg. Chem., 18 (1979) 1576.
103 C.E. Holloway, D.V. Stynes and C.P.J. Vuik, J. Chem. Soc., Dalton Trans., (1979) 124.
104 I. Collamati, Inorg. Chim. Acta, 35 (1979) L303.
105 C. Ercolani, F. Monacelli and G. Rossi, Inorg. Chem., 18 (1979) 712.
106 S. Maroie, M. Savy and J.J. Verbist, Inorg. Chem., 18 (1979) 2560.
107 K.C. Pati, R. Soundarajan and V.R.P. Verneker, Proc. Indian Acad. Sci., 88A (1979) 211.
108 A. Anagostopoulos, D. Nicholls and J. Reed, Inorg. Chim. Acta, 32 (1979) L17.
109 F. Capitan, E.J. Alonso and R.M. Jimenez, Afinidad, 35 (1978) 25 (Chem. Abstr., 90 (1979) 161393).
110 D. Kovacs and R.E. Shepherd, Inorg. Biochem., 10 (1979) 67.
111 B. Crociani, M. Nicolini and R.L. Richards, J. Chem. Soc., Dalton Trans., (1978) 1478.
112 M. Nagao, H. Inoue and S. Yanagisawa, J. Inorg. Nucl. Chem., 40 (1978) 1686.
113 R.C. Paul, R.C. Kumar and R.D. Verma, J. Indian Chem. Soc., 56 (1979) 251.
114 U. Russo, S. Calogero, N. Burriesci and M. Petrera, J. Inorg. Nucl. Chem., 41 (1979) 25; U. Russo, R. Graziani, S. Calogero and U. Castellato, Transition Met. Chem., 4 (1979) 82.
115 D.G. Batyr and M.V. Shopron, Koord. Khim., 5 (1979) 618.
116 M.P. Starysh, I.I. Bulgak and D.K. Batyr, Koord. Khim., 4 (1978) 1690.
117 H.C. Rai, A.K. Jena and B. Sahoo, Inorg. Chim. Acta, 35 (1979) 29.
118 J.T. Wrobleski and D.B. Brown, Inorg. Chem., 18 (1979) 498.
119 M. Mohan, H.C. Khera, S.G. Mittal and A.K. Sirivastava, Gazz. Chim. Ital., 108 (1978) 523.
120 A.N. Speca, L.S. Gelfand, F.J. Iaconianni, L.L. Pytlewski, C.M. Mikulski and N.M. Karayannis, Inorg. Chim. Acta, 33 (1979) 195.
121 D.E. Chasan, L.L. Pytlewski, C. Owens and N.M. Karayannis, J. Inorg. Nucl. Chem., 40 (1978) 1019.
122 D.E. Chasan, L.L. Pytlewski, C. Owens and N.M. Karayannis, J. Inorg. Nucl. Chem., 41 (1979) 13.
123 L.S. Gelfand, L.L. Pytlewski, D.L. Cosgrove, C.M. Mikulski, A.N. Speca and N.M. Karayannis, Inorg. Chim. Acta, 32 (1979) 59.
124 F.J. Iaconianni, L.S. Gelfand, L.L. Pytlewski, C.M. Mikulski, A.N. Speca and N.M. Karayannis, Inorg. Chim. Acta, 36 (1979) 97.
125 C.M. Mikulski, J. Unruh, L.L. Pytlewski and N.M. Karayannis, Transition Met. Chem., 4 (1979) 98.
126 C.M. Mikulski, L.L. Pytlewski and N.M. Karayannis, Inorg. Chim. Acta, 32 (1979) 263.
127 C.M. Mikulski, W. Henry, L.L. Pytlewski and N.M. Karayannis, J. Inorg. Nucl. Chem., 40 (1978) 769.
128 I.A. Rozanov, L.Y. Medvedeva and E.N. Beresnev, Zh. Neorg. Khim., 23 (1978) 2259.
129 D. Coucouvanis, D. Swenson, P. Stremple and N.C. Baenziger, J. Am. Chem. Soc., 101 (1979) 3392.
130 C.A. Yong, B.W. Fitzsimmons, L.F. Larkworthy and S.E. Al-Mukhtar, Inorg. Chim. Acta, 33 (1979) 249.

