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4. COPPER

Paul O'Brien

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INTRODUCTION

The Editorial brief to produce a "comprehensive" review of copper co-ordination chemistry (even for a single year) is daunting. I hope I have covered the vast majority of published work, but, almost inevitably, something has probably been missed and to those authors my apologies. The review covers the major journals for 1982, lesser known and/or foreign journals for the period covered by Chemical Abstracts Volumes 96 and 97.

The style of this review is rather different from Professor Hathaway's recent elegant contributions to this series. I hope that by adopting a fairly laconic style to have produced an article as comprehensive as possible but still of manageable length. The divisions within the review must to some extent reflect the predjudice of the author and be rather arbitrary. Papers are generally only cited once, this of course creates problems, examples are obvious do theoretical or crystallographic papers on macrocycles appear in the section for the technique or for macrocycles? I have tried to make such placements as logical as possible but ,I fear, readers may have their own (different) opinions on such matters. I hope that by scanning the review most readers will find some useful literature they might otherwise have missed and thus make the effort of producing the article worthwhile.

4.1 COPPER(I)

Relative bond dissociation energies for two-ligand complexes of Cu(I) with organic molecules in the gas phase have deen determined [1]. A pulsed-laser volatization/ionization source was used to generate copper(I). The results established Cu(I) to be softer than H^+, Al^+, Li^+ and $CpNi^+$; as would be expected.

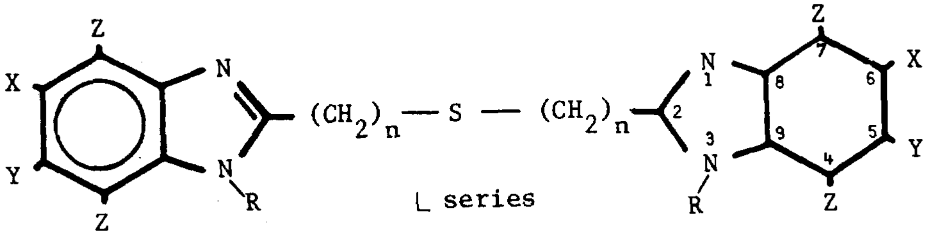
An ab initio molecular orbital study of bonding by carbon dioxide to $[Cu(I)(PH_3)_2]^+$ has been undertaken, end on co-ordination of CO_2 should be favoured [2].

4.1.1 Structural Papers

Many papers whose major content is the determination of a crystal structure have appeared. In bis(tetrabutylammonium) di-μ-iodo-diiodocuprate(I) $[N(C_4H_9)_4]_2$ $[Cu_2I_4]$ [3], the $[Cu_2I_4]^{2-}$ anion is a discrete centrosymmetric dimer with r(Cu-I) (bridging) 2.566(2) and 2.592(2)Å; r(Cu-I) terminal 2.574(2)Å and r(Cu...Cu) 2.726(4)Å. Tetrapyridinecopper(I) perchlorate is composed [4] of discrete $[Cu(C_5H_5N)_4]^+ClO_4^-$ units; co-ordination at copper(I) is close to tetrahedral with r(Cu-N) 2.046(4)Å. The structure of cuprous iodide polytype 12R has been determined [5], the iodine atoms are close packed with the copper atoms disordered; average r(Cu-I) is 2.616(5)Å. The type 2H polytype of β-copper(I) thiocyanate has been investigated [6]. The acrylonitrile complex of copper(I) chloride consists of undulating chains of copper and chloride ions interlinked by bidentate C_3H_7N ligands [7a], an unusual polymeric structure has been reported for the thiopyrilium salt of the infinite chain $[Cu_2I_3^-]$ [7b]. The structures of $[N(C_4H_9)_4][CuCl_2]$ and $[N(C_4H_9)_4][CuBr_2]$ have been determined [8].

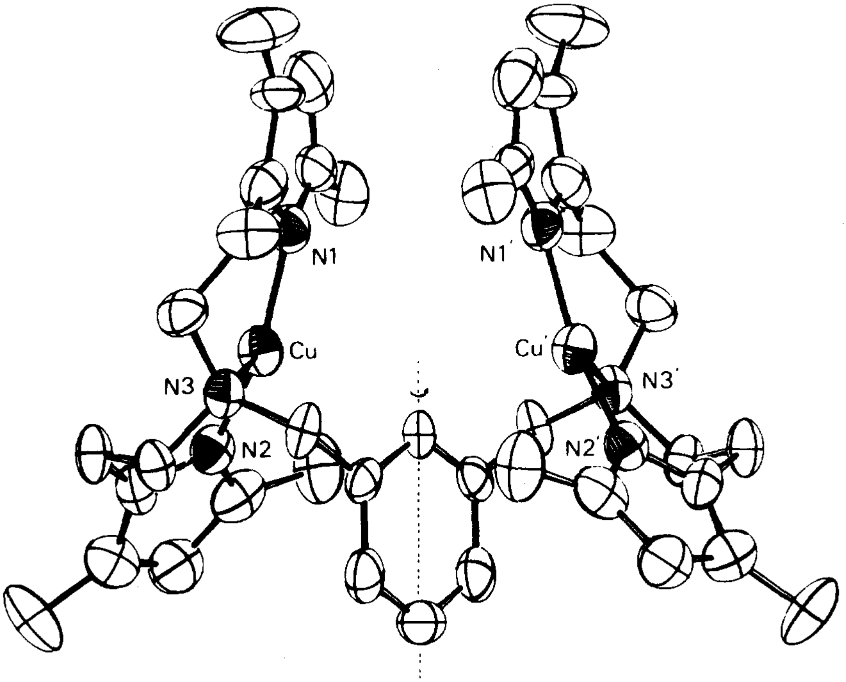
Interesting studies of copper(I) complexes with bulky ligands intended to mimic various metalloenzymes continue to appear, including crystal structures of the copper(I) complexes of 1,7-bis(2-benzimidazolyl)- 2,6-dithiaheptane (bbdh) [9], N,N,N',N'-tetrakis(2-benzimidazolymethyl)-1,2-diaminoetane [10] and 1,6-bis(N-benzylimidazol-2-yl)2,5-dithiahexane [11]. The preparation and structure of tetrakis(6-methyl-2-oxypyridine)tetracopper(I) $[Cu_4(mhp)_4]$ [12], reveals a puckered square of copper atoms each edge bridged by a single mhp ligands with r(Cu-Cu) between 2.656(1) and 2.709(1)Å. The structure of the copper(I) complex of 2,2'-bis(2-(propylbenzimidazolyl)) diethyl sulphide is a three coordinate T shaped copper(I) cation [13] with 2N and 1S donors (1).

The long Cu-S distance, 2.469 Å, is attributed to the misalignment of the sp^3 lone pair on sulphur with the Cu-S vector. Ligands of the kind illustratedbelow have been used to estimate the intrinsic Cu-N and Cu-S bond distances for histidine and methionine in copper proteins. The relevance of this to bonding in metalloproteins is discussed. Reaction of the ligand N,N,N',N'-tetrakis(2-pyridylmethyl)-1,2-diamminoethane (tpen) with $[Cu(CH_3CN)_4][BF_4]$ produces a binuclear complex $[Cu_2(tpen)]^{2+}$. The complex reversibly binds two molecules of carbon monoxide; the structures of both CO adduct and complex are reported. In the adduct each copper is pseudotetrahedral, in the complex the environment of each copper(I) is highly distorted with r(Cu-Cu) 2.78 Å [14].



1

The copper(I) complexes of thiourea $[Cu\{SC(NHC_2H_5)_2\}_3].[SO_4]_{0.5}$ [15] $[Cu_4\{SC(NH_2)_2\}_6][HSO_4]_2[SO_4].H_2O$ [16] and $[Cu_2\{SC(NH_2)_2\}_6][SO_4].H_2O$ [17] have been studied. The crystal and molecular structure of catena-μ-iodo-(1,2-cyclohexanedionedioxime)copper(I) reveals tetrahedral co-ordination at the metal by two nitrogens and two bridging iodine atoms [18]. The complex catena-poly[copper(I)-di-μ-bromo-copper(I)-2,3:2,4-[bis-μ-(1,4-oxathiane-S:S][di-μ-bromo-dicopper(I)]-3,1:4,1-[bis-μ-(1,4-oxathaine-S:S)] contains $\{Cu_2Br_2\}$ rings linked by S-bridging 1,4-oxathiane molecules into infinite chains; r(Cu-Br) 2.44-2.52 Å, r(Cu-S) 2.27-2.33 Å. There may be weak Cu....Cu interations [19]. Copper(II) oxathian complexes have been studied both crystallographically and by thermal analysis [20]. The non isomorphous complexes $[Cu(1,4\text{-thioxane})]_3[ClO_4]$ and $[Cu(1,4\text{-thioxane})_4][BF_4]$ have been studied, a hydrated form of the tetrafluoroborate salt was also isolated [21]. The only bridging copper(I) carbonyl to date has been prepared from [22] copper(I) benzoate in the presence of either N,N,N',N'-tetra-methylethylenediamine (tmen) or N,N,N',N',-tetramethylpropylenediammine (tmpn) by carbonylation. A considerable number of papers are concerned with polynuclear clusters. The complex $[(denc)CuX_4]$ [23] (denc =N,N-diethylnicotinamide; X = Cl, Br or I), has for the iodide a $\{Cu_4I_4\}$ distorted "cubane-like" core r(Cu-I) 2.6299-2.7493 Å, spectral measurements indicate that complexes with other halogens have similar structures with denc. The reactions with of dioxygen with these complexes are simple second order processes; rates decrease in the order Cl>Br>>I. A series of binuclear complexes involving xylene bridges which react reversibly with molecular oxygen have been reported, crystallographic results have been presented for related complexes [24].



2

A three co-ordinate copper(I) complex with the ligand prepared from the reaction of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine with α,α'-dibromo-m-xylene (mnx) has been studied [25] and is illustrated above (2).
The very "fine tuning" of redox properties observed for such model complexes suggests that such results should be very carefully considered.
A three co-ordinate copper(I) complex modelling deoxyhaemocyanin and deoxytyrosinase has been reported [26].

