Coordination Chemistry Reviews, 120 (1992) 325–359
Elsevier Science Publishers B.V., Amsterdam

Model systems containing pyrazole chelates and related groups: recent developments and perspectives

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(Received 18 November 1991)

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ABBREVIATIONS

biz	benzimidazole
iz	imidazole
py	pyridine
pz	pyrazole
Hc	hemocyanin
His	histidine
Hr	hemerythrine
Tyr	tyrosine
CA	carbonic anhydrase
PAP	purple acid phosphatase
NaOTs	toluene-4-sulphonic acid sodium salt
MPDP	*m*-phenylenedipropionate
bpeap	2-{bis[2-(pyrazol-1-yl)ethyl]amino}phenol
BICOH	bis(1-methylimidazol-2-yl)carbinol

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BiPhMe	bis(1-methylimidazol-2-yl)phenylmethoxymethane
$HBpz_3$	hydrotris(pyrazol-1-yl)borate
H_2Bpz_2	dihydrobis(pyrazol-1-yl)borate
$HB(3,5\text{-}Me_2pz)_3$	hydrotris(3,5-dimethylpyrazol-1-yl)borate
$HB(3,5\text{-}iPr_2pz)_3$	hydrotris(3,5-diisopropylpyrazol-1-yl)borate
$HB(3\text{-}t\text{-}but\text{-}5\text{-}Mepz)_3$	hydrotris(3-*t*-butyl-5-methylpyrazol-1-yl)borate
Hbpeac	2,6-bis{bis[2-(pyrazol-1-yl)ethyl]amino}-*p*-cresol
Hbimp	2,6-bis[bis(1-methylimidazol-2-ylmethyl)aminomethyl]-*p*-cresol
HCAB-Me	2,6-bis[bis(1-methylbenzimidazol-2-ylmethyl)aminomethyl]-*p*-cresol
HL-Et	*N*,*N*,*N*′,*N*′-tetrakis(1-methylbenzimidazol-2-ylmethyl)-2-hydroxy-1,3-diaminopropane
$mxyN_6$	α,α′-bis{bis[2-(3,5-dimethylpyrazol-1-yl)ethyl]amino}-*m*-xylene
$m\text{-}XYLPy_6$	α,α′-bis{bis[2-(2-pyridyl)ethyl]amino}-*m*-xylene
np_3	tris[2-(diphenylphosphino)ethyl]amine
timm	tris(1-methylimidazol-2-yl)methoxymethane
TIP	tris(imidazol-2-yl)phosphine
TMIP	tris(1-methylimidazol-2-yl)phosphine
2-TIC	tris(1-methylimidazol-2-yl)carbinol
4-TIC	tris(1-methylimidazol-4-yl)carbinol

A. INTRODUCTION

During my post-doctoral training under the guidance of Prof. L. Sacconi, it was my duty to investigate the virtually unexplored coordination chemistry of vanadium(II) and chromium(II). In the course of that work, I found that pyrazole and imidazole were suitable ligands for the stabilization of both vanadium and chromium in their oxidation number of two. Those early studies started my own interest in pyrazole and imidazole as ligands in the coordination chemistry of transition metals [1–10]. Later, having in mind Sacconi's well-known np_3 tripodal ligand [11] and its synthetic scheme, my coworkers and I synthesized the tetradentate ligands tris (3,5-dimethylpyrazol-1-ylmethyl)amine [12] and tris[2-(3,5-dimethylpyrazol-1-yl)-ethyl]amine [13] (ligands **XVIII** and **XVI**, see Table 3) and investigated their complexes with most of the 3d metals [14–19].

Numerous transition metal complexes with polydentate ligands containing pyrazole and related groups such as imidazole and benzimidazole have been reported and their number has greatly increased in recent years [20,21]. Apart from their intrinsic interest to the field of coordination chemistry, the polypyrazolyl ligands have been investigated for the purpose of synthesizing model complexes which mimic the metal environment in those metallo-enzymes and metallo-proteins that are known

or are supposed to contain imidazole groups from histidine bound to the metal at the active site. A number of comprehensive reviews concerning some aspects of the natural systems and of their modelling have appeared very recently [22–31].

This review is intended as a survey of the work which has been done in the last decade in the field of polydentate ligands containing pyrazole and imidazole (or related groups) as main donor groups and of their metal complexes which may be relevant to an understanding of the active site structure and, what is most important, of the mechanisms of reactions promoted by the metal centre in the natural complexes.

The imidazole bonding in metallo-proteins is often simulated, in model complexes, by chelating ligands containing pyridine, pyrazole, or benzimidazole donors because of their relative ease of preparation. The five-membered ring of pyrazole is reminiscent of that of imidazole, but their basicity is quite different (pK_b: pz = 11.52; iz = 7.05, [32]). The advantage of pyridine and benzimidazole is due to their basicity, which approaches that of histidine (pK_b: py = 8.75; biz = 8.47; His = 7.96 [32]). Presumably, imidazole provides the best approximation to histidine as a ligand, but the synthesis of imidazole-containing ligands is, in general, rather difficult and may require specific multistep procedures which hamper the use of such ligands.

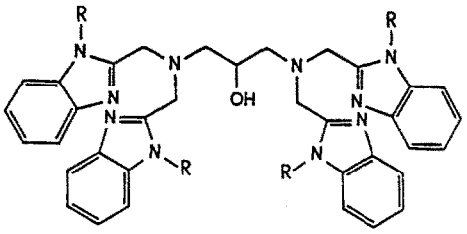
B. DINUCLEATING LIGANDS

A number of metal proteins are known to have an active site containing two metal ions coordinated to imidazole groups from histidine residues and held together by bridging groups. Perhaps, the best known examples are the dicopper proteins hemocyanin and tyrosine and the non-heme diiron protein hemerythrin. In their oxidised form (or met-form), the dicopper(II) proteins contain two metal centres bridged by an exogenous peroxo group and by an endogenous oxygen-donating ligand [23]; on the other hand, the diiron(III) protein hemerythrin has an oxo and two carboxylato bridges [22]. These bridging groups mediate strong antiferromagnetic coupling between the metals.

The best strategy to mimic the multihistidinyl binding of these natural systems has been to design multidentate ligands where two chelating units, separated by a suitable aromatic or aliphatic bridge, are held together. The length and the structure of the bridge have been chosen to fulfil two main requirements: (a) the ligand must allow two metal atoms to be accommodated at an appropriate distance from each other in such a way that ancillary ligands may coordinate to both metals and (b) the ligand should provide an endogenous donor group bridging the metal atoms. Moreover, the ligands must be sufficiently flexible to accommodate different metal ions, such as copper, iron, or manganese, which have different structural and electronic preferences depending on their oxidation states. A summary of ligands satisfying the aforementioned requirements is given in Table 1. The synthetic strategy based on

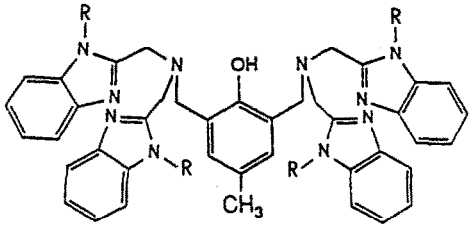
TABLE 1

Dinucleating ligands with abbreviations and references



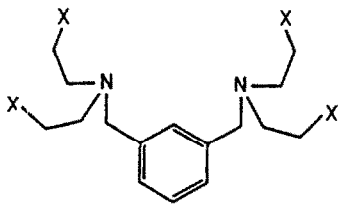
R = H: HL I-A [33]

R = Et: HL-Et I-B



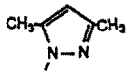
R = H II-A [34]

R = Me: HCAB-Me II-B [35]

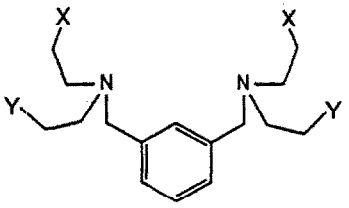


X =  III-A [36]

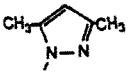
X =  m-XYLPy$_2$ III-B [37]

X =  mxyN$_6$ III-C [38]

X =  III-D [36]

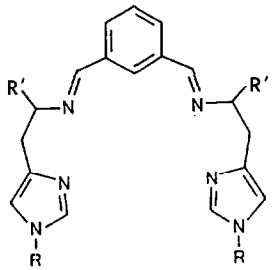


X =  Y =  IV-A [36]

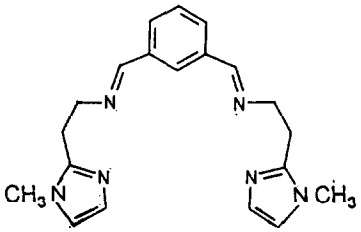
X =  Y =  IV-B

X =  Y =  IV-C

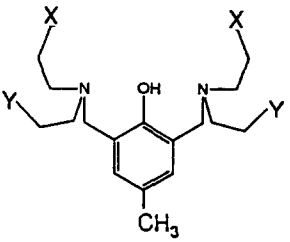
TABLE 1 (*continued*)



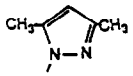
R = Me, R' = H V-A [39]
R = Me, R' = COOMe



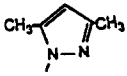
V-B [40]

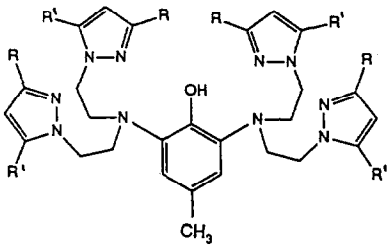


X = Y =  VI-A [41]

X = Y =  VI-B

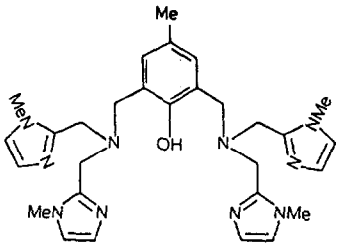
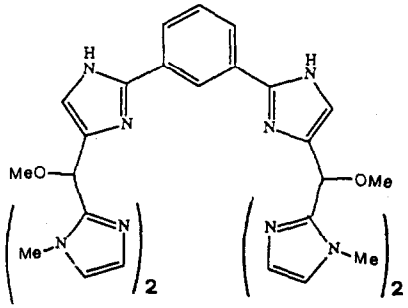
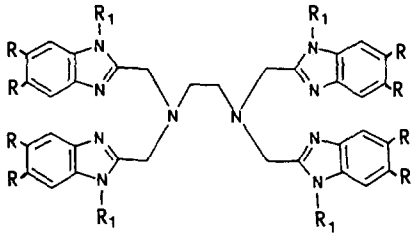
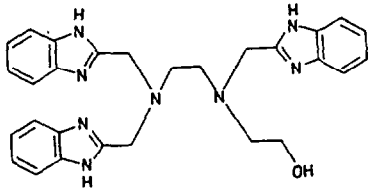
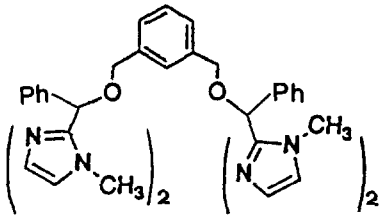
X =  Y =  VI-C [42]

X =  Y =  VI-D



R = R' = H: Hbpeac VII-A [43]
R = R' = Me VII-B [44]
R = C_6H_5, R' = H VII-C [44]
R = t-C_4H_9, R' = H VII-D [44]

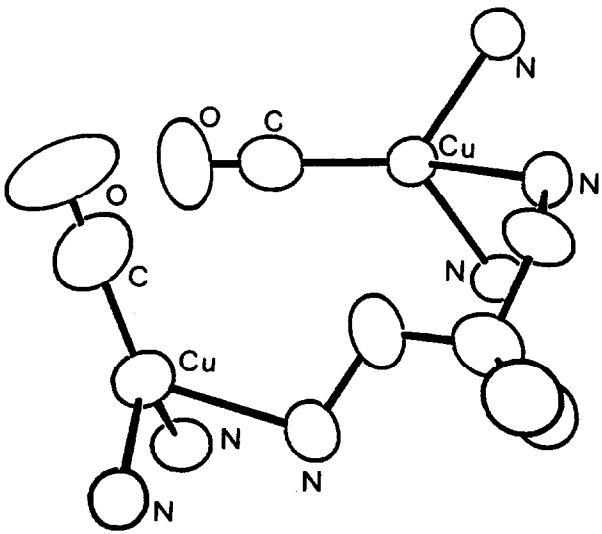
TABLE 1 (*continued*)

	Hbimp	VIII	[45]
		IX	[46]
	R = H, Me R_1 = H, Me, CH_2Ph	X	[47]
		XI	[48]
		XII	[49]

pre-organized dinucleating ligands has been successfully applied, in particular, to assemble dicopper model systems.