131 S.D. Ittel, A.D. English, C.A. Tolman and J.P. Jesson, Inorg. Chim. Acta, 33 (1979) 101.

132 C.S. Creaser and W.C. Kaska, Inorg. Chim. Acta, 30 (1978) L325.

133 R.V. Parish and B.F. Riley, J. Chem. Soc., Dalton Trans., (1979) 482.

134 P.M. Treichel and D.C. Molzahn, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 21.

135 M. Goodgame and K.W. Johns, J. Chem. Soc., Dalton Trans., (1978) 1294.

136 R.G. Bhattacharya and I. Bhaduri, J. Inorg. Nucl. Chem., 40 (1978) 733.

137 (a) K.A. Idress, M.M. Seleim and M.M. Khalil, Monatsh. Chem., 109 (1978) 1383; (b) M.J. Blandmer, J. Burgess, R.I. Haines, F.M. Mekhail and P. Askalani, J. Chem. Soc., Dalton Trans., (1978) 1001.

138 S.E. Wenk and F.A. Schultz, J. Electroanal. Chem. Interfacial Electrochem., 101 (1979) 89 (Chem. Abstr., 91 (1979) 99125).

139 M. Vidali, G. Rizzardi, P. Vigato, U. Castellato, S. Kida and H. Okawa, Inorg. Chim. Acta, 34 (1979) 19.

140 N. Torihara, H. Okawa and S. Kida, Chem. Lett., (1979) 683.

141 K.G.K. Warrier, C. Pavithran and P.K. Pillai, J. Inst. Chem. (India), 50 (1978) 221 (Chem. Abstr., 91 (1979) 48692).

142 K.K. Narang and A. Bindal, J. Sci. Banaras Hindu Univ., 28 (1978) 139 (Chem. Abstr., 90 (1979) 214464).

143 N.S.V.S. Rao, M.C. Ganorkar, B.K.M. Murali and C.P. Ramaswamy, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 27 (1979) 29.

144 M. Mohan, H.C. Khera, S.G. Mittal and A.K. Srivastava, Gazz. Chim. Ital., 109 (1979) 65.

145 K.P. Dubey, C.N. Kachru and B.L. Wazir, J. Chin. Chem. Soc. (Taipei), 26 (1979) 37 (Chem. Abstr., 91 (1979) 67736).

146 S.E. Livingstone and J.E. Oluka, Transition Met. Chem., 3 (1978) 261.

147 N.K. Sankhla, C.P. Gupta and R.K. Mehta, Curr. Sci., 47 (1978) 850 (Chem. Abstr., 90 (1979) 65924).

148 R.C. Aggarwal, N.K. Singh and R.P. Singh, Inorg. Chim. Acta, 32 (1979) L87.

149 R.C. Aggarwal and R.T. Rao, J. Inorg. Nucl. Chem., 40 (1978) 1177.

150 R.C. Aggarwal and B. Singh, J. Inorg. Nucl. Chem., 40 (1978) 1174.

151 A. Akbar Ali and S.G. Teoh, J. Inorg. Nucl. Chem., 40 (1978) 2013.

152 R.C. Aggarwal and B. Singh, Z. Anorg. Allg. Chem., 445 (1978) 227.

153 (a) H.K.J. Powell and J.M. Russell, Aust. J. Chem., 31 (1978) 2409; (b) R.B.S. Rao, S. Gupta and A. Chakravorty, Transition Met. Chem., 4 (1979) 42.

154 G. Ferey, A.M. Leclerc, R. De Pape, J.P. Mariot and F. Varret, Solid State Commun., 29 (1979) 477.

155 E. Banks, S. Nakajima and G.J.B. Williams, Acta Crystallogr., B35 (1979) 46.

156 N.W. Gregory, J. Phys. Chem., 83 (1979) 688.

157 Y. Saeki, R. Mutsuzaki and S. Fujiwara, Bull. Chem. Soc. Jpn., 51 (1978) 3527.

158 L.D. Arutyunyan, L.I. Atovmyan, E.A. Lavrent'eva, I.P. Lavrent'eva, V.I. Ponomarev and M.L. Khidekel, Dokl. Akad. Nauk SSSR, 243 (1978) 948.