4.1.2 Synthetic and Spectroscopic Studies

The effect of substituents on the charge transfer bands of a series of copper(I) complexes with 4-substituted pyridines has been investigated [27]. Monomeric and binuclear complexes could be identified and a reversible reaction of CO with the $[CuL_4]$ complex derived from $[CuCl(CH_3CN)_2]$ was observed. The complex of 1,8-di(2-pyridyl)-3,6-dithiaoctane (pdto) with CuCl and CuBr have been studied, by electronic and ^1H NMR spectroscopy [28]. The equilibrium between $[Cu(pdto)]^+$ and [CuX(pdto)] is discussed; [CuX(pdto)] is readily oxidised by molecular oxygen.

The reaction between chlorotris(methyldiphenylphosphine) coppper(I) and several hydroborates has been studied; a new complex [({acetoxy)trihydroborato}tris(methyldiphenylphosphine)copper(I)] was isolated and characterised by IR and NMR spectroscopy [29].

Vibrational studies have been undertaken on copper(I) aminobenzothiazoles [30], 3,5-diamino-1,2,4-dithiazolium halides (thiouret hydrohalides) [31] and bis(thiocyanato)cuprate(I) [32a]; in the last study [32a] vibrational results were used to argue that discrete $[Cu(SCN)_2]^-$ ions did not exist in the solid state, NQR frequencies for $[N(PPh_3)_2][Cu(SCN)_2]$ were in the region expected for diagonal or trigonal co-ordination of copper and the bonding in $K[Cu(CN)_2]$ was also studied by ^{14}N and ^{63}Cu NQR spectroscopy [32b].

Exposure of $K_3[Cu(CN)_4]$ to ^{60}Co γ-rays at 77 K gave rise to an electron-gain centre $[Cu(CN)_3]^{3-}$ [33]; having a planar structure with 70% of the extra electron in $4p_z$ of copper; this was compared with isoelectronic Ag, Zn, Cd and Hg centres. On warming the electron-loss centre undergoes a series of alterations, one important species being five-co-ordinate $[Cu(CN)_5]^{3-}$ with a d_{z^2} ground state. The influence of anion, solvent and temperature on the ^{63}Cu NMR of copper(I) complexes in solution has been investigated [34]. Exchange processes with complexes of lower (less than T_d) symmetry were concluded to be responsible for the large variation in line width and chemical shift parameters. Solid-state ^{13}C NMR spectroscopy has been used to characterize the bonding of thiocyanate in copper(I) complexes [35].

Copper(I) chloride complexes with pyridine, 4-methylpyridine, 2,4-

dimethylpyridine and 2,2'-bipyridyl in ether irreversibly take up molecular oxygen [36]. Copper(I) (and silver(I)) complexes of N-methyl- and N-amino rhodanine have been synthesised [37]. Phosphine functionalised macrocycles have been suggested to provide a new type of ligand for the synthesis of heterometallic complexes [38]. The fluorescence properties of copper(I) carboxylates have been investigated [39].

4.1.3 Thermodynamic and Kinetic Studies

The molecular species formed by the reaction of copper(I) trifluoroethanoate[CuT] with alkenes and benzene in the solid and liquid state are monomeric [CuT(C_2H_4)] and dimeric [$Cu_2T_2(C_6H_6)_2$]. Various enthalpy changes were measured [40]. Mixed-ligand complexes of bipyridine , copper(I) with pyridine, phospine or phosphite ligands have been studied ^1H and ^{13}C NMR [41] chemical shifts were correlated with metal to ligand bonding. The stability of $[Cu(bipy)_2]^+$ in both non aqueous [42] and aqueous [43] solution has been investigated. Kinetic studies of the oxidation of bis(1,10-phenathroline)copper(I) complexes by various cobalt(III) complexes in aqueous and micellar sodium dodecyl sulphate solutions have been undertaken [44]. The oxidation of the related bisbipyridine complex has been studied in dimethylmethamamide [45].

The formation of copper(I) has been studied in water/acetonitrile mixtures [46a,46b] ; the equilibrium:

$$Cu^{2+} + Cu^{o} \rightleftharpoons 2Cu^{+}$$

can be tuned by the choice of system [46a]. This may form the basis of a cheap method for the recovery of copper from crude samples.

The rate law:

$$\text{rate} = K_D.k_2[CuClL]_2\ [O_2]$$

was found to hold in a study of the rate of reaction of dioxygen with copper(I) pyridine complexes [47]. The effect of copper ions on the interaction of other metals with

2,4-dithiobiuret was studied [48] and the copper(I) complexes of 2-mercaptobenzothiazole investigated [49]. Photosensitization of cis,cis,-1,5-cyclooctadione [50] and norbornadiene [51a,51b] by copper(I) complexes has been studied.

Long range electron transfer occurs in Co(III)/Cu(I) binuclear ions [52] copper(I) complexation with cis-1,3,5-triaminocyclohexane in ethanenitrile leads to a tetra-co-ordinate solvated species [53]. Ligand and metal oxidation are linked in this complex. Dinuclear copper(I) benzotate complexes combining with alkynes react with molecular hydrogen to produce unusual species [54].

Electrochemical studies have been reported on the Cu(II)/Cu(I)/Cu(0) thiocyanate system in acidic solution [55,56] and on 5,5-dimethylcyclohexane-2-arylhydrazono-1,3,-dione complexes[57]. Mass spectrometry was used to study the alkali chloride/copper(I) chloride system[58]. A tripod ligand [59] has been used to investigate the redox chemistry of a pseudo-tetrahedral copper(I) complex; this may be relevant to copper co-ordination in redox enzymes.

4.2 COPPER(II)

4.2.1 Structural Papers

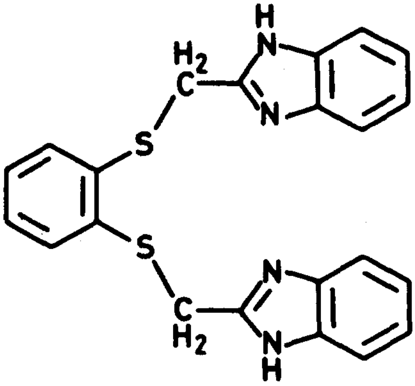
A hugenumber of crystallographic studies appeared during 1982. In this section some of the more interesting structures are described; followed by a tabulation of many other papers.

The study of "simple" copper(II) complexes, most notably halides remains popular. Electron density distribution in crystals of potassium trifluorocuprate(II) has been investigated [60]. The effect of hydrogen bonding on chlorocuprate(II) geometry was studied in bis(N-benzylpiperaziniumchloride) tetrachlorocuprate(II); $[CuCl_4]^{2-}$ shows a slight tetrahedral distortion[61]. The structure of $Cu(AlCl_4)_2$ has been determined [62]; copper atoms are tetragonally coordinated in centrosymmetric $[Cu(AlCl_4)_2]$ molecules, in contrast to the related Co(II) system copper(II) may be viewed as having a trans configuration. The complex salt $[Co(NH_3)_6][CuCl_5]$ has trigonal bipyramidal co-ordination at [63] copper(II), r(Cu-Cl)(ax) 2.301 A, r(Cu-Cl)(eq) 2.409 Å. The complex [64] $[(denc)(CuCl)_4][CO_3]]$ has been prepared by the aprotic oxidation of the corresponding copper(I) species [23]. Reaction with N,N,N',N'-tetramethyl-1,3-propanediamine (tmpd) in dichloromethane/benzene (25% v/v) produces dark green enantiomeric forms of the complex (syn-μ-carbonato)-*trans*-dichlorobis(tmpd)dicopper(II). The racemic form crystallized in the monoclinic space group $P2_1/n$, a = 16.9224, b = 7.9417 and c = 17.3433 Å, β= 99.73°; z= 4.

There continue to be many structural studies of complexes involving N-heterocycles; chlorobis[3,6-di(2-pyridyl)pyridazine]copper(II) chloride [65] consists of mononuclear $[Cu(C_{14}H_{10}N_4)_2Cl]^+$ cations; with a trigonal bipyramidal at copper(II). The complex [bis(2-pyridyl)amine]dibromocopper(II) involves a distorted tetrahedron with two-fold symmetry r(Cu-N)=1.96, r(Cu-Br) = 2.40 Å; best described as a compressed tetrahedron [66]. Crystal structures of copper(II) mixed complexes with thiodietanoate and 2,2'-bipyridine or 2,2':6',2''-terpyridine have been determined [67]. The bipyridine complex is monomeric with distorted octahedral co-ordination at copper(II); the terpy complex consist of polymeric trigonal bipyramidal co-ordinated copper(II) centre, with bridging carboxylates. Polymorphs of mixed 2,2'bipyridine oxalate complexes of copper(II) have been further investigated [68]. A monomeric complex $[Cu(ox)(bipy).H_2O].2H_2O$ is basically a square pyramid, symmetrically co-ordinated by bipyridine (mean r(Cu-N) 1,989Å) and oxalate (mean r(Cu-OO) 1.53 Å; with the water molecule at 2.341 Å above the plane of the chelating ligands. A second form involves an elongated rhombic octahedral stereochemistry at copper(II) with symmetrically co-ordinated bipyridine (mean r(Cu-N), 2.007 Å) and unsymmetrically co-ordinated *catena* bridging oxalates r(Cu-O), 1.988 and 2.302 Å). The resolution of the electronic spectrum of the polymeric form into two bands (93000 and 14500 cm^{-1}) in contrast to the single broad envelope (15600 cm^{-1}) for the monomer suggests an "electronic criterion of stereochemistry". In a search for Cu(I)/Cu(II) complexes with a common ligand environment, the structures of copper(II) (and copper(I)) complexes of 4,4',6,6'-tetramethyl-2,2'-bipridine (tmbp) have been determined [69]. In both hydrated and anhydrous forms of the complex copper has trigonal bipyramidal co-ordination; completed by a molecule of water in the hydrate or in the anhydrous form by a perchlorate ion. The crystal structure was used to argue for five co-ordinate species in solution studies of complexes of this type.