(i) Copper(I) and copper(II) complexes as models for the active site of O_2-activating copper proteins [23,24]

A number of dinuclear copper(I) complexes of the type $[Cu_2(L)X_2]Y_2$ (L= **I-A**, **I-B**; X=CO, CH_3CN; Y=CF_3SO_3, ClO_4, BF_4. L=**II-B**; X=CH_3CN; Y=CF_3SO_3; see Table 1 for the key to the ligands) have been prepared and structurally characterized by X-ray investigations [50]. These complexes are good approximations to the distorted copper(I) coordination environment in deoxy-hemocyanin where two histidines are strongly bound to copper(I) and a third histidine may be bound more weakly [51]. For example, in the carbonyl derivative $[Cu_2(HL-Et)(CO)_2](CF_3SO_3)_2$ (**1**) (Fig. 1), the copper(I)–tertiary amine bonds are 2.59(1) and 2.31(1) Å compared with the bond lengths of the copper(I)-heterocyclic amines in the range 1.96(1)–2.03(1) Å [50]. However, in contrast to compound **1**, carbon monooxy-Hc has a CO:Cu ratio of 1:2, presumably as a consequence of the steric constraints at the active site [23,52]. The copper(I) complexes with most of the ligands reported in Table 1 (the exception being the copper(I) complex with the ligand **III-B** [53]) are reported to react irreversibly with O_2, in contrast to the reversible activation of O_2 promoted by the reduced forms of both Hc and Tyr.



(1)

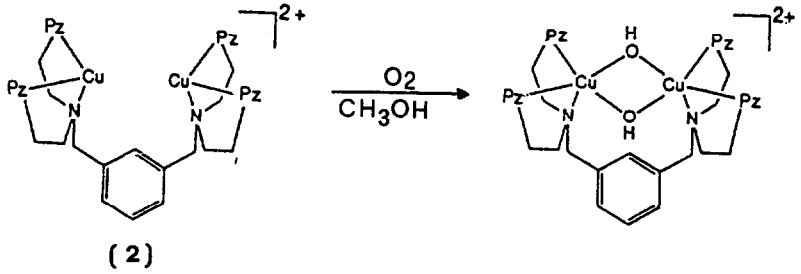
Fig. 1. Scheme of the coordination spheres in the cation $[Cu_2(HL-Et)(CO)_2]^{2+}$ (1) (HL-Et = **I-B**). (Adapted with permission from ref. 50.)

Modelling the oxygen activation by means of low-molecular weight and structurally simple complexes presumably requires a subtle and not yet foreseeable tuning of the steric and electronic properties at the metal centre [37,38,44]. This is nicely shown by the different reactivity toward O_2 (Fig. 2) of the two structurally analogous copper(I) complexes $[Cu_2(mxyN_6)](BF_4)_2$ (**2**) [38] and $[Cu_2(m\text{-}XYLPy_2)](PF_6)_2$ (**3**) [37] ($mxyN_6$ and m-$XYLPy_2$, respectively, stand for ligands **III-C** and **III-B** in Table 1). The insertion of an oxygen atom in a C–H bond of the aromatic ring in the ligand **III-B**, formally simulates the *o*-hydroxylation reaction of phenols, promoted by tyrosinase. Dinuclear copper(I) complexes analogous to **2** and **3**, having pz or N-Meiz donor groups (ligands **III-A** and **III-D**, Table 1) and mixed donor groups (ligands **IV-A**–**IV-C**), display different reactivity toward O_2 depending on the experimental conditions, but neither hydroxylation of the aromatic ring nor reversible O_2 binding has been detected [36,40]. On the other hand, copper(I) complexes with the ligands **V**, which contain either imidazol-2-yl [40] or imidazol-4-yl [39] groups, do react with O_2 undergoing ready aromatic hydroxylation (**4**, Fig. 2).

In order to mimic the function of Hc, the dinuclear copper(I) complexes $[Cu_2(L)](PF_6)$ (**5**) (HL = **VI-C** and **VI-D**) and $[Cu_2(HL)](PF_6)_2$ (**6**) (HL = **VI-A**–**VI-D**) have been reacted with O_2 [42]. A scheme of the reactions is reported in Fig. 3. The supposed peroxo- (**7**) and hydroperoxo-derivatives (**8**) fail, however, to reproduce the spectroscopic properties of the oxy-hemocyanin. In the case of the sterically hindered ligands **VII-B**–**VII-D** (Table 1), the dinuclear copper(I) complexes $[Cu_2(L)](BF_4)$ are inert to dioxygen [44].

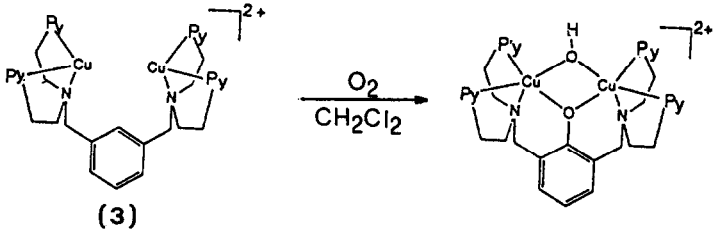
In conclusion, the picture emerging from the numerous investigations on dinuclear copper(I) derivatives and on their reactions with O_2 [23,37–40,42,44,47,54] is that, in modelling the function of a metallo-protein, the approach based on the structural resemblance between the donor groups in the active site of the natural system and those in the coordination environment of the synthetic complex is neither the only one possible nor necessarily the best one. As previously shown [37], in some model complexes the pyridine groups may be better approximations than imidazole to the histidine coordination.

Starting from copper(II) salts and some of the ligands reported in Table 1 (**I-B**, **II**, **VI-A**, **VII-X**), dinuclear complexes have been prepared for the purpose of modelling the strong antiferromagnetic coupling between the two copper(II) atoms occurring in the oxidised form of hemocyanin [33,34,41–47,55,56,57]. The X-ray structures of a number of such complexes have been determined to investigate how the nature of the exogenous bridging acetato, azido, nitrito, pyrazolato, methoxo, or hydroxo groups and the length of the ligand backbone influence the extent of the antiferromagnetic coupling between the two copper(II) atoms. Details on the structural data and the exchange coupling constant values are given in Table 2. The two structurally similar azido complexes $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ (**9**) (HL-Et = **I-B**, Table 1) [33,56] and $[Cu_2(bpeac)(N_3)](ClO_4)_2 \cdot THF$ (**10**) (Hbpeac = **VII**) [43] (Fig. 4) are essentially



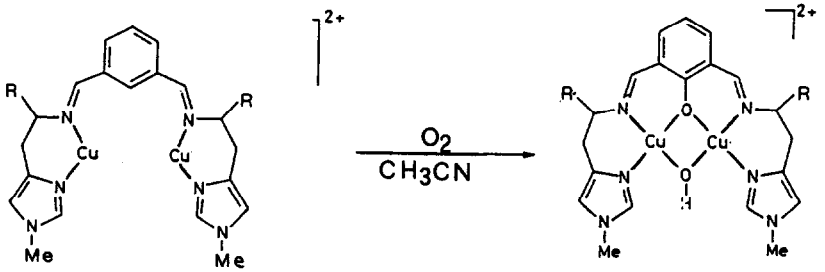
(2)

Pz = pyrazole, 3,5-dimethylpyrazole



(3)

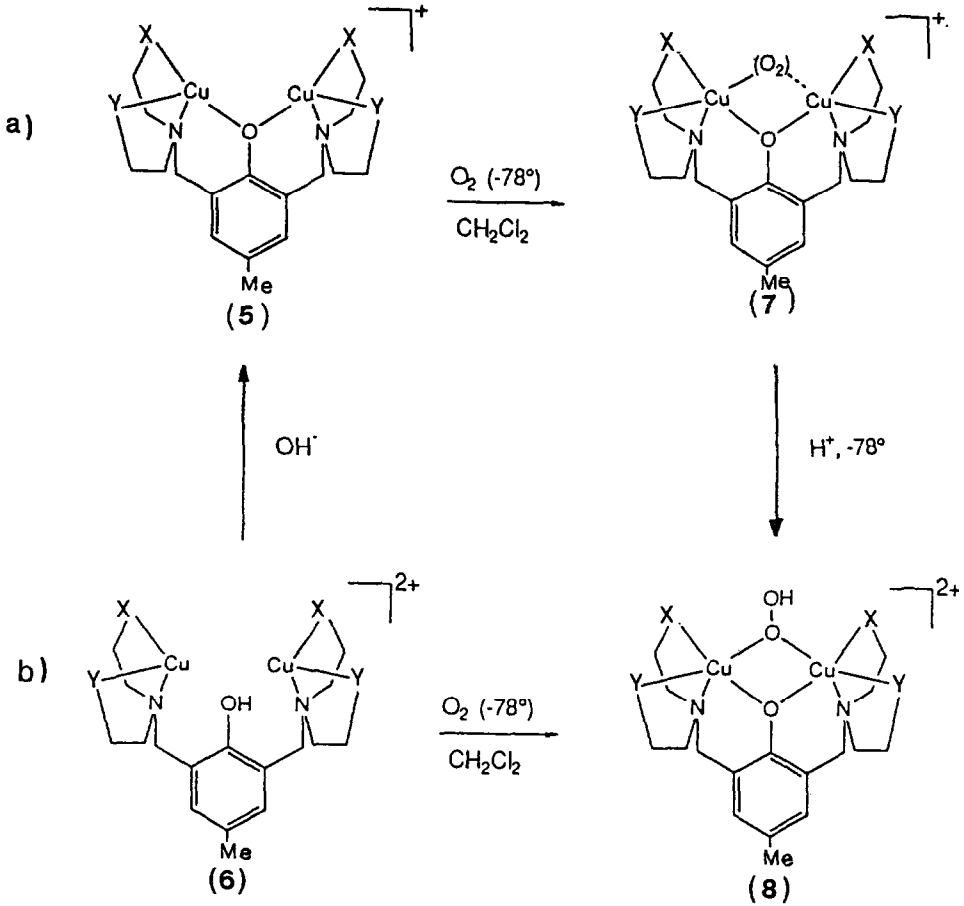
Py = pyridine



(4)

R = CO_2Me

Fig. 2. Reactions with O_2 of some dinuclear copper(I) complexes.



a) X = pz; Y = py. X = 3,5-Me_2pz; Y = py

b) X = Y = pz. X = Y = 3,5-Me_2pz. X = pz; Y = py
X = 3,5-Me_2pz; Y = py

Fig. 3. Summary of some reactions undergone by copper(I) and copper(II) complexes.

diamagnetic whereas in the analogous $[Cu_2(bimp)(N_3)](ClO_4)_2$ complex (Hbimp = **VIII**) [45], there is no appreciable exchange interaction between the copper(II) ions. Complexes **9** and **10** match some essential features of the azido derivative of oxy-Hc, such as the diamagnetism and UV-VIS spectra [58]. The alkoxide bridge in complex **9** and the phenoxide bridge in complex **10** could model the endogenous bridging ligand in oxy-Hc.