159 B.N. Figgis, C.L. Raston, R.P. Sharma and A.H. White, Aust. J. Chem., 31 (1978) 2717.

160 P.W. Smith and R. Stoessiger, J. Magn. Reson., 31 (1978) 431.

161 M.T. Kovarnechan, J. Roziere and D. Mascherpa-Corral, J. Inorg. Nucl. Chem., 40 (1978) 2009.

162 N. Caswell and S.A. Solin, Solid State Commun., 27 (1978) 961.

163 Y. Nishida, A. Sumita, K. Hayasida, H. Kyushu, S. Kida and Y. Maeda, J. Coord. Chem., 9 (1979) 161.

164 A.C. Melnyk, N.K. Kildahl, A.R. Rendina and D.H. Busch, J. Am. Chem. Soc., 101 (1979) 3232.

165 W.S. Walters, R.D. Gillard and P.A. Williams, Aust. J. Chem., 31 (1978) 1959.

166 M.E. Fernandopulle, P.A. Gillespie and W.R. McWhinnie, Inorg. Chim. Acta, 29 (1978) 197.

167 H. Drevs, Z. Chem., 19 (1979) 31.
168 A.A. Abushamleh and H.A. Goodwin, Aust. J. Chem., 32 (1979) 513.
169 S.A.A. Zaidi and M.A. Neyazi, Transition Met. Chem., 4 (1979) 164.
170 M. Magini, J. Chem. Phys., 70 (1979) 317.
171 G.N. Goncharov, A.A. Efimov, A.V. Kalyamin and S.B. Tomilov, Zh. Obshch. Khim., 48 (1978) 2398.
172 C. Delmas, R. Olazcuaga, F. Cherkaoui, R. Brochu and G. Le Flem, C.R. Acad. Sci., Ser. C, 287 (1978) 169.
173 A.Z. Berlina, K.M. Zhumanova, Z.M. Muldakhmetov and A.V. Bobrov, Zh. Neorg. Khim., 24 (1979) 2255.
174 I.P. Lorenz, Inorg. Nucl. Chem. Lett., 15 (1979) 127.
175 J.V. Singh, N.C. Jain and R.C. Mehrota, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 79.
176 A. Treciak, T. Szymanska-Buzar and J.J. Ziolowski, Pol. J. Chem., 53 (1979) 981.
177 R.A. Stukam, K.I. Turta, A.V. Ablov and S.A. Bobkova, Koord. Khim., 5 (1979) 95.
178 G. Roewer, G. Kempe, K. Kretschmer and E. Wieser, J. Prakt. Chem., 321 (1979) 75.
179 J.T. Wrobleski and D.B. Brown, Inorg. Chim. Acta, 35 (1979) 109.
180 (a) S.K. Dhar and S. Sickak, J. Inorg. Nucl. Chem., 41 (1979) 126; (b) J.J. Habeeb, D.G. Tuck and F.W. Walters, J. Coord. Chem., 8 (1978) 27.
181 M.P. Granchi and B.E. Douglas, J. Coord. Chem., 8 (1978) 149.
182 D.E. Chasan, L.L. Pytlewski, C. Owens and N.M. Karayannis, Chem. Chron., 8 (1979) 53.
183 K.D. Ghuge, P. Umapathy and D.N. Sen, J. Indian Chem. Soc., 55 (1978) 864.
184 V. Vancova, M. Melnik and G. Ondrejovic, Proc. Conf. Coord. Chem., (1976) 273.
185 R.M. Buchanan, S.L. Kessel, H.H. Downs, C.G. Pierpont and D.N. Hendrickson, J. Am. Chem. Soc., 100 (1978) 7894; D.G. Brown and W.L. Johnson, Z. Naturforsch., 34B (1979) 712.
186 J. Albertson, A. Oskarsson and M. Nyren, Acta Crystallogr., B35 (1979) 1473.
187 D.F. Evans and T.A. James, J. Chem. Soc., Dalton Trans., (1979) 723.
188 J. Stach, W. Dietzsch and R. Kirmse, Z. Chem., 19 (1979) 73.
189 D. Sellman, P. Kreutzer, G. Huttner and A. Frank, Z. Naturforsch., 33B (1978) 1341.
190 P.M. Treichel, D.C. Molzahn and K.P. Wagner, J. Organomet. Chem., 174 (1979) 191.
191 A.R. Amundsen, J. Whelan and B. Bosnich, Inorg. Chem., 18 (1979) 206.
192 E.M. Holt, S.L. Holt and M. Vlasse, Cryst. Struct. Commun., 8 (1979) 645.
193 A. Malek, G.C. Dey, A. Nasreen, T.A. Chowdhury and E.C. Alyea, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 145.
194 D.K. Rastogi, S.K. Dua, V.B. Rana and S.K. Sahni, J. Inorg. Nucl. Chem., 40 (1978) 1323.
195 R.N. Kapadia, Indian J. Chem., 16A (1978) 1103.
196 H.H. Pandey, L. Mishra and V.J. Ram, Acta Chim. Acad. Sci. Hung., 98 (1978) 77.
197 B.B. Kaul and K.B. Pandeya, J. Inorg. Nucl. Chem., 40 (1978) 1035.
198 N.I. Belichuk, V.V. Zelentsov, V.N. Kaftanat, A.K. Stroeska and R.A. Stukan, Koord. Khim., 5 (1979) 1025.
199 L.R. Gahan and M.J. O'Connor, Inorg. Chim. Acta, 31 (1978) 465.
200 D. Petridis, D. Niarchos and B. Kanellakopulos, Inorg. Chem., 18 (1979) 505.
201 Y. Tsuda and S. Nakajima, Chem. Lett., (1978) 1397.
202 L.L. Shorina and A.V. Polishchuk, Vopr. Khim. Khim. Tekhnol., 53 (1978) 30.
203 P. Peshev and M. Pecheva, Mater. Res. Bull., 13 (1978) 1167.
204 G. Pouillard, M.S. Alam, M.C. Trinel-Dufour and P. Perrot, C.R. Acad. Sci., Ser. C, 288 (1979) 517.
205 T. Ishiguro, K. Tanaka, F. Marumo, M.G.M. Ismail, S. Hirano and S. Somiya, Acta Crystallogr., B34 (1978) 3346.
206 B. Durrand and J.M. Paris, Ann. Chim., 4 (1979) 123.
207 R.R. Zakirov, B.I. Popov and A.D. Tsyganov, React. Kinet. Catal. Lett., 9 (1978) 61.