Copper(II) amino acid complexes are the subject of many reports; dichloro(L-histidine)copper(II) [70] consists of chains of molecules with the carboxylic oxygen, the amino nitrogen atom and the two chlorides forming an approximate square plane at copper(II). The mixed complex (L-aspartato)(imidazole)copper(II) dihydrate crystallizes in the orthorhombic space group [71] $P2_12_12_1$ with z=4; there is a polymeric two dimensional network in which each copper atom has distorted square-pyramidal geometry. The crystal structure of $CuL_2(im)_2$ (L = hippurate = benzoylglycinate)[72] shows square planar co-ordination <u>via</u> two centrosymmetric imidazole nitrogens and carboxylic oxygens; two weak interactions(at 2.736 Å) with carboxylic oxygens complete a very distorted tetragonal bipyramid. In bis(N-ethanoyl-α-alaninato)bis(N-methylimidazole)copper(II) dihydrate co-dination is square planar $\{N_2O_2\}$ [73]. The Schiff base complex of pyridoxal, histidine and copper(II) has been investigated [74]; cyclisation to tetrahydropyrido[3,4-d]imidazole derivative occurs.

A number of complexes of copper(II) with bulky ligands or sterically crowded ligands intended to mimic copper(II) co-ordination in metalloproteins have appeared. They include a copper(II) bbdh complex [75] (Cu(I)bbdh[9]) and the complex of copper(II) with 1,2Bis(benzamidazol-2'-ylmethylthio)benzene [76] (bbtp) (3) $[Cu(bbtp)(H_2O)]$ $[ClO_4].5C_2H_5OH$:



bbtb

3

In the bbtp complex copper(II) has trigonal bipyramidal co-ordination $\{\underline{S}_2\underline{N}_2\underline{O}\}$, a related dimeric system has also been studied [77]. Tripyridylamine)copper(II) bis(trifluoromethonesulphonate) and its bis acetonitrile adduct have been studied [78]. Four nitrogen atoms are coordinated to copper in a strict square plane, optical and EPR results were also presented. The syntheses of tris[2-(1-pyrazolyl)ethyl]amine (trpyn) and its 3,5-dimethylpyrazolyl and 3,5-di-ter-butylpyrazolyl derivatives have been described [79]. The ligands form trigonal bipyramid copper(I) complexes and square pyramidal copper(II) complexes, $E_{0.5}$ values for the Cu(I) complexes are 0.49, 0.67 and 0.94 V vs. SCE respectively; the last is the highest such potential ever recorded for a $\{CuN_4\}$ species. $[Cu(trpyn)H_2O][BF_4]_2$ is triclinic, space group P1; z = 1; a = 9.967, b = 12.956, c = 9.4734 Å; $\alpha = 91.24$, $\beta = 103.45$ $\gamma = 106.70^{\circ}$. The oxygenation of [tris(2-pyridyl)amine](trifluoromethanesulphonato)copper(I) produces a cubane like cluster [80].Many other structural papers have appeared during 1982, and these are summarised in Table 1.

The crystal structures of a number of macrocyclic complexes including: (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 7,6 diethanoicacid)copper(II) [120], aqua(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7,-diene)-copper(II) hexafluorophosphate [121], chloro[(2R,5S;8R,11S)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) chloride, chloroform solvate [122] , *N*,*N*'propylenebis[2-hydroxy-1-napthyl)methanimato]copper(II) -0.5 dmso[123], bis aqua(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,8-tetraane)copper(II) nitrate [124], chloro[(2R,5R,8R,11R)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) chloride [125], (N-methylimidazole)(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) hexafluorophosphate [126], aqua(3,7-diaza-2,7-nonadiene-2,8-dicarboxylato-*O*,*O*^{1},*N*,*N*^{1})copper(II) [127] and various (tetraazacyclotetradecatetraenato)copper(II) complexes have been determined [128].

There has recently been a rather close interplay between crystallographic studies and thinking on electronic structure. The dynamic *pseudo*-Jahn-Teller effect may be used to explain the temperature dependence of many copper(II) structures; such work has been excellently reviewed by Professor Hathaway [129,130,131]. Recent work in this area includes further investigations of the low-temperature phases of copper(II) pyridine *N*-oxides [132], studies of successive Jahn-Teller transitions in $RbCuCl_3$[133] and detailed investigation of $[Cu(phen)_2(O_2CMe)]X$ (X = BF_4, ClO_4^-, NO_3) [134]. In this last study [134], four cation distortion isomers were investigated; X-ray and EPR data were consistent with a fluxional

TABLE 1 CRYSTAL STRUCTURE DETERMINATIONS

Complex	Formulae	Coordination	Reference
tetraammine copper(II)tetraiodide	$[Cu(NH_3)_4I_4]$	$\{CuN_4I_2\}$	[81]
mixed binuclear 1,2-diaminoethane complexes	e.g. $[Cu_2(en)_2(H_2O)_2].4H_2O$	polynuclear	[82]
bis[μ-(2-methylaminopyridine 1-oxide)-μ-O]-bis [dichloro(2-methylaminopyridine 1-oxide)copper(II)]	$[Cu_2(C_6H_8N_2O_4)]_2$	-	[83]
bis[2-(methylaminomethyl)pyridine 1-oxide]copper(II) diperchlorate	$[Cu(C_7H_{10}N_2O)_2][ClO_4]_2$	$\{CuN_2O_4\}$	[84]
bis(3-aminopyridine)copper cyanate monohydrate	$[Cu(NCO)_2(3ampy)_2(H_2O)]$	$\{CuO_3N_2\}$	[85]
β-aqua[*N*,*N*'-bis(2'-pyridinecarboxamido)-1,3-propane] copper(II) dihydrate	$[CuC_{15}H_{20}N_4O_5]$	$\{CuN_4O\}$	[86]
diaquabis(picolinato N-oxido)copper(II)	$[Cu(NpicO)_2(H_2O)_2]$	$\{CuN_2O_2\}$	[87]
potassium bis(nitroethanato(2-)]copper(II)	$K_2[Cu(nac)_2].H_2O$	$\{CuN_2O_2\}$	[88]
bis(*N*-isopropyl-5,6-benzosalicylideneaminato)copper(II)	CuL_2	$\{CuN_2O_2\}$	[89]
di-μ_3-hydroxo-μ-sulphato-tetrakis-μ-(isonicotinato-N-oxide)tetraaqua-tetracopper(II)	$[Cu_4(N\text{-}inicO)_4SO_4(OH)_2](H_2O)_4$	tetranuclear	[90]
diaquo-di-μ-hydroxo-bis-μ-(nicotinato-*N*-oxide)-bis-μ-(nicotinato-N-oxide)tricopper(II)	$[Cu_3(N\text{-}nicO)_4(OH)_2(H_2O)_2]_n$	polymeric	[91]

TABLE 1 contd. CRYSTAL STRUCTURE DETERMINATIONS

Complex	Formulae	Coordination	Reference
bis(*N*^{1}-isopropyl-2-Methyl-1,2-diaminpropane) copper(II) salicylate	$[CuL_2][sal]^-$	$\{CuN_2O_2\}$	[92]
ethanol[salicylato(2-)](*N*,*N*,*N*',*N*'-tetramethyl-1,2diamino ethane)-copper(II)	$[Cu(sal)(2\text{-}me\text{-}en)].C_2H_5OH$	$\{CuN_2O_3\}$	[93]
bis(benzoato-μ-(2-diethylaminoethanolato-N,-μ-O)copper(II)	$Cu_2[(C_2H_5)_2NC_2H_4O]_2$	$\{CuN_2O_3\}_2$	[94]
diaquabis(aminooxyethanoate)copper(II) dihydrate	$[Cu(C_2H_4NO_3)_2(H_2O)_2]2H_2O$	$\{CuN_2O_4\}$	[95]
trans-bis(*N*-butyl-pyridoxylideneiminato)copper(II)	CuL_2	$\{CuN_2O_2\}$	[96]
bis(purpurato)copper(II) "octahydrate"	$[Cu(C_8H_4N_5O_6)_2]\ 7.6H_2O$	$\{CuN_2O_2\}$	[97]
di-μ-chloro-bis[chloro(2-ethyl-2hydroxymethyl-1,3-propanediol)copper(II)]	$[Cu(C_6H_{14}O_3)Cl_2]_2$	$\{CuO_2Cl\}_2Cl_2$	[98]
[biuretato(2-)-N^1,N^5](1,2-diaminoethane)copper(II)	$[Cu(en)(C_2H_3N_2O_2)]$	$\{CuN_4\}$	[99]
teta-μ-ethanato-bis[benzimidazolecopper(II)]	$[Cu(CH_3COO)_2(C_7H_6N_2)]_2$	$\{CuO_4N_2\}$	[100]
ethanato(*N*-methyl-*N*'-salicylidene-1,3-diaminopropane) copper(II)	$[Cu(C_{11}H_{15}N_2O)(C_2H_3O_2)]_2$	$\{CuO_4N_2\}$	[101]
(2-dimethylaminoethanolato)(trifluorethanato)copper(II)	$[Cu_4(C_2F_3O_2)_4(C_4H_{10}NO)_4]$	$\{CuO_5N\}$	[102]