TABLE 2

Distances and angle within the Cu–O–Cu fragment and exchange coupling constant in some dinuclear copper(II) complexes

Complex[a]	Cu–O–Cu (degree)	Cu···Cu (Å)	Cu–O[b] (Å)	$-2J$[c] (cm^{-1})	Ref.
$[Cu_2(bpeac)(CH_3CO_2)]^{2+}$	133.2	3.562	1.905 1.976	0	43
$[Cu_2(bpeac)(N_3)]^{2+}$	138.2	3.765	2.017 2.013	1800	43
$[Cu_2(L)(OH)]^{2+}$[d]	101.9	3.053	2.002 1.927	420	41
$[Cu_2(L\text{-}Et)(N_3)]^{2+}$	136.9	3.615	1.944	>1100	33
$[Cu_2(L\text{-}Et)(NO_2)]^{2+}$	127.1	3.325	1.87 1.85	278	57
$[Cu_2(L\text{-}Et)(CH_3CO_2)]^{2+}$	130.6	3.459	1.89 1.92	−24[e]	33
$[Cu_2(bimp)(CH_3O)]^{2+}$	98.7	3.026	1.994	94	45
$[Cu_2(L)(OH)(CH_3CO_2)]^{2+}$[f]	109.3	3.156	1.934	−2.6[e]	46

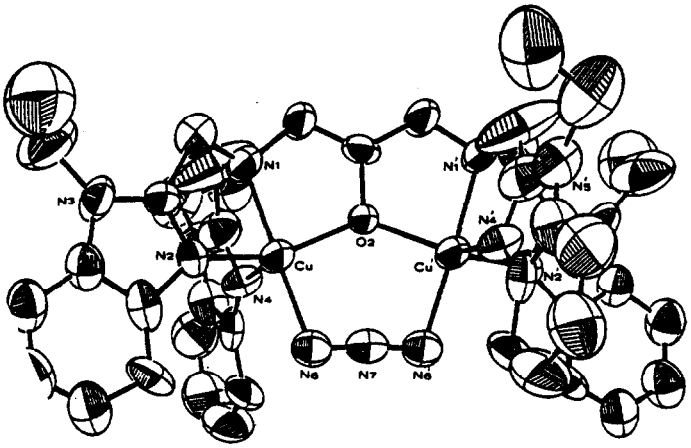
[a]Key to the ligands in Table 1.
[b]Endogenous bridging oxygen except the exogenous hydroxo group in the last complex.
[c]The spin-exchange Hamiltonian has the form $H = -2JS_1 \cdot S_2$.
[d]HL = **VI-A**.
[e]Ferromagnetic exchange coupling.
[f]L = **IX**.

C. CAPPING TRIDENTATE AND TETRADENTATE LIGANDS

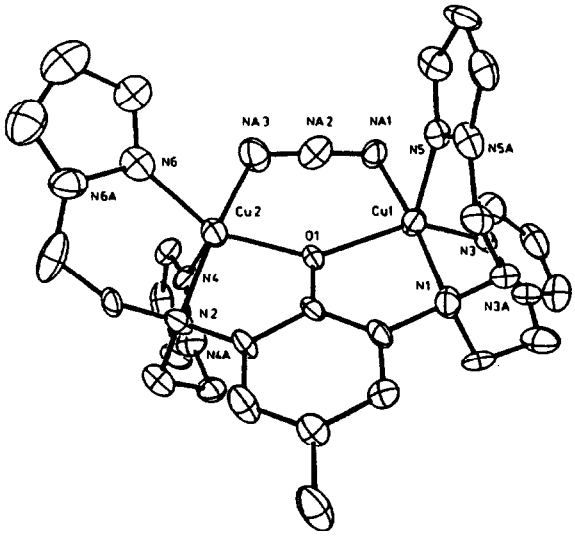
Instead of using pre-organized dinucleating ligands, other authors have used either specifically designed or already known tridentate ligands to assemble dinuclear complexes of copper, manganese and particularly iron. This strategy is based on the "spontaneous self-assembly" [59] capacity of some metal ions in the presence of capping tridentate ligands and in suitable reaction conditions. These ligands are summarized in Table 3 together with other bi-, tri-, tetradentate and mixed-donor ligands. Tri- and tetradentate ligands obviously also fulfil the requirements for the formation of mononuclear complexes and to this purpose have been extensively employed.

(i) Dinuclear copper complexes

Dinuclear copper(I) complexes have been prepared with the ligands **XIII-B**, $[Cu(timm)]_2(BF_4)_2$ [60], **XIV-A** and **XIV-B**, $[Cu(L)]_2$ [76], as possible models for deoxy-Hc. In particular, $[Cu(timm)]_2^{2+}$ reacts with CO affording a carbonyl derivative, $[Cu(timm)CO]^+$, which has the same luminescence properties as the CO-



(9)



(10)

Fig. 4. ORTEP plot of the cations $[Cu_2(L\text{-}Et)(N_3)]^{2+}$ (**9**) (HL-Et = **I-B**) and $[Cu_2(bpeac)(N_3)]^{2+}$ (**10**) (Hbpeac = **VII**). (Reproduced with permission from refs. 56 and 43, respectively).

derivative of Hc, in spite of the different CO : Cu ratio. Dinuclear μ-oxo and μ-peroxo complexes of copper(II) with the ligands **XIV-B** and **XIV-C** are reported in Fig. 5 together with some of the reactions they undergo. The spectroscopic features of the complexes $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (**11**) [77,78] and $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(O_2)$ (**12**) [ν-(O—O): **11**, 731 cm^{-1}; **12**, 741 cm^{-1}; oxy-Hc, 744–752 cm^{-1} [79]; electronic spectra: **11**, 530 nm ($\varepsilon = 840\ cm^2\ mmol^{-1}$), 338 nm ($\varepsilon = 2.08 \times 10^4\ cm^2\ mmol^{-1}$);

TABLE 3
Di-, tri- and tetradentate ligands with abbreviations and references

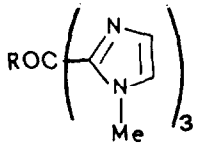
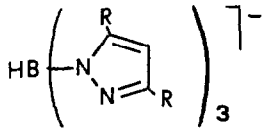
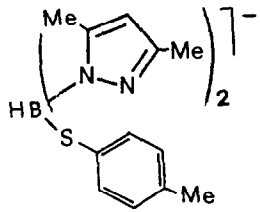
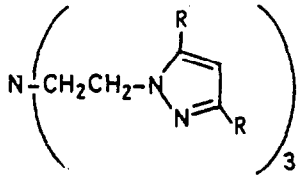
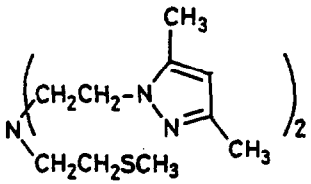
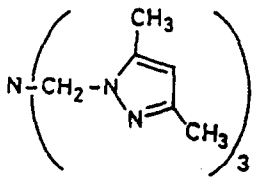
	R = H	XIII-A	[60]
	R = Me: timm	XIII-B	
	R = H: $HBpz_3$	XIV-A	[61]
	R = Me: $HB(3,5\text{-}Me_2pz)_3$	XIV-B	[62]
	R = $CHMe_2$: $HB(3,5\text{-}iPr_2pz)_3$	XIV-C	[63]
		XV	[64]
	R = H	XVI-A	[17]
	R = Me	XVI-B	[13]
	R = $t\text{-}C_4H_9$	XVI-C	[65]
		XVII	[66]
		XVIII	[12]

TABLE 3 (*continued*)

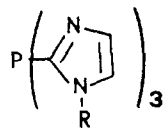
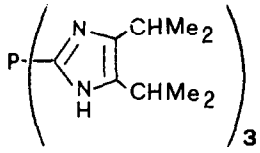
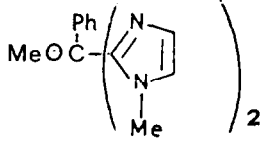
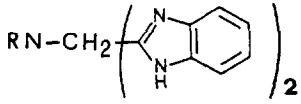
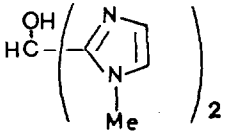
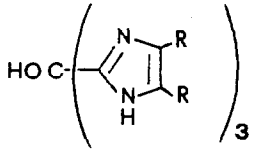
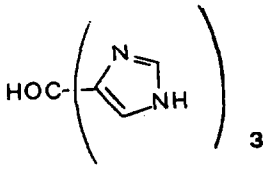
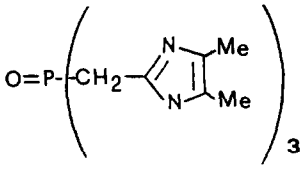
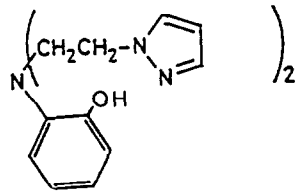
	XIX	R = H:	TIP	[67]
		R = Me:	TMIP	[67, 68]
			XX	[67]
			BiPhMe XXI	[69]
		R = H	XXII-A	[70]
		R = Me	XXII-B	
			BICOH XXIII	[71]
	XXIV	R = H:	2-TIC	[71,72]
		R = Me		
			4-TIC XXV	[71]

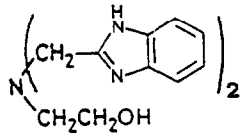
TABLE 3 (*continued*)



XXVI [73]

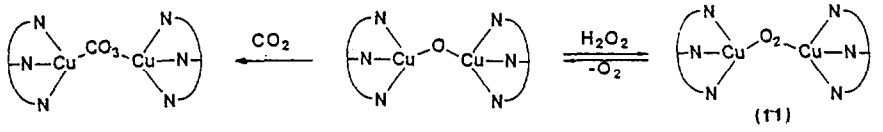


bpeap XXVII [74]

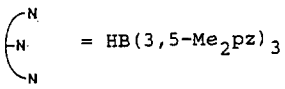


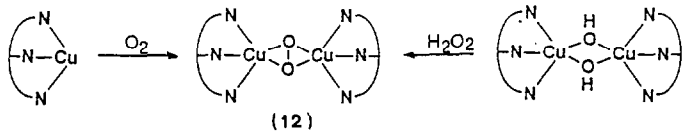
XXVIII [75]

12, 551 nm ($\varepsilon = 790\ cm^2\ mmol^{-1}$), 345 nm ($\varepsilon = 2.0 \times 10^4$); oxy-Hc, 570 nm ($\varepsilon = 1.0 \times 10^3\ cm^2\ mmol^{-1}$), 345 nm ($\varepsilon = 2.0 \times 10^4\ cm^2\ mmol^{-1}$) [80]] and their diamagnetism match the spectromagnetic properties of oxy-Hc in spite of the absence in complexes **11** and **12** of an endogenous bridging group which is believed to occur in



(11)





(12)