208 E. Koyama, I. Wakai and K. Nagashima, Nippon Kagaku Kaishi, (1979) 793 (Chem. Abstr., 91 (1979) 101213).

209 G.N. Stepanov and V.N. Agartanova, Magnit. Svoistva Plenoch Masivn. Materialou, (1977) 37 (Chem. Abstr., 90 (1979) 47597).

210 N. Ravi and R. Jagannathan, J. Phys. Chem. Solids, 39 (1978) 1337.

211 M.P. Gupta, A.P.B. Smith and S.K. Dat, J. Phys. Chem. Solids, 39 (1978) 1321.

212 L. Maijs and I. Vevere, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1979) 59 (Chem. Abstr., 90 (1979) 19332).

213 A.A. Morozov, A.K. Rozanov and G.A. Sidorenko, Dokl. Akad. Nauk SSSR, 242 (1978) 1352.

214 P. Taylor and D.W. Shoesmith, Can. J. Chem., 56 (1978) 2797.

215 L.E. Rendon-Diazmiron and H. Steinfink, J. Solid State Chem., 27 (1979) 261.

216 J.C. Jumas, E. Philippot and M. Mauria, Acta Crystallogr., B35 (1979) 2195.

217 A. Leclerc and M.G. Townsend, J. Phys. Chem. Solids, 39 (1978) 687.

218 M. Sugitani, N. Kinomura, M. Koizumi and S. Kume, J. Solid State Chem., 26 (1978) 195; W. Jeitschko and D.J. Braun, Acta Crystallogr., B34 (1978) 3196.