TABLE 1 contd. CRYSTAL STRUCTURE DETERMINATIONS

Complex	Formulae	Coordination	Reference
1,4-di(2'-pyridyl)aminophthalazine complexes	-	various	[103]
trans-dichlorobis(7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepin-2-one)copper(II)	$[Cu(C_{16}H_{13}ClN_2O)_2Cl_2]$	$\{CuN_2Cl_2\}$	[104]
dichloro(bis-2-benzimidazolmethyl)amine copper(II) methanol	$[Cu(ibz)Cl_2].CH_3OH$	$\{CuCl_2N_3\}$	[105]
N,N-bis(2-benzoimidazolylmethyl)ethanolamine copper(II) perchlorate	$[Cu(ibzen)X]ClO_4.CH_3OH$	$\{CuN_3OCl\}$	[106]
bis(dibenzylamine)bis(ethylthioethanato)copper(II)	$[CuL_2L'_2]$	$\{CuN_2O_2\}$	[107]
bis(isopropylthioethanato)tris(isoquinoline)copper(II)	$[CuL_2L'_2]$	$\{CuN_2O_3\}$	[108]
bis(1,4 thioxane)dichlorocopper(II)	$[Cu(1,4\text{-thioxane})_2Cl_2]$	$\{CuCl_2S_2O_2\}$	[109]
bromo-(trismethylthioethylamine)copper(II) perchorate	$[Cu(ns)_3Br][ClO_4]$	$\{CuS_2NBr\}$	[110]
bis(4-chloro-2-nitrophenato)copper(II)	$[Cu(4Cl,2\text{-Npheo})_2]$	-	[111]
isothiocyanatobis(1,2-diaminoethane)copper(II) bromide	$[Cu(en)_2(NCS)]Br$	$\{CuN_4S_2\}$	[112]
bis2-(2'-thiazolylazo)-5ethylaminophenolcopper(II)	$[CuL_2]$	-	[113]

TABLE 1 contd. CRYSTAL STRUCTURE DETERMINATIONS

Complex	Formulae	Coordination	Reference
2-,3- and 4-pyridinecarboxamide complexes of copper(II)	various	-	[114]
bis(1,2-diaminoethane)(nitrate)copper(II)selenocyanate	$[Cu(en)_2(NO_3)][SeCN]$	$\{CuN_4O_2\}$	[115]
aquabis(1,2-diaminoethane)copper(*II*)-*tris*(cyano)(*seleno*-cyanato)dicuprate(I)	$[Cu(H_2O)(en)_2][Cu_2(CN)_3(SeCN)]$	$\{CuN_4O\}$	[116]
(1,4-bis{(2pyridyl)amino}phthalazine N^1,N^3,N^4,N^6)-μ-chloro-dichloro-μ-hydroxy dicopper(II)sesquihydrate	$[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)]1.5H_2O$	$\{CuN_2Cl_2O\}$	[117]
aquabis(4-chloro-2-methylphenoxyethanato)bis(pyridine)copper(II)	$[CuC_{28}H_{28}Cl_2N_2O_7]$	$\{CuN_2O_3\}$	[118]
trans-bis(ethanato)bis(collidine)copper(II)	$[Cu(CH_3CO_2)_2(C_8H_{11}N)_2]$	$\{CuN_2O_3\}$	[119]

$Cu\underline{N}_4\underline{O}_2$ structure best described as pseudo-cis-distorted octahedral copper(II) in three of the complexes, and a square pyramidal distorted octahedron (4+1+1) in the fourth.

Studies of other phase transitions have been published. Two forms of N-(2-ammonioethyl)morpholinium tetrachlorocuprate(II), both stable at room temperature have been isolated [135]. In the green form two crystallographically independent $[CuCl_4]^{2-}$ ions, one a flattened tetrahedron and the other square planar, are found; in the yellow form only $[CuCl_4]^{2-}$ distorted tetrahedra are present. Reversible thermochromism has been observed [136a] for the complex bis(1,5 diaza-cyclooctane) copper(II) nitrate at 90 °C. The phase transition was attributed to co-ordination of NO_3 in the high temperature form. This is in marked contrast to the well known [136b] transitions in N,N'-substituted 1,2-diaminoethane complexes of copper(II), in which conformational changes of the ligand explain thermochromism. If reliable this is a most interesting phase transition. Phase transitions in cobalt(II) and iron(II) fluorosilicates have been probed by doping with copper(II) and investigating using EPR spectroscppy [137]. Phases transitions in hexanitrocomplexes of Copper(II) (Cobalt(II) and Nickel(II)) have been correlated with axial and equatorial bond distances [138].

4.2.2 Theoretical Studies

Many papers have apeared which report the results of MO calculations. The contributions of Gazo and Boca on the manifestation of equitorial-axial interactions are particularly notable and they have published an interesting review of their work [139]. Related papers deal with hexafluoro complexes[140], hexahalo complexes [141] and thiocyanates [142]. Forty dioxygen complexes, including several copper systems, were investigated [143] by CNDO-UHF and MO-LCAO-SCF calculations; the same methods were used to investigate N,N-ethylenebis(thioacetylacetoneiminato)copper(II) complexes [144]. In the latter study results were related to XPES data; for copper(II), Koopmans theorem is qualitatively valid.

A perturbation configuration interaction using localized orbitals (PCILO) was extended to overcome the limitations of a two centre approach to bonding [145], several systems were investigated including $[CuBr_4]^{2-}$. Iterative extended Huckel methods and CNDO have been used to study copper(II) maleonitriledithiolate [146]; the results were correlated with redox properties. The role of d-s mixing in hexa-co-ordinated copper(II) and nickel(II) complexes has been investigated by angular overlap calculations, kinetic and thermodynamic properties were related to the results [147].

Copper, silver and gold porphyrin complexes have been investigated by X_α calculations, excellent agreement between observed and calculated spin Hamiltonean parameters was obtained [148]. The interaction between metal and porphrin ligand has also been investigated by the CNDO/2 method [149]. Finally, a most interesting series of HOMO-LUMO approximations have lead to the conclusion[150] that ,in general, trans rather than cis geometries at copper(II) are more stable. This theoretical result is in accord with the known thermal reactivity of cis-bis(glycinato)copper(II) monohydrate[151].

4.2.3 General and Synthetic

This section is structured (approximately) by ligand type. Simple copper(II) species reported during the past year include, a new modification of copper orthophosphate [152], various phosphate, phosphonate and tetrafluoroborates [153] and dihydrazide and pseudohalide complexes [154]. Hexafluoroarsenates $2CuF_2.3AsF_5$ and $CuF_2.AsF_5$ have been prepared [155], and their thermal decomposition [156] and vibrational spectra studied [157]. The structural and magnetic properties of fluoro-bridged coordination compounds of first row transition metal ions, including copper(II) have been studied [158]. The effect of imidazole on the bonding of cyanato copper(II) complexes has been investigated [159], isomeric complexes $[Cu(NCO)_2(2\text{-ethyl-benzimidazole})_2]$ are produced. At low concentrations copper(II) ions inhibit the thermal decomposition of ammonium perchlorate [160], at higher concentrations a catalysed decomposition is observed.

Addition complexes of copper(II)ethanoate with both pyridine and picolines occur in both monomeric and dimeric forms [161]. Desorption mass spectra of transition-metal complexes of β-diketonates including copper(II) have been studied [162]. The interaction of sterically hindered phenols with copper(II) produces a variety of products [163]. Copper and barium tartrate complexes derived from $Ba_3[Cu_4L_2(HL)]_2.12H_2O$ have been investigated [164], water is lost at 110-130 °C; the product $Ba_3[Cu_4L_2(HL)]_2$ is EPR silent. Copper(II) succinate acid dihydrazide and bis(pentane-2,4-dionato)complexes have been prepared and studied by thermal methods [165,166]. The thermal decomposition of oxalatocuprates [167] and copper(II) oxalate hydrazinate has been reported [168].

Co-ordination complexes of copper(II) with tricyanomethines have been described [169]. A terdentate N,N,N, donor derived from 2,6-diacetylpyridine produces a variety of copper complexes [170] $CuL(NO_3)_2$, $CuLCl(NO_3)$, $[CuL(en)NO_3]NO_3$ and $[CuL_2](NO_3)_2$; these have been characterized by conductivity, vibrational and electronic spectral measurements. Bis(theophyllinato)copper(II) dihydrate and its anhydrous form have been prepared [171]; the magnetic behaviour of the hydrated form is explained by the Curie law; antiferromagnetic exchange occurs in the anhydrous form.

Copper(II) complexes of N,N,N',N'-tetrakis[(2-benz[d]imidazolyl)-methyl]alkanediamines have been isolated [172]; copper(II) lies in a distorted tetrahedral geometry. Various complexes have been isolated from the Cu(II)/NCO^-/3,4,5-trimethylpyrazole system [173], coligand isomerism was used to describe this phenomenon. Complexes with 1,2-dicyano-1,2-diaminocyclohexane have been investigated [174].

{Bis(4-aminosalicyl)hydroxyborate}copper(II) has been prepared, and investigated by IR spectroscopy and thermal decomposition [175]; similar techniques were used to study copper(II) complexes with pyridine-4-aldehyde [176]. The complexation of substituted diamines with copper(II) has been investigated using EPR both 1:4 and 1:2 complexes are formed [177]. The tetradentate ligand 3,6-bis(2'-pyridyl)pyridazine forms dinuclear complexes $[Cu_2LCl_4]$, the exact state of hydrolysis and hydration depending on the reaction conditions [178]. Nitrogen donors have also been studied in imidazoline derivatives [179], benzimidazole complexes [180] and pyridinecarboxaldehyde derivatives [181]. Cluster complexes of copper(II) have been described with bis(3-hydroxyimino-2-butylidene)phenylenediamine [182] and 3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone [183].

The complex forming properties of pyridine-carbohydroxamic acids and 1-oxide-pyridinecarbohydroxamic acids have been described [184]. Square planar structures have been suggested for the copper(II) complexes of

N,N'ethylenebis(2-hydroxy-4-methylpropiophenoneimine) [185a] and 1,5-diamino-3-pentanol[185b]; the latter is binuclear. In marked contrast the 2,2'-bi-8-quinolinol copper(II) complex was concluded on the basis of spectral measurements to be tetrahedral [186]. Complexes of diacetyl bis(dimethylhydrazone) have been prepared [187].