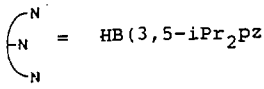
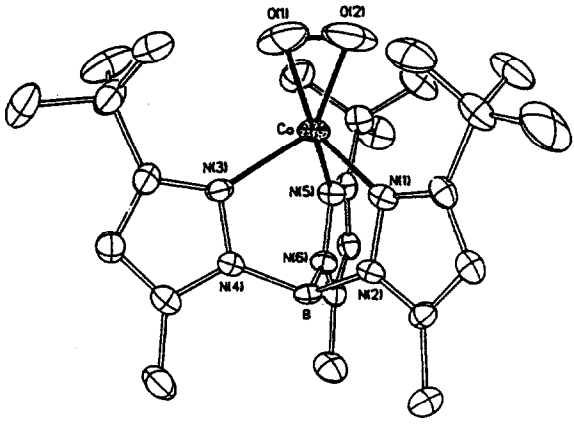


Fig. 5. Summary of some reactions undergone by copper complexes with ligands **XIV-B** and **XIV-C**.

the natural systems. The structure of complex **12** revealed the presence of a peroxide ion symmetrically coordinated in an unusual doubly side-on fashion (also described as μ-η^2:η^2). A remarkable feature of this complex is the Cu···Cu distance, of 3.56 Å, very close to the 3.58–3.66 Å values in oxy-Hc and oxy-Tyr, estimated by EXAFS analysis [81,82], and much shorter than those found for μ-1,2-peroxo complexes (4.359 Å [83]). It is therefore suggested [84] that the bridging peroxide ion in both oxy-Hc and oxy-Tyr may have this type of coordination instead of the 1,2-coordination usually accepted. In this connection it should be noted that, in the cobalt



(13)

(Reproduced with permission from ref. 85.)

complex **13** [85], the dioxygen group is side-on coordinated as a superoxide. Also, the complex $[Cu\{HB(3,5Me_2pz)_3\}O_2]\cdot 1/8Et_2O$ [86] is supposed to contain dioxygen as superoxide.

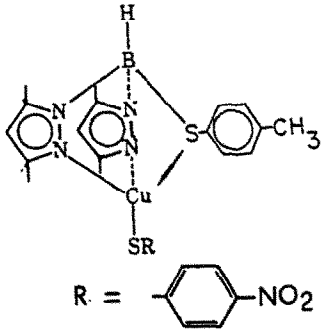
The oxidative reactivity of the peroxo-complex **11** toward a variety of substrates has been investigated [87]. In anaerobic conditions, phenols and catechol are oxidatively coupled.

(ii) Copper(II) complexes relevant as models for the active site of blue-copper proteins [29,30]

A recent review by Bouwman et al. [29] is entirely devoted to the synthetic models of the blue-copper proteins formed by a variety of mixed donor N_xS_y synthetic ligands. Consequently, in this section only the most recent model complexes and other complexes which were not included in the aforementioned review will be reported.

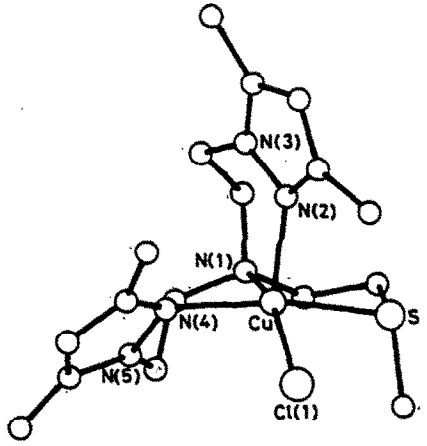
The active site of plastocyanin and other blue-copper proteins is formed by a copper atom pseudotetrahedrally coordinated by two imidazole nitrogens from

histidines, a thioether sulphur from a methionine and a thiolate sulphur from a cysteine [88]. The first synthetic complex which nicely mimics the donor groups in the active site of blue-copper (or type I) proteins was synthesized a decade ago [64] with the ligand **XV** and *p*-nitrobenzenthiolate as the ancillary ligand. The intense blue-coloured complex [Cu(L)(*p*-S-$C_6H_4NO_2$)] (**14**) has a strong absorption band



(14)

at 595 nm ($\varepsilon = 4.1 \times 10^3$ cm^2 mmol^{-1}), reminiscent of that at about 600 nm ($\varepsilon = 1.5 \times 10^3 - 5.0 \times 10^3$ cm^2 mmol^{-1}) of some blue-copper proteins [89]. The complex

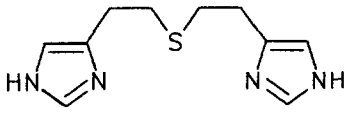


(15)

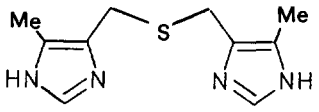
(Reproduced with permission from ref. 66.)

[Cu(L)Cl]Cl·2H_2O (**15**) L = **XVII**) is five-coordinate with an N_3SCl donor set [66] and the comparison of its electronic spectrum with that of the complex [Cu(L)Cl]BPh_4 (L = **XVI-A**), having a N_4Cl donor set [66], confirms that the 600 nm absorption in the blue-copper proteins is a thiolate S→Cu(II) LMCT transition. The

complex [Cu(L)(*t*-BuS)] (L = **XIV-C**; *t*-BuS = *t*-butyl thiolate) [90], which has not yet been isolated in the solid state, gives rise to an EPR signal similar to that found in the natural systems (Fig. 6). Two promising tridentate thioether-imidazole ligands have been prepared [91,92]. These ligands act as tridentate in a number of copper(II) complexes, namely $[Cu(L)X_2]$ (L = **XXIX-A**, **XXIX-B**; X = Cl, Br, NCS, NO_3), $[Cu(L)Cl]_2(ClO_4)_2$ (L = **XXIX-A**) and $[Cu(L)_2]Y_2$ (L = **XXIX-B**; Y = Cl, Br, NO_3,



XXIX-A



XXIX-B

BF_4). Other examples of thioether-imidazole ligands and of their copper complexes have been reported by Reed and co-workers [93] and Driessen and can be found in ref. 29. On the other hand, the paucity of copper(II) complexes containing thiolate groups is due to the easy reduction of copper(II) in low molecular weight compounds in the presence of these reducing species.

(iii) Dinuclear iron(II) and iron(III) complexes as models for diiron centres in natural systems [22,28]

Hemerythrin is a reversible O_2 carrier which has a (μ-oxo)bis(μ-carboxylato) diiron(III) core in its oxidised form [22]. The coordination of the two iron(III) atoms

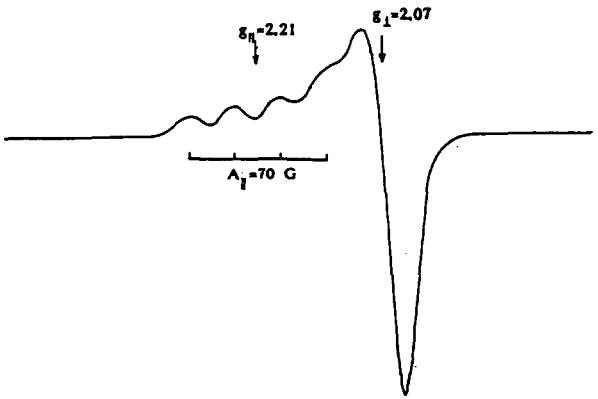


Fig. 6. EPR spectrum of the complex [Cu{HB(3,5-iPr$_2$pz)$_3$} (*t*-Bus)] (*t*-Bus = *t*-butyl thiolate) at 77 K in CH_2Cl_2. (Reproduced with permission from ref. 90.)

is completed by a total of five imidazoles from histidine residues and by a hydroperoxide anion. The two iron(III) atoms are strongly antiferromagnetically coupled.

Some of the tridentate ligands of Table 3 have been successfully employed to assemble diiron(III) complexes containing both oxo- and carboxylato bridging groups and their structural and spectromagnetic properties have been carefully investigated. The complexes $[Fe_2(O)(RCO_2)_2(HBpz_3)_2]\cdot CH_3CN$ (Fig. 7) ($HBpz_3$ = **XIV-A**; R = H, CH_3, C_6H_5), reported by Lippard and his group [94,95], are among the first synthetic complexes which accurately mimic the coordination environment and the physical properties of the active site of oxy-Hr. Analogous diiron(III) complexes have been reported with neutral imidazolyl phosphines and benzimidazolyl amines (ligands **XIX** and **XXII**, Table 3) acting as tridentate ligands [68,70,96]. Examples of such complexes are reported in Table 4. The short Fe—O (μ-oxo) bonds in these model complexes mediate a strong antiferromagnetic coupling between the iron(III) atoms. Distances and angles within the diiron(III) cores and antiferromagnetic interactions (Table 4) are not substantially influenced by the nature of the terminal donor groups (imidazole, pyrazoles or benzimidazoles) provided by the tridentate ligands and can be assumed to be typical values for the $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]$ fragment. The diiron(III) model complexes for which the X-ray structure determination and magnetic investigations have been carried out have been found to possess relatively short Fe···Fe distances and, consequently, a reduced antiferromagnetic exchange coupling

TABLE 4

Distances and angles within the $[Fe_2(O)(RCO_2)_2]$ and $[Fe_2(O)(MPDP]$ cores, and exchange coupling constant in some diiron(III) complexes

Complexes[a]	Fe—O—Fe (degree)	Fe···Fe (Å)	Fe—O (μ-oxo, Å)	$-2J$[b] (cm^{-1})	Ref.
$[Fe_2(O)(CH_3CO_2)_2(TIMP)_2]^{2+}$	122.7	3.158	1.79	240[c]	68
$[Fe_2(O)(CH_3CO_2)_2(HBpz_3)_2]$	123.6	3.146	1.780 1.788	242	94
$[Fe_2(O)(HCO_2)_2(HBpz_3)_2]$	125.5	3.168	1.777 1.785	–	94
$[Fe_2(O)\{(CH_3)_3CCO_2\}_2(L)_2]^{2+}$[d]	117.0	3.075	1.803	232	70
$[Fe_2(O)(C_6H_5CO_2)_2(L)_2]^{2+}$[d]	118.7	3.079	1.777 1.802	234	96
$[Fe_2(O)(MPDP)(BiPhMe)_2Cl_2]$[e]	125.9	3.183	1.783 1.790	243	100
$[Fe_2(O)(MPDP)(HBpz_3)_2]$[e]	123.4	3.161	1.797 1.793	249	100

[a]Key to the ligands in Table 3.
[b]The spin-exchange Hamiltonian has the form $H = -2JS_1\cdot S_2$.
[c]Estimated in CH_3CN solution.
[d]L = **XXII-A**.
[e]MPDP = **16**.