219 J.A. Linn and A.F. Schreiner, Inorg. Chim. Acta, 35 (1979) L339.

220 I.B. Bersuker, S. Stavrov and B.G. Vekhter, Biofizika, 24 (1979) 413 (Chem. Abstr., 91 (1979) 51453).

221 J.R. Budge, P.E. Ellis, R.D. Jones, J.E. Linard, F. Basolo, J.E. Baldwin and R.L. Dyer, J. Am. Chem. Soc., 101 (1979) 4760.

222 M. Momenteau, B. Loock, J. Mispelter and E. Bisagni, Nouv. J. Chim., 3 (1979) 77.

223 H. Ledon and Y. Brigandat, J. Organomet. Chem., 165 (1979) C25.

224 J.P. Collman and K.S. Suslick, Pure Appl. Chem., 50 (1978) 951.

225 F.C. Mills, G.K. Ackers, H.T. Gaud and S.J. Gill, J. Biol. Chem., 254 (1979) 2875; F.C. Mills and G.K. Ackers, J. Biol. Chem., 254 (1979) 2881.

226 J.S. Valentine and E. McCandlish, Front. Biol. Energy, Int. Symp., 2 (1978) 933.

227 T. Mincey and T.G. Traylor, J. Am. Chem. Soc., 101 (1979) 765.

228 J.W. Buchler, W. Kokisch, P.D. Smith and B. Tonn, Z. Naturforsch., 33B (1978) 1371.

229 G.B. Jameson and J.A. Ibers, Inorg. Chem., 18 (1979) 1200.

230 W.R. Scheidt, I.A. Cohen and M.E. Kastner, Biochemistry, 18 (1979) 3546.

231 K. Hatano and W.R. Scheidt, Inorg. Chem., 18 (1979) 877.

232 K.M. Adams, P.G. Rasmussen, W.R. Scheidt and K. Hatano, Inorg. Chem., 18 (1979) 1892.

233 A. Vogler, B. Rethwisch, H. Kunkely and J. Huettermann, Angew. Chem., 90 (1978) 1011.

234 M. Chikira, H. Kon and K.M. Smith, J. Chem. Soc., Chem. Commun., (1978) 906.

235 D. Ostfeld and J.A. Colfax, in F.R. Longo (Ed.), Porphyrin Chem. Adv., Symp., (1979) 273.

236 E.W. Ainscough, A.W. Addison, D. Dolphin and B.R. James, J. Am. Chem. Soc., 100 (1978) 7585.

237 S.P. Cramer, J.H. Dawson, K.O. Hodgson and L.P. Hager, J. Am. Chem. Soc., 100 (1978) 7282.

238 V. Ullrich, H. Sakuri and H.H. Ruf, Acta Biol. Med. Ger., 38 (1979) 287.

239 T.G. Traylor and T. Mincey, Acta Biol. Med. Ger., 38 (1979) 351.

240 C. Bonfils, P. Debey and P. Maurel, Biochem. Biophys. Res. Commun., 88 (1979) 1301.

241 H. Ledon, C.R. Acad. Sci., Ser. C, 288 (1979) 29; (a) C.K. Chang and M.S. Kuo, J. Am. Chem. Soc., 101 (1979) 3413.

242 R.F. Pasternak, Biochem. Soc. Trans., 6 (1978) 1342; R.F. Pasternak and B. Halliwell, J. Am. Chem. Soc., 101 (1979) 1026.