Salicylamide ($HOC_6H_4CONH_2$) complexes of the composition [$CuLCl_2(H_2O)$] have been investigated [188], on the basis of spectroscopic and other measurements a pseudo-octahedral environment for copper(II) is suggested. The N-aryl-salicylideneaminato complex (closely related to many solvent extraction reagents) bis[N-2,6-diisopropylphenyl)salicylideneaminato]-copper(II) is planar, a five co-ordinate adduct is formed in pyridine [189]. Copper(II) halides form 1:1 adducts with α,ωdione dioximes in non aqueous media [190], mono (β-aminoketone) complexes of 4,4,12,12-tetramethyl-5,8,11-triazapentadecane-2,14-dione are formed in acetone [191] and pyridinecarboxamide complexes are formed from copper(II) acetoacetate in methanol [192]. The 8-hydroxyquinoline derivative, N,N-bis(8-hydroxy-2-quinolyl)butylamine forms complexes with copper(II) [193], and copper(II) complexes of acetylaminobenzoic acids [194] and hydroxybenzoates [195] have also been described.

Studies of Schiff's base complexes of copper(II) are, as ever, popular, an excellent review of both conformation and interconversion has appeared [196]. The polydentate Schiff's bases complexes of N,N'-bis(salicylidene)-1,2-diaminoetane and N,N'-bis(salicylidene) hexamethylenediamine with copper(II) have been prepared, 1:1 complexes are formed [197]. A similar 1:1 complex has been prepared from 1,2-phenylenediamine, aziodialdehyde and copper(II) [198], and from the tridentate system derived from salicylaldehyde(s) and 2-aminomethylpyridine or 2-aminoethylpyridine [199]. From hydroquinone, formaldehyde and benzylamine the so called "Mannich" base, 2,5-bis(benzylaminomethyl) hydroquinone may be synthesised [200]; a polymeric 1:1 complex is obtained with copper(II).

The copper(II) complexes of the Schiff's bases N-(4-methyl-2-pyridyl)salicylaldmine and N-(6-methyl-2-pyridyl)salicylaldimine have been synthesised, reaction products depend markedly on the solvent system [201]. The complex between N,N'-(1,3-trimethylene)bis(2-oxy-1-napthaldinine) copper(II) and 7,7',8,8'-tetracyanoquinodimethane has been investigated [202]. The complex is tetrahedral with a 26.5^{o} angle between CuNO planes.

The binuclear copper(II) complex formed by the ligand 1,2,3,4-

tetrakis(R-salicylideneamino)-2,3-dimethylbutane, have been investigated by magnetic, spectroscopic and electrochemical methods [203]; electron delocalization throughout the system of the two $\{CuN_2O_4\}$ chromophores is used to explain the observations. Other Schiff's base complexes studied include mixed complexes of 1,10-phenanthroline 2,2'-bipyridine and salicylaldehyde or 2-hydroxyacetophonene [204], the bis(salicylidene)-O-alkyl-aminourea complex [205] and the hydrazine-S-methylcarbodithioate Schiff base derived from dicarbonyl compounds [206].

Various Schiff's bases derived from amino acids have been synthesised. Complexes with abnormally low magnetic moments were prepared from salicylaldehyde with L-methionine and L-leucine [207]. Other complexes with amino acids have been studied [208,209] and amino sugar Schiff's bases synthesised [210].

Complexes with the following sulphur containing ligands have been prepared and characterized, O-butyl-N-methylthiocarbamate [211], tetradithiocarbamate [212], 4 benzoylthiosemicarbazone-3-methyl-1-phenyl-2-pyrazolin-5-one [213], 1-isonictinoyl-4-allyl-3-thiosemicarbazide [214], and thiocyanate [215]. Diaquabis(ethylthioethanato)copper(II) $[Cu(C_4H_7SO_2)_2(H_2O)_2]$ is a chelate $\{S_2O_4\}$ complex; a distorted octahedron is attributed on the basis of a CT band due to the strong copper-sulphur bond [216]. The copper(II) complex of N-2-phenylsalicylaldimine $[SC_4H_3CH_2N{=}CHC_6H_4OH]$ is binuclear ($J = -175\ cm^{-1}$, $g = 2.4$)[217].

Copper(II) complexes of 2-amino-1,3,4-thiadiazole, 2-ethyl-1,3,4-thiadiazole [218a], 2-mercapto-5-methyl-1,3,4-thiadiazole, 2,5-bis(methyl mercapto)-1,3,4 thiazole [218b] and 5-benzylthio-1,2,4-triazole [219] are monomeric, several of the salts isolated were suggested to be pseudo tetrahedral. Five and six co-ordinate complexes have been isolated with sulphur containing α,ω diamines [220] and the co-ordination chemistry of copper(II) with a series of thioethers derived from aromatic systems related to imidazole studied [221]. Twenty copper(II) complexes formed with 3 and 4-(diphenylarsino) benzoic acids have been synthesised and characterized [222].

Synthetic studies of a number of complexes with low molecular weight biologically relevant ligands have been reported. The DL-lysine complex of copper(II), $[Cu(II)(H_3NC_5H_{10}CHNH_2COO)_2][HgI_3]_2$ is held to spontaneously resolve on the basis of X-ray powder data [223]. The interaction of cyanocuprates with methionine have been studied [224] and dicarboxy-N,N'-glutamic acid complexes reported [225]. The N,N'-bis-(aceto-glucose)-1,2-

diaminoethane complex of copper(II) has been synthesised [226], and vitamin-U (S-methymethionine) [227], 2-guanidino-benzimidazole [228] and vinylimidazole [229] complexes have been studied. Ferrocenyl hydrazone complexes have been investigated because of their relation to biologically active derivatives of antibiotics [230], the biological activity of 4,4'-bis(benzoyl thiourea)benzene complexes has been studied [231].

Polymer-supported copper(II) complexes studied include : polyazomethane chelate polymers [232], polystyrene anchored pentane-2,4-dionato [233], poly(2,6-dimethyl-1,4-phenylene oxide) [234], a salicylic acid urea-formaldehyde copolymer [235] and a poly(iminoethylene)dithiocarbamate copolymer [236]. Other synthetic studies have been made involving the following ligands: S-methylsemicarbazones of substituted salicylaldehyde [237], tetraphthalaldehyde bis-(semicarbizone) [238], methoxy-di(2,4-dinitrophenol) [239] 1-methoxy-2,6-ditert-butylphenyl-4-N-salicylaldimates [240], morpholine carboxylates[241], 4,4'-diamino-diphenyl-sulphide-N-methylene-keto)methane [242], benzil semicarbazone [243,244] and ethylxonthate [245].

4.2.4 EPR Spectroscopy and Related Resonance Techniques

Resonance techniques but most notably EPR are very popular methods for studying copper(II) systems. This section deals with those papers whose main contribution is a study of EPR, ENDOR, NMR or NQR spectra. The applications of these methods range from solid state physics to the study of metalloenzymes; limited EPR studies will also have been undertaken on many complexes reported in the structual, general and synthetic and biological sections. The use of EPR spectroscpoy in one and two dimensions has been reviewed, the information to be gained from the lineshape of dipole broadened exchange narrowed signals summarized [246]. The experimental approaches available for the analysis of copper(II) EPR, particularly for biological samples, has been reviewed [247]. The measurement of spin-spin separations from the intensity of EPR half field transitions [248] has been outlined (M_s= +2); various calibration checks were undertaken.

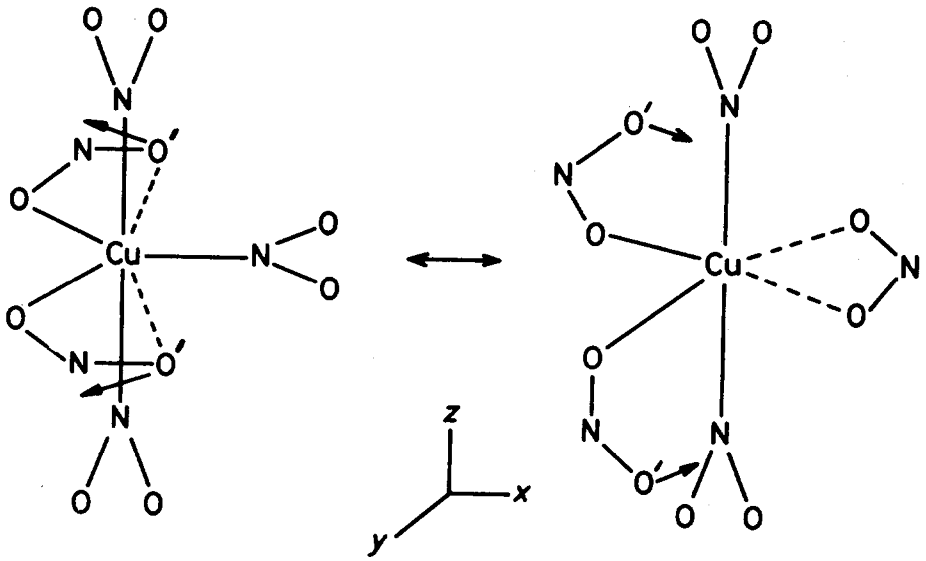
Physically orientated studies of copper(II) systems are now summarized. In an EPR study of copper(II) doped $[NH_4]_2\ [C_2O_4].H_2O$ single crystals [249], two different lattice sites were identified, each giving rise to a set of four hyperfine lines. Copper(II) doped ammonium iodide crystals [250], investigated by EPR spectra show that copper(II) substitutes for $[NH_4]^+$, polymorphs with different metal ion habitats were isolated. Single crystals of copper(II) fluorosilicate hexahydrate contain three distorted octahedral sites for copper(II) ($g = 2.390$, $g = 2.093$) and one regular octahedral site ($g = 2.093$). The temperature dependence of the EPR spectrum was not studied [251]. Various copper(II) carboxylates [252] and their pyridine adducts have been studied, as have $CuPO_4.H_2O$ and $Cu_4H(PO_4)_3.3H_2O$ [253].