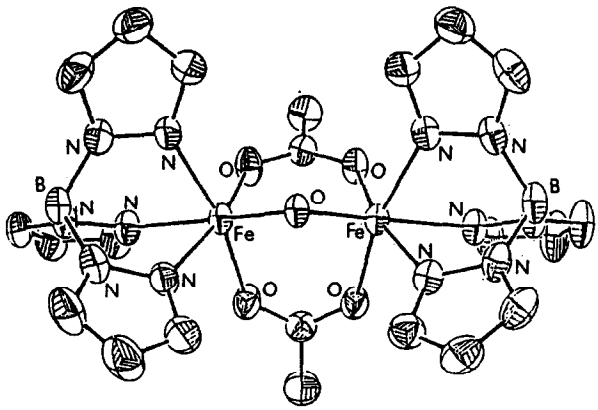
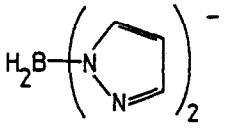


Fig. 7. ORTEP plot of the complex $[Fe_2(O)(CH_3CO_2)_2(HBpz_3)_2]CH_3CN$. (Adapted with permission from ref. 94.)

compared with that found for met-Hr (Fe···Fe = 3.21 Å; $2J = -268\ cm^{-1}$ [97]). This must be taken into account in the efforts to improve the functionality of the models. Most important, functional models for the reduced form of Hr must possess a vacant coordination site at one iron(II), thus allowing the reversible binding of an oxygen molecule (as a peroxide or hydroperoxide anion). For the purpose of assembling a coordinatively unsaturated diiron centre, the bidentate ligand $H_2Bpz_2^-$ (**XXX**) [61]



XXX

was used in addition to, or in place of, the tridentate one $HBPz_3^-$ ligand. However, the tetranuclear iron(III) complexes $[Fe_4(O)_2(RCO_2)_7(H_2BPz_2)_2]Et_4N$ ($R = CH_3$, C_6H_5) were obtained [98]. These complexes contain the $(Fe_4O_2)^{8+}$ core (Fig. 8). Attempts were also made to assemble diiron(III) complexes with a coordination site vacant or occupied by a labile ligand by using specifically designed asymmetric ligands. This approach gave the dinuclear complex $[Fe_2(O)Cl_3(L)]Cl \cdot 2EtOH$ (L = **XI**, Table 1) [48] and the tetranuclear complex $[Fe_4(O)_2(C_6H_5CO_2)_4(BICOH)_2(BICO)_2]Cl_2$ (Fig. 9) (BICOH = **XXIII**, Table 3) [99]. The latter results seem to indicate that the unsaturation of the coordination environment around one iron centre in synthetic models results in self-aggregation with the formation of tetranuclear species, unless some steric hindrance is provided by the terminal donor groups. In the natural systems, the self-aggregation of the diiron moieties is presumably hindered by the steric demands of the protein envelope. The use of the very specific dicarboxylate ligand $MPDP^{-2}$ (**16**), which has suitable steric requirements to occupy the

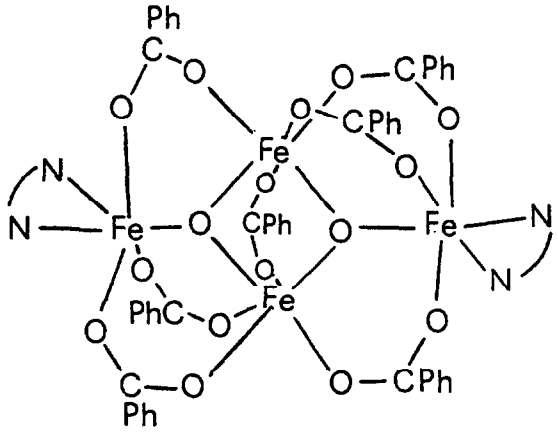
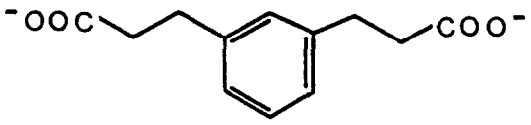


Fig. 8. Scheme of the structure of $[Fe_4(O)_2(C_6H_5CO_2)_7(H_2Bpz_2)_2]^-$.



(16)

positions of both acetate groups in the $[Fe_2(O)(CH_3CO_2)_2]$ moiety, and of the ligands **XIII** and **XXI** (Table 3) has enabled the assembly of compounds such as $[Fe_2(O)(MPDP)(BiPhMe)_2Cl_2]$ (**17**) (Fig. 10 and Table 4)) [100] and

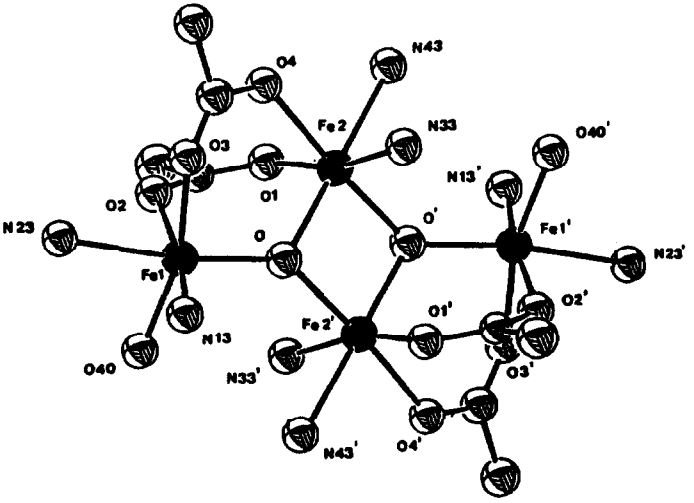
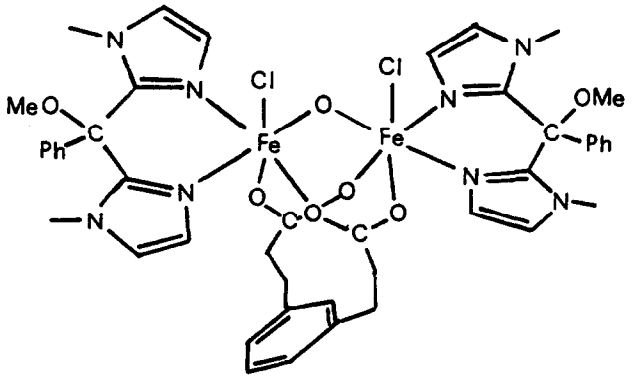


Fig. 9. Scheme of the inner coordination sphere of the cation $[Fe_4(O)_2(C_6H_5CO_2)_4(BICOH)_2(BICO)_2]^{2+}$ (BICOH = **XXIII**). (Reproduced with permission from ref. 99.)



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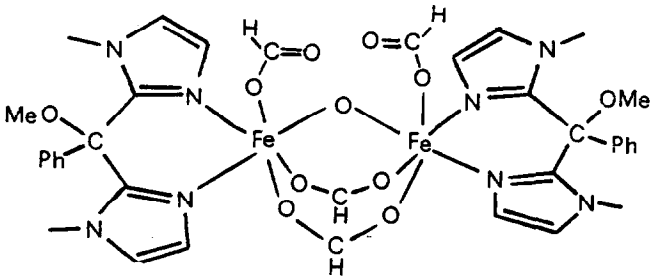


(18)

Fig. 10. Schemes of the structures of $[Fe_2(O)(MPDP)(BiPhMe)_2Cl_2]$ (**17**) and $[Fe_2(O)(HCO_2)_4(BiPhMe)_2]$ (**18**) (BiPhMe = **XXI**; MPDP = **16**).

$[Fe_2(O)(MPDP)(timm)_2Cl_2]$ [101] where the sixth coordination position around each iron(III) is occupied by a labile monodentate ligand. An analogous complex, $[Fe_2(O)(HCO_2)_4(BiPhMe)_2]$ (**18**) (Fig. 10), was obtained by air oxidation of the parent diiron(II) complex [102].

Even if the stability of a moiety such as $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2]$ enables it to be obtained by a "spontaneous self-assembly" [59], dinucleating ligands facilitate this assembly. The complex $[Fe_2(C_6H_5CO_2)_2(L)](ClO_4)_3$ (HL = **I-A**; $2J = -52\ cm^{-1}$; HL = **I-B**; Table 1) [103] has an endogenous bridging alkoxo group in the place of the exogenous oxo group. The ligand **XII** (Table 1), which contains two chelating units analogous to **XXI** (Table 3), failed to give the usual μ-oxo diiron group; instead, the tetranuclear derivative $[Fe_4(\mu\text{-}O)_2(\mu\text{-}HCO_2)_4(HCO_2)_4(L)_2]$ has been obtained

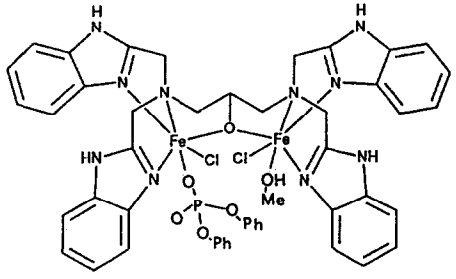
[49]. The ^1H NMR behaviour of $[Fe(L)_2]X_3$ (L = **XIII-A, XIII-B**) has been investigated [104,105].

Dioxygen adducts of iron complexes are scarce and no X-ray structure is yet available. The iron(II) complex $[Fe(C_6H_5CO_2)\{HB(3,5\text{-}iPr_2pz)_3\}]$ is reported to bind dioxygen in toluene reversibly at −20°C [106], whereas $[Fe_2(L\text{-}Et)(C_6H_5CO_2)](BF_4)_2$ (HL-Et = **I-B**, Table 1) reacts irreversibly with O_2 [107]. In both cases, the formation of peroxo-bridged diiron(III) species has been proposed on the basis of spectroscopic data. On the other hand, the iron(III) complex $[Fe_2(L)(OH)(NO_3)_2](NO_3)_2$ (HL = **I-A**, Table 1) [108,109] on reaction with H_2O_2 affords a compound formulated as $[Fe_2(L)(\mu\text{-}O_2)(NO_3)_2](NO_3)$ (HL = **I-A**) [108].

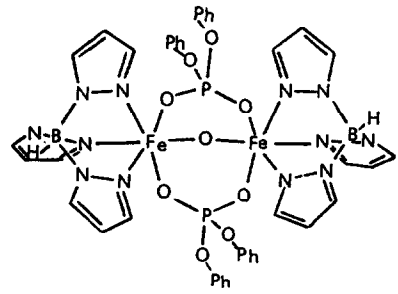
Mixed valence iron(II) iron(III) complexes have been prepared and characterized as synthetic approximations to the active form of purple acid phosphatases (PAP). In the complexes $[Fe^{II}Fe^{III}(bimp)(CH_3CO_2)_2](ClO_4)_2\cdot 2H_2O$ (Hbimp = **VIII**, Table 1) [110] and $[Fe^{II}Fe^{III}(L)(C_6H_5CO_2)_2](BF_4)_2$ (HL = **II**, Table 1) [111], the high-spin iron(II) and iron(III) ions are weakly antiferromagnetically coupled. The heterobimetallic complex $[Mn^{II}Fe^{III}(bimp)(CH_3CO_2)_2](ClO_4)_2$ has also been reported [112]. To model the coordination of phosphate in the oxidized form of PAP, the complexes $[Fe_2Cl_2\{O_2P(OPh)_2\}(L)(CH_3OH)](ClO_4)_2\cdot 3MeOH$ (HL = **I-A**) (**19**, Fig. 11) [113] and $[Fe_2(O)(O_2PR_2)_2(HBpz_3)_2]$ (R = OPh, Ph) (**20**) [114] have been prepared. However, because of the differences between the spectral features of the latter model complexes and those of PAP, it is suggested that the natural system may not contain bridging phosphato groups [114].

(iv) Cobalt and zinc complexes as spectroscopic and functional models for carbonic anhydrase

Carbonic anhydrase has a water molecule and three hystidinyl imidazoles in the zinc-coordination sphere and catalyzes the hydration of CO_2 according to



(19)



(20)

Fig. 11. Schemes of the structures of $[Fe_2Cl_2\{O_2P(OPh)_2\}(L)(CH_3OH)]^{2+}$ (**19**) (L = **I-A**) and $[Fe_2(O)\{O_2P(OPh)_2\}_2(HBpz_3)_2]$ (**20**). (**19** is adapted with permission from ref. 113.)