243 L. Castle and J.R. Lindsey-Smith, J. Chem. Soc., Chem. Commun., (1978) 704.

244 H. Yamamoto, H. Takei, T. Yamamoto and M. Kimura, Chem. Pharm. Bull., 27 (1979) 789.

245 A. Labhardt and C. Yeun, Nature (London), 277 (1979) 150; (a) D.A. Buckingham and T.B. Rauchfuss, J. Chem. Soc., Chem. Commun., (1978) 705.
246 C.A. Reed, T. Mashiko, S.P. Bentley, M.E. Kastner, W.R. Scheidt, K. Spartalian and G. Lang, J. Am. Chem. Soc., 101 (1979) 2948.
247 R.K. Poole, A.J. Waring and B. Chance, FEBS Lett., 101 (1979) 56.
248 I. Tabushi, K. Yamamura and T. Nishiga, J. Am. Chem. Soc., 101 (1979) 2785.
249 B. Chance, L. Powers and J.S. Leigh, in F.R. Longo (Ed.), Porphyrin Chem. Adv., Symp., (1979) 9.
250 T.S. King, L. Yu, C.A. Yu and Y.H. Wei, Dev. Biochem., (1979) 53.
251 F. Adar and M. Erecinska, Biochemistry, 17 (1978) 5484.
252 R. Schulman, P. Eisenberger, B.K. Teo, B.M. Kincaid and G.S. Brown, J. Mol. Biol., 124 (1978) 305.
253 K.D. Watenpaugh, L.C. Sieker and L.H. Jensen, J. Mol. Biol., 131 (1979) 509.
254 T. Tuskihara, K. Fukuyama, H. Tahara, Y. Katsube, Y. Matsuura, N. Tanaka, M. Kakudo, K. Wada and H. Masubara, J. Biochem., 84 (1978) 1645.
255 J.G. Norman, B.J. Kalbacher and S.C. Jackels, J. Chem. Soc., Chem. Commun., (1978) 1027.
256 F.A. Armstrong and G.A. Sykes, J. Am. Chem. Soc., 100 (1978) 7710.
257 G. Cristou and C.D. Garner, J. Chem. Soc., Dalton Trans., (1979) 1093.
258 J.M. Berg, K.O. Hodgson and R.H. Holm, J. Am. Chem. Soc., 101 (1979) 4586.
259 C.J. Coles, R.H. Holm, D.M. Kurtz, W.H. Orme-Johnson, J. Rawlings, T.P. Singer and G.B. Wong, Proc. Natl. Acad. Sci. U.S.A., 76 (1979) 3805; B.L. Trumpower and C.E. Edwards, FEBS Lett., 100 (1979) 13.
260 D.C. Stout, J. Biol. Chem., 254 (1979) 3598.
261 S. Seki, M. Hagiwara, K. Kudo and M. Ishimoto, J. Biochem., 85 (1979) 833.
262 G. Cristou, B. Ridge and H.N. Rydon, J. Chem. Soc., Chem. Commun., (1979) 20.
263 J.L. Lambert and J.V. Paulstelis, Report 1977, Contrib.-194W78-08141 OWRR-A-062 Kan(1) (Chem. Abstr., 90 (1979) 112930).
264 R.G. Bowman and R.L. Burwell, J. Am. Chem. Soc., 101 (1979) 2877.
265 S.R. Scott, G. Cristou, C.D. Garner, T.J. King, F.E. Mabbs and R.M. Miller, Inorg. Chim. Acta, 35 (1979) L337.
266 G. Cristou, C.D. Garner, F.E. Mabbs and M.G.B. Drew, J. Chem. Soc., Chem. Commun., (1979) 91.
267 E.P. Paques, A. Paques and R.R. Crichton, J. Mol. Catal., 5 (1979) 363.
268 S.R. Cooper, J.V. McArdle and K.N. Raymond, Proc. Natl. Acad. Sci. U.S.A., 75 (1978) 3551.
269 W.R. Harris, C.J. Carrano and K.N. Raymond, J. Am. Chem. Soc., 101 (1979) 2213.
270 C.J. Carrano, S.R. Cooper and K.N. Raymond, J. Am. Chem. Soc., 101 (1979) 599.
271 W.R. Harris, C.J. Carrano and K.N. Raymond, J. Am. Chem. Soc., 101 (1979) 2722.
272 F.L. Weitl and K.N. Raymond, J. Am. Chem. Soc., 101 (1979) 2728; W.R. Harris, F.L. Weitl and K.N. Raymond, J. Chem. Soc., Chem. Commun., (1979) 177.
273 P.M. Gormley, J.S. Loehr, B. Brinhall and M.A. Hermodson, Biochem. Biophys. Res. Commun., 85 (1978) 1360.
274 Y. Suguica, Biochem. Biophys. Res. Commun., 87 (1979) 649.