EPR spectroscopy has been used to investigate the darkening of copper-cadmium halide photochromic glasses [254]. Ultra violet light induces an EPR spectrum from the basically $CdCl_2$:CuCl phase, colloidal copper produce from the disproportionation of copper(I) is suggested to explain the photochromism. (Tetraphenylporphinato)copper(II) orientated in stretched polymer films has been investigated by EPR and polarized absorption spectroscopy; EPR indicates uniaxial orientation of the porphyrin molecules [255].

Dynamic spin phenomena within impurity doped $[(CH_3)]_4NMnCl_3:Cu^{2+}$ (TMC) have been studied by X and Q band EPR [256]. Deviations from the point dipolar model have been investigated for the proton relaxation rate of $CuSO_4.5H_2O$ by NMR spectroscopy [257].

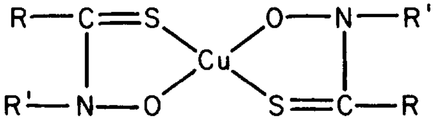
Polarized single crystal electronic and electron spin resonance spectra of $K_3[Cu(NO_2)_5]$ have been determined [258]. The results are consistent with two copper(II) environments; *seven* co-ordinate $[Cu(\underline{N}O_2)_3(\underline{O}N\underline{O})_2]^{3-}$ and a *cis*-distorted six co-ordinate $[Cu(\underline{N}O_2)_2(\underline{O}NO)_2(\underline{O}NO)]^{3-}$ (4).

Studies of monomeric copper(II) complexes in solution (and/or glasses) abound. Electron spin resonance has been used to study thiohydroxamate and 1-phenyl-3-imino-2-(1H-pyridinethione) complexes of copper(II) [259]. Both classes of compound have square-planar geometries, *trans*-$\{S_2O_2\}$ (5) and *cis*-$\{S_2N_2\}$ (6); electrochemical and electronic spectral studies were reported. The EPR spectra of a series of salicylate Schiffs base complexes



4

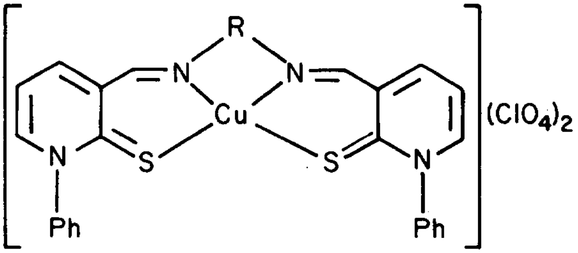
with amino acids [260] at 110 K are consistent with an $\{N_2O_2\}$ distorted planar structure; solvent effects on planarity were discussed.



I

R = H, aryl; R' = H, Me, Ph

5



II

R = $-CH_2-CH_2-$

6

The speciation of copper(II) in the organic phase arising from solvent extraction with the Shell reagent SME529 (principally anti-5-nonyl-2-hydroxyacetophenone) has been studied by EPR spectroscopy [261,262]. The formation of five co-ordinate adducts with nitrogenous bases was demonstrated; no evidence for the displacement of oxime by ammonia could be obtained, all complexes were monomeric. The resolution of these spectra was excellent. In the bis(1-phenyl-3-methyl-4-phenylazo-pyrazol-5-thione) complexes of copper(II), well resolved *N*-hyperfine coupling on the isotropic copper(II) spectrum provided evidence for a square planar structure with two equivalent nitrogen atoms [263]. Excellent resolution is again observed in the isotropic spectrum of a copper(II) cyclam derivative [264].

Adduct formation by bis-(dithiocarbonate)copper(II) has been studied using EPR spectroscopy, $\langle N_2S_2\rangle$ and $\langle S_4\rangle$ chromophores were found to differ from $\langle O_4\rangle$ and $\langle N_2O_2\rangle$ chromophores. The former react in halogen containing hydrocarbons to produce as the final product CuX_2 (X = Cl or Br) [265]. The reaction between NO and copper(II) dithiocarbonates, dithiophosphates and bis(8-mercaptquinolinates) results in the formation of adducts, in contrast NO_2 oxidises the ligands [266]

Other EPR studies include work on various derivatives of acetophenone [267], 2-phenolic oximes [268], 2,5-diphenyloxazole complexes [269], 2,6 dihydroxybenzoates [270], phthalocyanine/iodide species [271], sarcosine complexes [272], pyridine and picoline complexes [273], dithiocarbamates [274] and Shiff's bases [275]. Yet another EPR study of the complexes of composition $[Cu(bipy)_2]$ has appeared [276]. The complex (ethylenebisguanidine)copper(II) chloride has been studied to investigate the effect on *g* values of ligand field strength [277].

A number of EPR studies are devoted to systems of coupled copper(II) centres. A one-dimensional Heisenberg paramagent $[(CH_3)_4N]Mn_{1-x}Cu_xCl_3$ has been studied for values of x between 0 and 0.5 [278]. The maximum line width occurs at x 0.3, in agreement with the altered diffusion model. Single crystals of the *quasi*-eclipsed structure of $[(NH_3(CH_2)_nNH_3)][CuCl_4]$ n = 2, 3 and 4 have been subjected to linewidth measurements between 100 and 333 K [279]. Frequency dependent EPR measurement 1-18 GHz were performed on TMMC doped with 1%, 4%, 7% and 9% copper(II), the exchange interaction constant J_{MnCu}/k_b was evaluated as 1.7(-0.4) K [280].

Tetra-butylammonium-(maleonitriledithiolato)(monoethyldithiophosphato)cuprate(II)/nickel(II) has been the subject of an ENDOR study [281] as have, diethyldithiocarbonates [282,283]. The ^{63}Cu,^{35}Cl and ^{79,81}Br NQR spectra copper (II) complexes involving amino alcohols studied [284]. The ^{63}Cu and ^{65}Cu ENDOR spectra of bis(2,4-pentanedionato) copper(II) (doped in the palladium complex) have been studied [285]; nuclear quadrupole coupling tensors reveal deviation from axial symmetry. Quadrupole interactions of ^{14}N nuclei in copper(II)-doped triglycine sulphate were investigated by ENDOR spectroscopy [286]. It appears that the bis(glycinato)copper(II) used for the doping was regarded as remaining intact, this is unlikely in view of the kinetic lability of copper(II) complexes. A detailed and most interesting ENDOR study of tetraimidazolecopper(II) has appeared, this may provide a model for the copper site of superoxide dismutase [287]. Nuclear quadrupole coupling in octahedral copper(II) has been investigated in an EPR study of $MgSO_4.7D_2O$ [288]; powder and single crystal methods were in good agreement.

A number of papers concern copper(II) nitroxide radical interactions studied by EPR methods [289,290,291]. The triplet EPR spectrum of the copper porphyrin radical cation has been studied [292].

4.2.5 Electronic Spectroscopy and Related Methods

The electronic spectrum of tetrachlorocuprates(II) of aminopyridinium cations, are consistent with D_{2d} symmetry [293]. The origin of the red colour in copper(II)-doped ethylenediammonium tetrachloromanganate(II) has been studied [294]. An intense absorption band at 20,800 cm^{-1} responsible for the colour is assigned to a Cl-Cu electron transfer transition, in a $\{CuCl_6\}$ centre of "strained" co-ordination. The electronic spectra of complexes of the form $[Cu(phen)_2]X_2$ have been studied [295], the authors hold that "electronic" criteria for stereochemistry needs careful interpretation [296]. Complexes of sulfadimesine [297] and phosphines [298] have been characterized by their electronic spectra.

Solution spectroscopic studies of the co-ordination of pyridine and piperidine to copper(II) porphyrins have been carried out[299]. A spectroscopic study of copper(II) chloro complexes in propylene carbonate and dimethyl sulphoxide has been undertaken. Calculated spectra for unsolvated $[CuCl_4]^{2-}$ are similar in both solvents [300]. The electronic structure of some copper(II) complexes with $\{S_4\}$ and $\{N_4\}$ ligand fields have been studied [301]; results are related to blue copper proteins. The electronic spectra of 5-co-ordinate mixed chelates of copper(II) containing N-alkylated 1,2diaminoetane, pentane-2,4-dione and halide ions have been measured [302], and interpreted in terms of a competition for the axial position between solvent and halide. Schiff's bases formed from pyridoxol and histamines in aqueous solution have been investigated spectrophotometrically [303]. Reduction potentials have been correlated with the frequency of the CT transition in alkoxo-bridged binuclear copper(II) complexes [304].

The use of chiroptic methods (CD,ORD) may have been less popular than in some recent years. Unsymmetrical Schiff's bases of (R)-1,2-diaminopropane with pentane-2,4-dione salicylaldehyde [305] and heptane-2,4,6-trione [306] have been studied; the results were interpreted in terms of exciton theory. An interesting polemic concerning the structure of such Schiff's base complexes has appeared. Jansen [307a] holds that tetrahedral distortions in O-aminobenzaldehyde/chiral diamine complexes are substantial; Waters [307b] proposes that these reach a maximum of 5-10°. The discussion again highlights how much of our real knowledge of the local molecular geometry of copper(II) is confined to crystal structure; the extrapolation of such solid state results to solution should always be cautious. The formation of polynuclear complexes in solution has been detected in a CD study of glyoxol bis[(2S)-pyrrolidin-2-ylmethylimene] metal species [308]

Deprotonated complexes have been detected in a study of the CD spectra of copper(II) L-threonine and L-allothreonine [309]. "New bands" detected in the UV region due to CT are similar to those first described some years ago by Tsangaris [310]. The origin of diastereomeric interactions has been commented on in a study of the Shiff's bases of (1R)-3-(hydroxymethylene)camphor and chiral 1,2-diamines [311].

The photoredox chemistry of copper(II) perchlorate in methanolic media is mediated via CT bands in the 200-250 nm region [312]. The reduction of copper(II) in various unsaturated chelates[313] has been investigated and structural and electron-transfer processes have been correlated with crystal field splitting parameters [314].