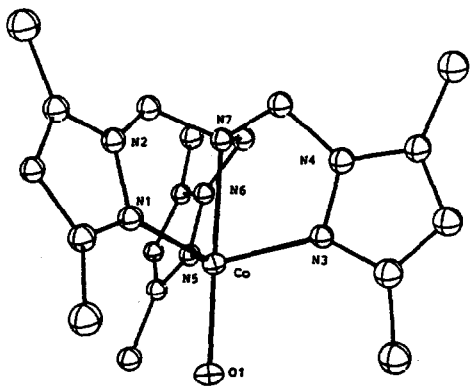
the reaction

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

The pK_a of the coordinated water is about 7.5 [115]. Cobalt(II) can be substituted for the native zinc, yielding a still-active enzyme with similar acid–base properties. A characteristic feature of the electronic spectrum of the cobalt substituted CA is its strong pH dependence.

A cobalt(II) complex containing a coordinated water molecule, $[Co(H_2O)(L)](ClO_4)_2$ (**21**) (L = **XVIII**), was synthesized [116,117] and its structure (Fig. 12) determined by X-ray diffraction [118]. The spectral behaviour as a function of the pH of the complex **21** (Fig. 13) presents a striking similarity with the spectra of cobalt-substituted CA. The deprotonation equilibrium of the cobalt-bound H_2O molecule in **21** is estimated to have a $pK_a = 8.9$ in water, and results in the formation of the corresponding hydroxo complex. This pK_a value, higher than that of CA, is presumably a consequence of the greater coordination number (5) of the synthetic complex with respect to that of CA (4) and prevents any catalytic activity towards CO_2 hydration in water solution at physiological pH. In fact, the mechanism of CO_2 hydration in the natural system is supposed to involve the formation of a zinc-bound hydroxide which acts as a strong nucleophile toward CO_2. The pseudotetrahedral model complex [Zn{HB(3-*t*-But-5-Mepz)$_3$}(OH)] does indeed react with CO_2, affording an unstable hydrogenocarbonate adduct [119].

Several cobalt(II) and zinc(II) complexes with the polyimidazole ligands **XX** and **XXVI** have been investigated in 80% ethanol–water solutions owing to the solubility requirements of the ligands [73,120,121]. Titrimetric investigations indicate that the deprotonation equilibrium of a coordinated water molecule has pK_a in the



(21)

Fig. 12. ORTEP plot of the cation $[Co(L)(H_2O)]^{2+}$ (**21**) (L = **XVIII**). (Reproduced with permission from ref. 118.)

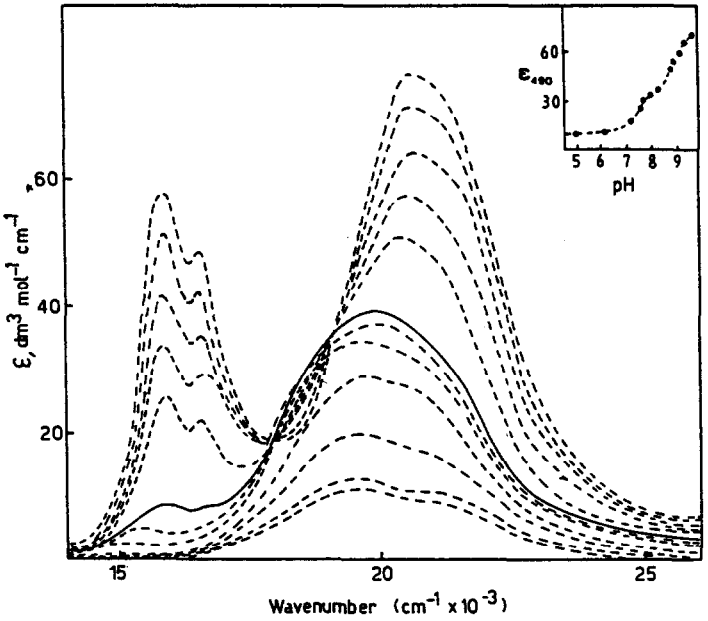


Fig. 13. pH dependence of the electronic spectra of complex **21** in water; pH values are (from the top) between 9.55 and 5.0. The pH of the solid line (8.3) is that of the solution of **21** at 10^{-3} mol dm^{-3} concentration. The insert shows the variation of ε_{490} with pH. (Reproduced with permission from ref. 117.)

range 7.6–7.8, depending on the ligand involved. These values are strictly similar to those found for CA. The zinc(II) complex with the ligand **XX** is reported to catalyze efficiently the hydration of CO_2 in a 80% ethanol–water solution at values of measured pH between 6.1 and 7.3 [120]. This result is, presumably, a direct consequence of the low polarity of the model system medium compared with water [122].

(v) Manganese and vanadium complexes as models for the active site in natural systems [25–27,31]

Complexes of manganese(II) [123], manganese(III), [75,124], and mixed valence manganese(II)–manganese(III) species [125] have been structurally characterized by X-ray diffraction. Details on structural parameters and exchange coupling constants for some of the complexes are reported in Table 5. While dinuclear complexes with a Fe^{III}–O–Fe^{III} bridge exhibit, in general, strong antiferromagnetic coupling, the metal ions are only weakly coupled in the dinuclear manganese derivatives. The oxidation of the complex $[Mn_2(O)(CH_3CO_2)_2(HBPz_3)_2]$ with I_2 produces a compound whose EPR spectrum exhibits a 16-line ^{55}Mn hyperfine pattern typical of the Mn(III)Mn(IV) trapped valence state and reminiscent of that found for an intermedi-

TABLE 5

Distances and angles within the Mn–O–Mn and Mn$<^{O}_{O}>$Mn fragments and exchange coupling constant in some dinuclear manganese complexes

Complexes[a]	Mn–O–Mn (degree)	Mn···Mn (Å)	Mn–O (bridg., Å)	$-2J$[b] (cm^{-1})	Ref.
$[Mn_2(bpeap)_2(THF)_2]^{2+}$	99.9	3.256	2.156 2.096	<0.4	123
$[Mn_2(O)(CH_3CO_2)_2(HBpz_3)_2]$[c]	125.1	3.159	1.773 1.787	1	124
$[Mn_2(CH_3CO_2)_2(bimp)]^{2+}$	116.8	3.54	2.258 1.887	9	125

[a]Key to the ligands in Tables 1 and 3.
[b]The spin-exchange Hamiltonian has the form $H = -2JS_1 \cdot S_2$.
[c]Values referred to the sample with $4CH_3CN$.

ate state of the manganese centre in photosystem II [124]. Photosystem II is a redox-active manganese enzyme which catalyses the photosynthetic water oxidation/oxygen evolution in green plants.

The manganese(II) complexes $[Mn_2(L)(OH)Br_2]$ and $[Mn_2(L)Cl_3]$ (HL = **I-A**, Table 1) [126] have not been structurally characterized, but their chemical behaviour is noteworthy because they catalyze the disproportionation reaction of H_2O_2. The reaction mechanism is supposed to proceed through the formation of a μ-oxo manganese(III) intermediate

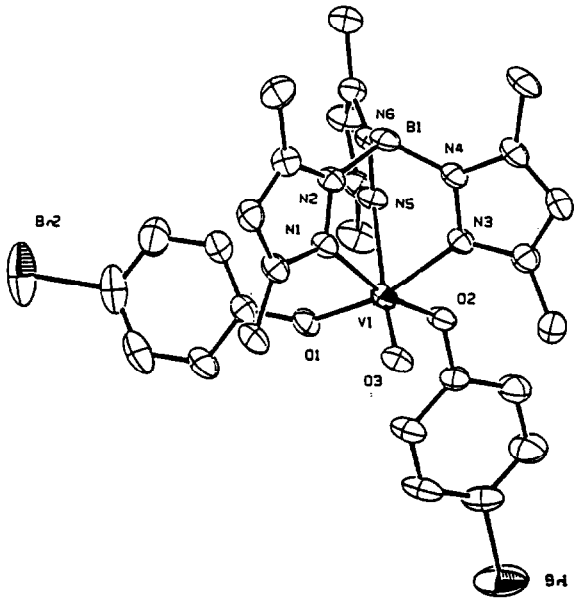
$$[Mn^{II}_2(L)Cl_3] + H_2O_2 \rightleftharpoons [Mn^{III}_2(L)(O)Cl_3] + H_2O$$

$$[Mn^{III}_2(L)(O)Cl_3] + H_2O_2 \rightarrow [Mn^{II}_2(L)Cl_3] + H_2O + O_2$$

These reactions can be assumed to be reasonable approximations to the mechanism of O_2 evolution in manganese pseudocatalase.

From EXAFS data, it is assumed that the binding site in the bromoperoxidase enzyme consists of a vanadium(V) atom six-coordinated by two histidinyl nitrogens, a terminal oxygen atom and three additional light donor atms, presumably oxygen atoms from unidentified groups [31].

Complexes of vanadium with polypyrazolyl ligands in oxidation states between two and four have been reported [3,6,127–130]. However, in order to model the binding site of the bromoperoxidase enzyme, complexes of vanadium(V) must be prepared. Starting from the vanadium(IV) complex $VO\{HB(3,5\text{-}Me_2pz)_3\}Cl \cdot DMF$ and sodium phenoxides, after exposure to the air the vanadium(V) complexes $VO\{HB(3,5\text{-}Me_2pz)_3\}(OC_6H_4\text{–}R)_2$ (R = H, *p*-Br (**22**), *p*-NO_2, *p*-OCH_3, *p*-$CH(CH_3)_2$)



(22)

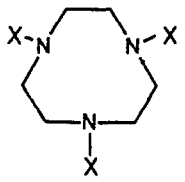
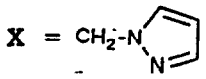
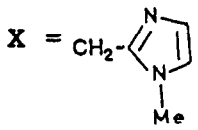
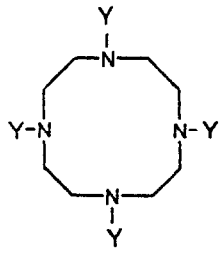
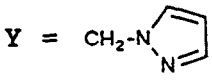
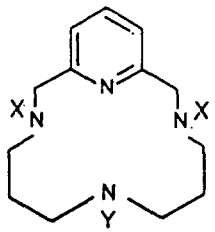
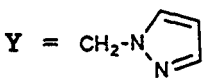
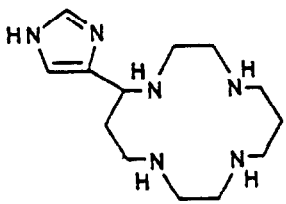
(Reproduced with permission from ref. 131.)

were obtained [131]. These vanadium(V) phenolato complexes are deeply coloured from green to violet owing to a strong LMCT band at about 400 nm. Since bromoperoxidase lacks this spectral behaviour, the phenolate oxygen from a tyrosine residue is not considered to be a possible donor atom in the active site of the natural system. Further studies are needed on both the natural system and model complexes for a better understanding of the structures of vanadium enzymes.