4.2.6 Vibrational Spectroscopy

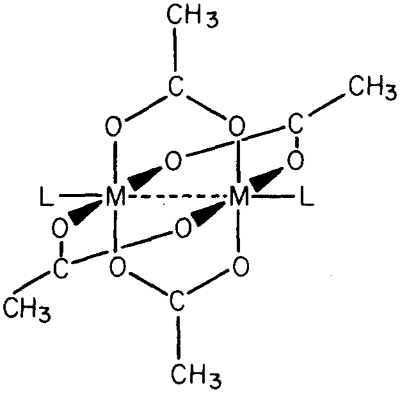
The pH dependence of the Raman spectra of 1:2 copper(II) histamine complexes in aqueous solution may be explained in terms of co-ordination via N(1) and N(3) of the ligand [315]. Protonated complexes exist in acidic solutions. Infra-red and Raman studies of thiosemicarbazide complexes of copper(II) indicate a trans-square planar structure [316]. Incoherent inelastic neutron scattering spectra confirm these results. Surface Raman spectroscopy has been used [317] to investigate the interaction of the dithizone (diphenylthiocarbazone) anion at the copper electrode in alkaline media. Comparisons with the spectrum of copper(II) dithizonate enable the approximate orientation of the anion at the interface to be proposed.

Infrared studies of a copper-urea complex [318], complexes of 2,fluoro,5-nitroaniline and 4,fluoro,2-nitroaniline species [319], the N-methyl-thiazolidine-2-thione complex [320] and 1-(2-pyridylazo)-2-napthol complex [321] have been reported. Infra red spectra have been reported for the thermal decomposition products of catena-diaquabis-μ-(nicotinato-N-oxido)copper(II)tetrahydrate [322] [cf 90]. A group theoretical treatment of the metal-ligand stretches in bis(aminoacidato)copper(II) complexes first suggested by Herlinger[323-4]has been adapted to form the basis of undergraduate practical exercise. The copper(II) complexes of soil humic substances have been isolated, -OH, -C=O as well as $-COO^-$ groups are indicate as co-ordination sites [325]. Infrared results are also reported for 4',4'diaminodiphenylmethane [326] and various triazole complexes [327].

4.2.7 Magnetic Measurements

The majority of contemporary magnetochemists are concerned with measurements on coupled copper(II) centres and ferromagnetic behaviour ; studies on dimeric and polymeric complexes have hence been collected in this section of the review. A major review of the relationship between structure and magnetic properties for oxo-bridge binuclear complexes has appeared [328]. Single crystal magnetic anisotropy measurements have been made on hexakis(pyridine-N-oxide)copper(II) (and cobalt(II)) using a superconducting quantum interference device (SQUID) [329], the $[Cu(C_5H_5NO)_6]$ centre studied is slightly distorted from regular octahedral stereochemistry. An alternative method of modelling the magnetic susceptibility of dimers has been reported; results are compared with those obtained using the Bleaney-Bowers formula [330].

The copper etanoate dimer (7) and its derivative have formed the subject of a variable temperature infrared and Raman study [331].



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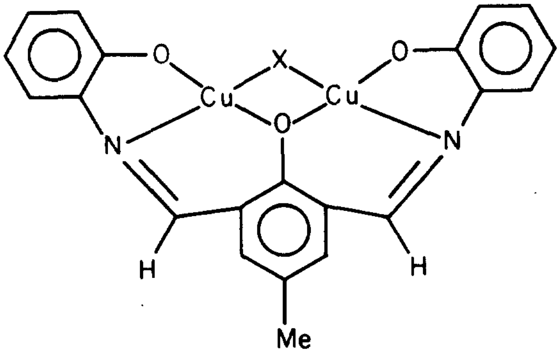
Isotopic ^{2}H, ^{18}O and ^{65}Cu substitution has been used; data on the pyridine and pyrazine derivatives reveals a temperature-dependent feature at 300 cm^{-1} in the aquo complex as a Cu-O stretch. Magnetic and spectroscopic studies of copper(II) N-methyl [332a] and N-benzoylvalinates [332b] are reported, 2J values are correlated with related complexes. Adducts of copper(II) ethanoate with triphenylphosphine and triphenylphosphine oxide have singlet/triplet energy level splitting of 371 and 319 cm^{-1} repectively [333].

Complexes with the binucleating ligand; 1,5-bis[1-(pyridin-2-yl)ethylideneamino]pentane-3-ol complex derived from the condensation of salicylaldehyde and pyridine-2-carboxaldehyde feature a single bridging ligand alkoxide group [334] (8).



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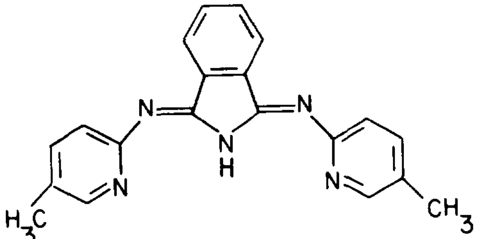
In the perchlorate complex the Cu-Cu separation is 2.928 A ; the Bleaney-Bowers equation with J = -142 cm^{-1} models the magnetic properties well. The complex μ-(benzotriazolato-N^1,N^3)-bis{[tris(N^1-methylbenzimidazol-2-ylmethyl)amine-N,N^3,$N^{3'}$,$N^{3''}$]copper (II)} trinitrate is an antiferromagnetic J = -18 cm^{-1} [335] (imidazolate and benzimidazolate complexes have similar properties(J = -28 and 10 cm^{-1} repectively). The complex has dimeric cations of C_2 symmetry with a bridging benzotriazolato ligand r(Cu-Cu) = 5.536 A. A copper(II) complex with two N,N,O,S sub units has been described [336]; J = -630 cm-1.



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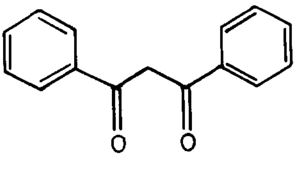

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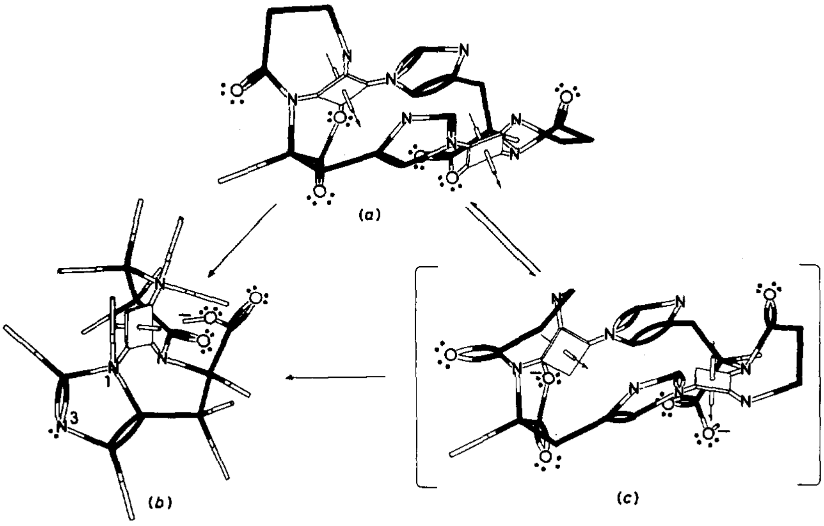
The ternary complex of copper(II) with dibenzoylmethane and 1,3-bis(2-pyridylimino)isoindolines (9,10); is a non-covalent dimer in which a spin exchange process operates [337]. The solid state EPR is of a spin coupled triplet, but above 77 K the susceptibility obeys the Curie-Weiss law.

Single crystal magnetic properties of the Y-form of bis N-(methylsalicylaldimine)copper(II) indicate a ferromagnetic exchange in the dimer [338]. The binuclear Schiff's base complexes derived from salicylaldehyde and various amines have been studied [339,340]. Centrosymmetric dimers are formed by the anhydrous [bis(dichlorobis(2-methylpyridine)copper(II) [341]. The magnetic properties of dimers of this chloride bridged general type are discussed in terms of the bond angle and distance between copper and chloride atoms. Pyrazolate bridged copper(II) complexes with diethylenetriamine have an antiferromagnetic interaction ($J=-21.5$ cm^{-1}) [342]. The alkoxy bridged binuclear complexes of 2-[2-(dialkylamino)ethylthio]ethanol. (For alkyls, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) have been prepared [343], magnetic properties were interpreted using the Bleaney-Bowes equation [343]. Other essentially binuclear complexes studied include those of, terpyridine [344], dibromobis(4-methyloxazole) [345], μ-oxamido-bis-2,2'-bipyridine [346], benzotriazoles [347], N,N'-bis(2-pyridylethyl)-oxamide [348] and di and triaminoguanidine [349]. The super exchange interaction has been studied in $[NH_3(CH_2)NH_3]$ $[CuX_4]$ (X = Cl and or Br), the strength of the copper-copper interaction indicates a 10th power dependance on halide-halide separations [350,351].



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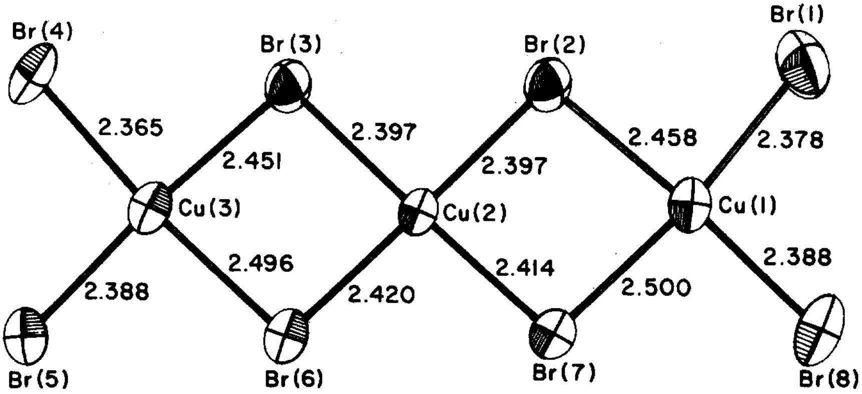
The pH dependance of the formation of simple imidazolate bridged binuclear copper(II) complexes has been investigated [352]. An apparent pka of 8.3 was observed; closely resembling the unusual properties of zinc free bovine erythrocyte super oxide dismutase. Copper(II) dimers in solution have also been investigated in a study of carnosine complexes by FTIR and EPR spectroscopic [353] evidence for the persistance of dimers in saturated aqueous solutions between 15 and 18 C was obtained (11).