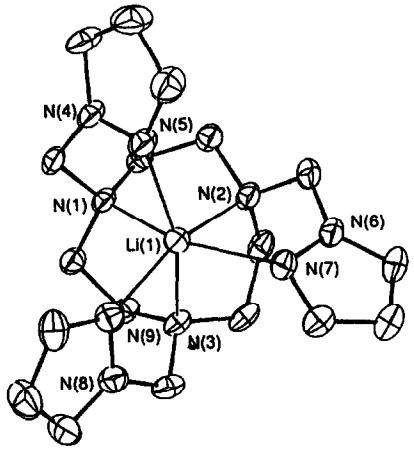
D. FUNCTIONALISED MACROCYCLES [132]

A recent development in the coordination chemistry of the polypyrazolyl ligands has been the attachment of the pyrazole or related groups to a macrocyclic framework. Besides their biochemical relevance in modelling the protein metal-binding sites, specifically designed functionalised macrocycles may have many potential uses as, for example, sequestering agents, metal chelating agents for medical applications, selective metal transport agents. Until now, few macrocyclic ligands functionalised with biomimetic pyrazole and imidazole groups are known. They are summarized in Table 6. Recently, general high-yielding routes have been devised which enable imidazole and pyrazole groups to be added to preformed macrocycles

TABLE 6

	X =  X = 	XXXI-A XXXI-B	[133]
	Y = 	XXXII	[138]
	X = CH_2Ph Y = 	XXXIII	[139]
		XXXIV	[140]

bearing secondary amine nitrogens [133]. Using these procedures, the ligands **XXXI** and **XXXII** were prepared and their metal complexes investigated [134–138]. A striking feature of these ligands is their ability to complex either transition or alkali metal ions giving stable complexes. The structure of the six-coordinated $[LiL]BPh_4$ **(23)** (L = **XXXI-A**) [135], $[NiL](ClO_4)_2$ **(24)** (L = **XXXI-B**) [133] (Fig. 14) and $[NiL]I_2$ (L = **XXXII**) [138] and of the eight-coordinated $[NaL]BPh_4$ **(25)** [135,136] and



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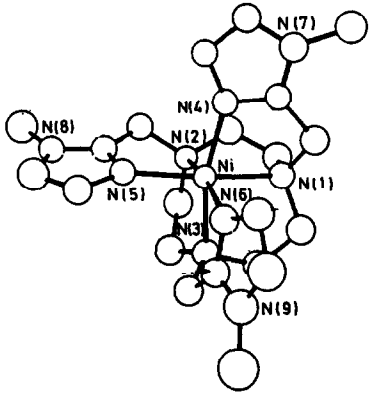
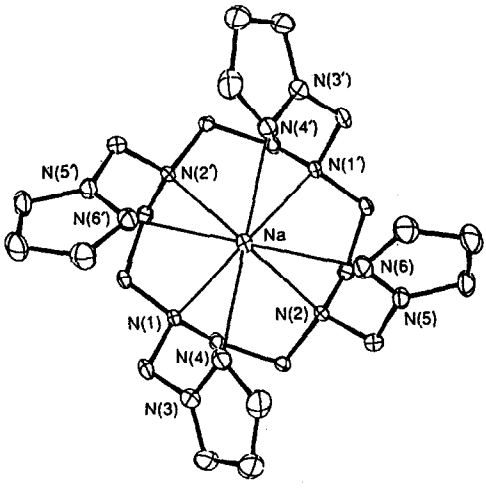


(24)

Fig. 14. Structures of the cations $[Li(L)]^+$ (**23**) (L = **XXXI-A**) and $[Ni(L)]^{2+}$ (**24**) (L = **XXXI-B**). (Reproduced with permission from refs. 135 and 133, respectively.)

$[MnL](PF_6)_2 \cdot (CH_3)_2CO$ (**26**) (L = **XXXII**) [137] (Fig. 15) have been determined by means of X-ray diffraction. Quite interestingly, the seven-coordinate $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$ and the six-coordinate $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$ (L' = **XXXV**) have been obtained because of the spontaneous replacement of one pendant pyrazole group by an ethoxo group, which occurred in ethanol–acetone solution [138].

Metal complexes formed by the ligands **XXXIII** [139] and **XXXIV** [140], having a single pendant arm, may approximate the metal binding site of natural systems, where the metal ion is surrounded by four N atoms in a plane and by an



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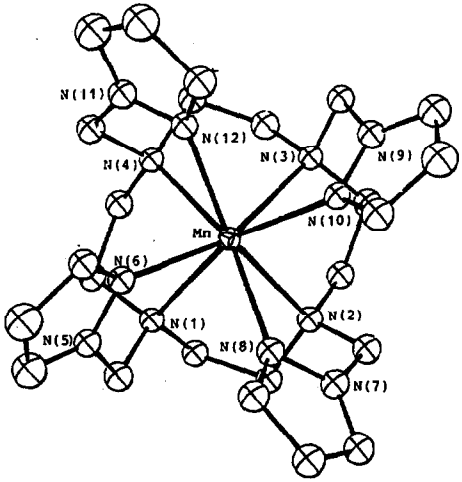
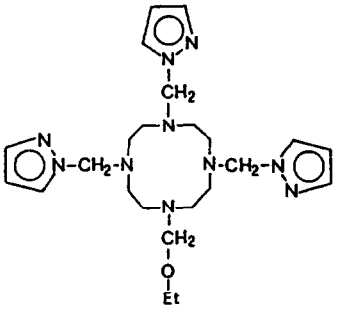


(26)

Fig. 15. Structures of the cations $[Na(L)]^+$ (**25**) and $[Mn(L)]^{2+}$ (**26**) (L = **XXXII**). (**25** is reproduced with permission from ref. 135.)



XXXV

additional donor group from a side-chain of the molecule, in the fifth coordination site.

REFERENCES

1 F. Mani and G. Scapacci, Inorg. Chim. Acta, 16 (1976) 163.
2 M. Ciampolini and F. Mani, Inorg. Chim. Acta, 24 (1977) 91.
3 P. Dapporto, F. Mani and C. Mealli, Inorg. Chem., 17 (1978) 1323.
4 F. Mani and R. Morassi, Inorg. Chim. Acta, 36 (1979) 63.
5 P. Dapporto and F. Mani, J. Chem. Res. (S), (1979) 374.
6 F. Mani, Inorg. Chim. Acta, 38 (1980) 97.
7 F. Mani, Inorg. Chim. Acta, 117 (1986) L1.
8 D. Ajo', A. Bencini and F. Mani, Inorg. Chem., 27 (1988) 2437.
9 M. Di Vaira and F. Mani, J. Chem. Soc. Dalton Trans., (1990) 191.
10 A. Bencini, M. Di Vaira and F. Mani, J. Chem. Soc. Dalton Trans., (1991) 41.
11 L. Sacconi and I. Bertini, J. Am. Chem. Soc., 90 (1968) 5443.
12 F. Mani and G. Scapacci, Inorg. Chim. Acta, 38 (1980) 151.
13 F. Mani and C. Mealli, Inorg. Chim. Acta, 54 (1981) L77.
14 L. Banci, C. Benelli, D. Gatteschi and F. Mani, Inorg. Chem., 21 (1982) 1133.
15 F. Mani and C. Mealli, Inorg. Chim. Acta, 63 (1982) 97.
16 M. Di Vaira, P. Stoppioni and F. Mani, J. Organomet. Chem., 247 (1983) 95.
17 M. Di Vaira and F. Mani, Inorg. Chim. Acta, 70 (1983) 99.
18 M. Di Vaira and F. Mani, Inorg. Chem., 23 (1984) 409.
19 A. Bencini and F. Mani, Inorg. Chim. Acta, 87 (1984) L9.
20 S. Trofimenko, Prog. Inorg. Chem., 34 (1986) 115.
21 J. Reedijk, in G. Wilkinson, R.D. Gillard and J.A. McCleverthy (Eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, Oxford, 1987, p.73.
22 S.J. Lippard, Angew. Chem. Int. Ed. Engl., 27 (1988) 344.
23 T.N. Sorrell, Tetrahedron, 45 (1989) 3.
24 Z. Tyeklar and K.D. Karlin, Acc. Chem. Res., 22 (1989) 241.
25 G.W. Brudvig and R.H. Crabtree, Prog. Inorg. Chem., 37 (1989) 99.
26 G. Christou, Acc. Chem. Res., 22 (1989) 328.
27 K. Wieghardt, Angew. Chem. Int. Ed. Engl., 28 (1989) 1153.
28 D.M. Kurtz, Jr., Chem. Rev., 90 (1990) 585.
29 E. Bouwman, W.L. Driessen and J. Reedijk, Coord. Chem. Rev., 104 (1990) 143.

30 A.G. Sykes, Adv. Inorg. Chem., 36 (1991) 377.
31 A. Butler and C.J. Carrano, Coord. Chem. Rev., 109 (1991) 61.
32 R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 67th edn., 1986, pp. D-159–D-161.
33 V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch and C.A. Reed, J. Am. Chem. Soc., 106 (1984) 4765.
34 H.P. Berends and D.W. Stepham, Inorg. Chem., 26 (1987) 749.
35 D.R. Chapman and C.A. Reed, Tetrahedron Lett., 29 (1988) 3033.
36 T.N. Sorrell, V.A. Vankai and M.L. Garrity, Inorg. Chem., 30 (1991) 207.
37 K.D. Karlin, J.C. Hayes, Y. Gultneh, R.W. Cruse, J.W. McKown, J.P. Hutchinson and J. Zubieta, J. Am. Chem. Soc., 106 (1984) 2121.
38 T.N. Sorrell, M.R. Malachowski and D.L. Jameson, Inorg. Chem., 21 (1982) 3250.
39 L. Casella, M. Gullotti, G. Pallanza and L. Rigoni, J. Am. Chem. Soc., 110 (1988) 4221.
40 T.N. Sorrell and M.L. Garrity, Inorg. Chem, 30 (1991) 210.
41 T.N. Sorrell, D.L. Jameson and C.J. O'Connor, Inorg. Chem., 23 (1984) 190.
42 T.N. Sorrell and V.A. Vankai, Inorg. Chem., 29 (1990) 1687.
43 T.N. Sorrell, C.J. O'Connor, O.P. Anderson and J.H. Reibenspies, J. Am. Chem. Soc., 107 (1985) 4199.
44 T.N. Sorrell, M.L. Garrity and D.J. Ellis, Inorg. Chim. Acta, 166 (1989) 71.
45 K.J. Oberhausen, J.F. Richardson, R.M. Buchanan, J.K. McCusker, D.N. Hendrickson and J.M. Latour, Inorg. Chem., 30 (1991) 1357.
46 W.B. Tolman, R.L. Rardin and S.J. Lippard, J. Am. Chem. Soc., 111 (1989) 4532.
47 H.M.J. Hendriks, P.J.M.W.L. Birker, J. van Rijn, G.C. Verschoor and J. Reedijk, J. Am. Chem. Soc., 104 (1982) 3607.
48 P. Gomez-Romero, G.C. DeFotis and G.B. Jameson, J. Am. Chem. Soc., 108 (1986) 851.
49 J.L. Sessler, J.D. Hugdal, V. Lynch and B. Davis, Inorg. Chem. 30 (1991) 334.
50 M.G. Patch, Hok-kin Choi, D.R. Chapman, R. Bau, V. McKee and C.A. Reed, Inorg. Chem., 29 (1990) 110.
51 W.P.J. Gaykema, A. Volbeda and W.G. Hol, J. Mol. Biol., 187 (1985) 255.
52 R.W. Root, J. Biol. Chem., 104 (1934) 239.
53 K.D. Karlin, R.W. Cruse, Y. Gultneh, A. Farooq, J.C. Hayes and J. Zubieta, J. Am. Chem. Soc., 109 (1987) 2668.
54 T.N. Sorrell and A.S. Borovik, J. Chem. Soc. Chem. Commun., (1984) 1489.
55 P.J.M.W.L. Birker, H.M.J. Hendriks, J. Reedijk and G.C. Verschoor, Inorg. Chem., 20 (1981) 2408.
56 V. McKee, J.V. Dagdigian, R. Bau and C.A. Reed, J. Am. Chem. Soc., 103 (1981) 7000.
57 V. McKee, M. Zvagulis and C.A. Reed, Inorg. Chem., 24 (1985) 2914.
58 J.E. Pate, P.K. Ross, T.J. Thamann, C.A. Reed, K.D. Karlin, T.N. Sorrell and E.I. Solomon, J. Am. Chem. Soc., 111 (1989) 5198.
59 R.H. Holm and J. Ibers, Science, 209 (1980) 223.
60 T.N. Sorrell and A.S. Borovik, J. Am. Chem. Soc., 109 (1987) 4255.
61 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3170.
62 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 6288.
63 N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, Chem. Lett., (1989) 421.
64 J.S. Thompson, J.L. Zitzmann, T.J. Marks and J.A. Ibers, Inorg. Chim. Acta, 46 (1980) L101.
65 T.N. Sorrell and D.J. Jameson, Inorg. Chem., 21 (1982) 1014.
66 M. Di Vaira and F. Mani, J. Chem. Soc. Dalton Trans., (1985) 2327.
67 N.J. Curtis and R.S. Brown, J. Org. Chem., 45 (1980) 4038.

68 Feng-Jung Wu, D.M. Kurtz, Jr., K.S. Hagen, P.D. Nyman, P.G. Debrunner and V.A. Vankai, Inorg. Chem., 29 (1990) 5174.
69 W.B. Tolman, A. Bino and S.J. Lippard, J. Am. Chem. Soc., 111 (1989) 8522.
70 H. Adams, N.A. Bailey, J.D. Crane, D.E. Fenton, J.M. Latour and J.M. Williams, J. Chem. Soc. Dalton Trans., (1990) 1727.
71 C.C. Tang, D. Davalian, P. Huang and R. Breslow, J. Am. Chem. Soc., 100 (1978) 3918.
72 R.S. Brown and J. Huguet, Can. J. Chem., 58 (1980) 889.
73 R.S. Brown, D. Salmon, N.J. Curtis and S. Kusuma, J. Am. Chem. Soc., 104 (1982) 3188.
74 T.N. Sorrell, A.S. Borovik, and C.C. Shen, Inorg. Chem., 25 (1986) 589.
75 Y. Nishida, N. Oshino and T. Tokii, Z. Naturforsch. Teil B, 43 (1988) 637.
76 C. Mealli, C.S. Arcus, J.L. Wilkinson, T.J. Marks and J.A. Ibers, J. Am. Chem. Soc., 98 (1976) 711.
77 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, J. Chem. Soc. Chem. Commun., (1988) 151.
78 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, J. Am. Chem. Soc., 113 (1991) 5664.
79 N.C. Eickman, E.I. Solomon, J.A. Larrabee, T.G. Spiro and K. Lerch, J. Am. Chem. Soc., 100 (1978) 6529.
80 R.S. Himmelwright, N.C. Eickman, C.D. LuBien and E.I. Solomon, J. Am. Chem. Soc., 102 (1980) 5378.
81 G.L. Woolery, L. Powers, M. Winkler, E.I. Solomon and T.G. Spiro, J. Am. Chem. Soc., 106 (1984) 86.
82 G.L. Woolery, L. Powers, M. Winkler, E.I. Solomon, K. Lerch and T.G. Spiro, Biochem. Biophys. Acta, 788 (1984) 155.
83 R.R. Jacobson, Z. Tyeklar, A. Farooq, K.D. Karlin, S. Liu and J. Zubieta, J. Am. Chem. Soc., 110 (1988) 3690.
84 N. Kitajima, K. Fujisawa and Y. Moro-oka, J. Am. Chem. Soc., 111 (1989) 8975.
85 J.W. Egan, Jr., B.S. Haggerty, A.L. Rheingold, S.C. Sendinger and K.H. Theopold, J. Am. Chem. Soc., 112 (1990) 2445.
86 J.S. Thompson, J. Am. Chem. Soc., 106 (1984) 4057.
87 N. Kitajima, T. Koda, Y. Iwata and Y. Moro-oka, J. Am. Chem. Soc., 112 (1990) 8833.
88 P.M. Colman, H.C. Freeman, J.M. Guss, M. Murata, V.A. Norris and J.A.M. Ramshaw and M.P. Venkatappa, Nature, 272 (1978) 319.
89 J.A. Fee, Struct. Bonding, 23 (1975) 1.
90 N. Kitajima, K. Fujisawa and Y. Moro-oka, J. Am. Chem. Soc., 112 (1990) 3210.
91 A.C. van Steenbergen, E. Bouwman, R.A.G. de Graaff, W. Driessen, J. Reediijk and P. Zanello, J. Chem. Soc. Dalton Trans., (1990) 3175.
92 M. Zoeteman, E. Bouwman, R.A.G. de Graaff, W.L. Driessen, J. Reediijk and P. Zanello, Inorg. Chem., 29 (1990) 3487.
93 J.V. Dagdigian, V. McKee and C.A. Reed, Inorg. Chem., 21 (1982) 1332.
94 W.H. Armstrong, A. Spool, G.C. Papaefthymiou, R.B. Frankel and S.J. Lippard, J. Am. Chem. Soc., 106 (1984) 3653.
95 W.H. Armstrong and S.J. Lippard, J. Am. Chem. Soc., 106 (1984) 4632.
96 P. Gomez-Romero, N. Casan-Pastor, A. Ben-Hussein and G.B. Jameson, J. Am. Chem. Soc., 110 (1988) 1988.
97 J.W. Dawson, H.B. Gray, H.E. Hoenig, G. Rossman, J.M. Schredder and R.H. Wang, Biochemistry, 11 (1972) 2003.
98 W.H. Armstrong, M.E. Roth and S.J. Lippard, J. Am. Chem. Soc., 109 (1987) 6318.
99 S.M. Gorun and S.J. Lippard, Inorg. Chem., 27 (1988) 149.

100 R.H. Beer, W.B. Tolman, S.G. Bott and S.J. Lippard, Inorg. Chem., 30 (1991) 2082.
101 R.H. Beer, W.B. Tolman, S.G. Bott and S.J. Lippard, Inorg. Chem., 28 (1989) 4559.
102 W.B. Tolman, A. Bino and S.J. Lippard, J. Am. Chem. Soc., 111 (1989) 8522.
103 Q. Chen, J.B. Linch, P. Gomez-Romero, A. Ben-Hussein, G.B. Jameson, C.J. O'Connor and L. Que, Jr., Inorg. Chem., 27 (1988) 2673.
104 S.M. Gorun, Ph.D. Thesis, Massachusetts Institute of Technology, 1986.
105 Feng-Jung Wu and D.M. Kurtz, Jr., J. Am. Chem. Soc., 111 (1989) 6563.
106 N. Kitajima, H. Fukui and Y. Moro-oka, J. Am. Chem. Soc., 112 (1990) 6402.
107 S. Menage, B.A. Brennan, C. Juarez-Garcia, E. Munck and L. Que, Jr., J. Am. Chem. Soc., 112 (1990) 6423.
108 B. Brennan, Q. Chen, C. Juarez-Garcia, A.E. True, C.J. O'Connor and L. Que, Jr., Inorg. Chem., 30 (1990) 1937.
109 Y. Nishida, M. Takeuchi, H. Shimo and S. Kida, Inorg. Chim. Acta, 96 (1984) 115.
110 M.S. Mashuta, R.J. Webb, K.J. Oberhausen, J.F. Richardson, R.M. Buchanan and D.N. Hendrickson, J. Am. Chem. Soc., 111 (1989) 2745.
111 M. Suzuki, A. Uehara and K. Endo, Inorg. Chim. Acta, 123 (1986) L9.
112 R.M. Buchanan, M.S. Mashuta, J.F. Richardson, K.J. Oberhausen, D.N. Hendrickson, R.J. Webb and M.A. Nanny, Inorg. Chem., 29 (1990) 1301.
113 B. Bremer, K. Schepers, P. Fleischhauer, W. Haase, G. Henkel and B. Krebs, J. Chem. Soc. Chem. Commun., (1991) 510.
114 P.N. Turowski, W.H. Armstrong, M.E. Roth and S.J. Lippard, J. Am. Chem. Soc., 112 (1990) 681.
115 S. Lindskog, L.E. Henderson, K.K. Kannan, A. Lijas, P.O. Nyman and B. Strandberg, The Enzymes, Vol. 5, Academic Press, New York, 3rd edn., 1971, p. 587.
116 I. Bertini, G. Canti, C. Luchinat and F. Mani, Inorg. Chim. Acta, 46 (1980) L91.
117 I. Bertini, G. Canti, C. Luchinat and F. Mani, Inorg. Chem., 20 (1981) 1670.
118 C. Benelli, I. Bertini, M. Di Vaira and F. Mani, Inorg. Chem., 23 (1984) 1422.
119 R. Alsfasser, S. Trofimenko, A. Looney, G. Parkin and H. Vahrenkamp, Inorg. Chem., 30 (1991) 4098.
120 R.S. Brown, N.J. Curtis and J. Huguet, J. Am. Chem. Soc., 103 (1981) 6953.
121 R.S. Brown, M. Zamkanei and J.L. Cocho, J. Am. Chem. Soc., 106 (1984) 5222.
122 R. Breslow, J.T. Hunt, R. Smiley and T. Tarnowski, J. Am. Chem. Soc., 105 (1983) 5337.
123 D.J. Hodgson, B.J. Schwartz and T.N. Sorrell, Inorg. Chem., 28 (1989) 2226.
124 J.E. Sheats, R.S. Czernuszewicz, G.C. Dismukes, A.L. Rheingold, V. Petrouleas, J.A. Stubbe, W.H. Armstrong, R.H. Beer and S.J. Lippard, J. Am. Chem. Soc., 109 (1987) 1435.
125 R.M. Buchanan, K.J. Oberhausen and J.F. Richardson, Inorg. Chem., 27 (1988) 973.
126 P. Mathur, M. Crowder and G.C. Dismukes, J. Am. Chem. Soc., 109 (1987) 5227.
127 F. Mani, Inorg. Chim. Acta, 65 (1982) L197.
128 P. Burchill and M.G.H. Wallbridge, Inorg. Nucl. Chem. Lett., 12 (1976) 93.
129 L.E. Manzer, J. Organomet. Chem., 102 (1975) 167.
130 E. Kime-Hunt, K. Spartalian, M. DeRusha, C.M. Nunn and C.J. Carrano, Inorg. Chem., 28 (1989) 4392.
131 S. Holmes and C.J. Carrano, Inorg. Chem., 30 (1991) 1231.
132 P.V. Bernhardt and G.A. Lawrance, Coord. Chem. Rev., 104 (1990) 297.
133 M. Di Vaira, F. Mani and P. Stoppioni, J. Chem. Soc. Chem. Commun., (1989) 126.
134 G. De Martino Norante, M. Di Vaira, F. Mani, S. Mazzi and P. Stoppioni, J. Chem. Soc. Dalton Trans., (1992) 361.
135 M. Di Vaira, B. Cosimelli, F. Mani and P. Stoppioni, J. Chem. Soc. Dalton Trans., (1991) 331.

136 G. de Martino Norante, M. Di Vaira, F. Mani, S. Mazzi and P. Stoppioni, J. Chem. Soc. Chem. Commun., (1990) 438.
137 M. Di Vaira, F. Mani and P. Stoppioni, Proceedings 15th Congress of the International Union of Crystallography, Bordeaux, 1990, p. C 214.
138 G. De Martino Norante, M. Di Vaira, F. Mani, S. Mazzi and P. Stoppioni, Inorg. Chem., 29 (1990) 2822.
139 N.W. Alcock, K.P. Balakrishnan, A. Berry, P. Moore and C.J. Reader, J. Chem. Soc. Dalton Trans., (1988) 1089.
140 E. Kimura, M. Shionoya, T. Mita and Y. Iitaka, J. Chem. Soc. Chem. Commun., (1987) 1712.