Several well defined polynuclear complexes have been synthesised. Poly-functional phthalazines produce well defined mono, di and tri nuclear complexes [354]. The tetranuclear complex produced by aerial oxidation of bis(3(5)-methylpyrazole)copper(I) nitrate has J = -202 cm^{-1} [355]. The Schiff's base formed from salicylaldehyde and bis(3-aminopropyl)methylamine contains two "inner" and two "outer" copper ions [356]. Magnetic exchange (anti ferromagnetic J=6.6 cm^{-1}) is determined by the two "inner" copper(II) centres. The ferromagnetic ground state of the tetrametric complex, of copper(II) with 3-hydroxy-5-hydroxymethyl-4-(4'-hydroxy-3'-methyl-4'-phenyl-2'-azabut-1'-en-1'-yl)2-methyl pyridine is characterized by g = 2.12, J_{13} =17.1 cm^{-1} and O = 1.1 K; in the Heisenberg/Dirac/van Vleck model [357]. The trimeric complex $[(C_2H_5)_2NH_2]_2$ $[Cu_3Br_8]$ $[CuBr_2].C_2H_5OH$ has two distinct copper(II) environments [358]. Three of the coppers are square planar and bridged by bromide, adjacent trimers are stacked to give octahedral (4+2) co-ordination. The other copper centre is involved in an unusual neutral $CuBr_2$ chain, magnetic results are interpreted in terms of antiferromagnetic coupling within the trimers (J_t/k = -100 K) and the chain (J_c/k = -20 K) (12):



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Polymeric systems attract an every increasing number of magnetic and related studies. The magnetic susceptibility of the polymer copper(II) chloride-1,4-dioxane(3:2) has been investigated between 4-300 K [359]. There are some similarities to the above study in that there are trimeric units, these are linked ferromagnetically intratrimer J/k = 94 k and antiferromagnetically inter-trimer J/k = -7.6 k. Spin waves in the one-dimensional Heisenberg ferromagnet $[CuCl_2]$.dmso have been investigated by neutron scattering [360], the spin line widths disagree with those predicted by classical methods, this is held to suggest that quantum corrections to the line widths are significant. In a separate study [361] ferromagnetic interaction coupling was measured as J/k = 45 K for $CuCl_2$ DMSO, interchain coupling was antiferromagnetic J/Pc = -1.6 K.

The compound bis(anilinium)copper tetrachloride $[C_6H_5NH_3]_2[CuCl_4]$ is a typical layered perovskite; layers of $[CuCl_4]^{2-}$ ions are sandwiched between bilayers of the organic ammonium cations [362]. Intra-layer exchange is ferromagnetic, EPR and NMR studies provide evidence for two dimensional spin diffusion. The ferromagentic quantum chains $[C_6H_{11}NH_3][CuCl_3]$ and $[C_6H_{11}NH_3][CuBr_3]$ are to good approximations S = 1/2, Heisenberg linear chains, J/k 50K[363]. The quasi one dimensional system $(CH_3)_4$ NMn_x Cu_{1-x} Cl_3 has been subjected to magnetic measurements for $0<x<1$ and down to 0.32K [364]. At 4.2 K the susceptibility starts to increase for values of x up to 0.1 and then decreases rapidly. The spin dynamics of $Rb_2[CuBr_4].2H_2O$ and related systems have been studied [365, 366, 367, 368].

Low dimensional magnetic interactions have been investigated in $[Cu(bipy)(H_2O)_2]SO_4$ linear chain complexes[369]. The complex catena-dichloro(3,6-dithiooctane)copper(II) has a unique chain structure [370], magnetic susceptibility is bestfittedby alternating chain theory S = 1/2 with alternation parameters -2.73 cm^{-1} and 0.69 cm^{-1} and g = 2.084.
There have been two studies of ferromagnetic coupling in copper(II) carbonates for $Na_2[Cu(CO_3)_2].3H_2O$ [371] and $K_2[CuCO_3]$[372]. In the former magnetic measurements were performed in the temperature range 1.8-42 K, for the later average and single-crystal measurements show ferromagnetic ordering at 6.6 K, above 15 K the data are well represented by the S=1/2 series expansion for the fcc lattice with g = 2.14 and J = 1.19 cm^{-1}.

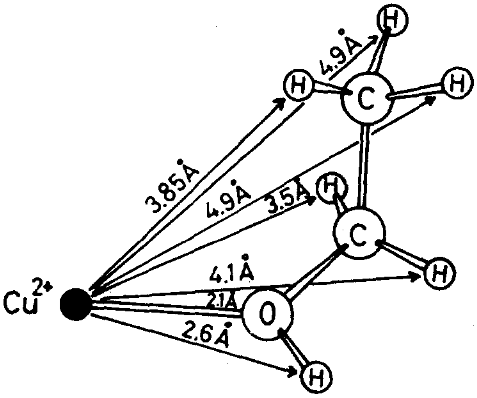
A number of studies of pyrazine carboxylic acid copper(II) complexes have appeared, $[C_4H_3N_2COO]^-$ complexes $[CuL_2]$ and $[CuL_2].H_2O$ have been investigated; magnetic properties indicate weak ferromagnetic interactions [373]. The complex (2,3-pyrazinedicarboxylato)copper(II)hydrochloride [374] shows a ferromagnetic intrachain exchange; with infinite chains propagated along the [011] axis of a $Pna2_1$ structure; magnetic parameters, g = 2.26, J/k = 1.9 K. In contrast the trihydrate [375] exhibits no magnetic interactions. Complexes of the type $[Cu_3AsS_3]$ and homologues have been studied [376].

The coupling of copper(II) centres to other paramagnetic transition metal ions has again attracted a considerable amount of work. Ferromagnetic interaction between copper(II) and chromium(III) has been observed [377] in a dinuclear complex, in which the "magnetic" orbitals are orthogonal; a triplet/quintet separation of 120 (+ 30) cm^{-1} was deduced. A similar interaction (J = 118 cm^{-1}) has been described for VO(II)/Cu(II) coupling in a related study [378]. With the Schiff's base derived from the condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol a series of binuclear complexes of copper(II) with Mn(II), Fe(II), Co(II) and Ni(II) have been prepared [379], antiferromagnetic exchange was observed with J -30, -71 and -103 cm^{-1} for Mn(II), Fe(II) and Ni(II) respectively. In studies of $[CuNi(fsa)_2en(H_2O)_2].H_2O$ [380] ($H_4(fsa)_2en$ = N,N'-Bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane) -3J/2 = 213 cm^{-1} between an $^2A_1$ ground state and $^4A_1$ excited state; copper is strictly planar $\{N_2O_2\}$and Nickel is pseudo octahedral $(\underline{O}_2,\underline{O}_2(H_2\underline{O})_2)$. Copper(II)/M(II) (M = Cu, Co, Cd, Hg) complexes have also been reported for N',N'-bis(5-t-butylsalicylidene)alkanediamines; redox behaviour was studied[381]. The behaviour of Ni(II)/Cu(II) coupled centre studied are a wide temperature range [382]. The complexes of a paramagnetic enamine ketone have been studied [383].

4.2.8 Solvation Studies

In recent years the application of diffraction techniques (X-ray or neutron) and EXAFS to solutions has begun to give real information about solvation. On the whole (for copper(II)) such work confirms the models which had long been considered by chemists, this is perhaps reassuring. It is important to remember that most structural information, to date, pertains to the solid state and that real structural information for copper(II) species in solution is desperately needed

A neutron diffraction study of copper(II) chloride in heavy water (4.32 molar) exhibits clear 2-4 character [384]. The two nearest neighbours are identified with heavy water molecules, r(Cu-O) = 2.05(+ 0.02) Å. The chloride separation is suggested to be 2.56 Å. Concentrated aqueous perchlorate solutions have been used in an X-ray diffraction study of the solvation of copper(II) [385] the co-ordination numbers six with a tetragonal distortion was concluded $r(Cu-O)_{eq}$ 1.97 - 1.98; $r(Cu-O)_{ax}$ 2.34 - 2.39 Å. Electron-Spin-Echo Modulation Analysis has been used in a detailed study of the solvation of copper(II) in ethanol [386]. The structure proposed for the ethanol solvate is illustrated below (13).



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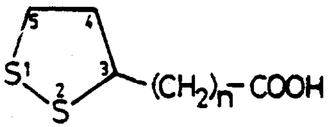
The complexes of copper(II) with chloride ions have been described in both DMSO and propylene carbonate [387]. The thermodynamic properties of a solution of copper sulphate in dioxan/water was described [388].

Inelastic light scattering has been used to study the properties of $[CuBr_2]$ in aqueous solution [389], local order in $[CuBr_2]$ solutions discussed on the basis of a vibrational study [390]. The use of EXAFS to investigate coordination in $CuBr_2$ reveals local ordering of copper and bromide ions, coordination number at copper is four with r(Cu-Br) 3.2-3.4 Å [391], temperature effects on the same systems [392] have been quantitatively analysed and a more qualitative study of the same system reported [393].

4.2.9 Equilibrium Studies

A major review of the co-ordinating ability of the amide bond [394] including much copper(II) chemistry has appeared. The hydrophobic and metal ion co-ordinating properties of α-lipoic acid (14) have been summarized [395].



n = 4 : Lipoic acid (LP)
n = 2 : Bisnorlipoic acid (BL)
n = 0 : Tetranorlipoic acid (TL)

14

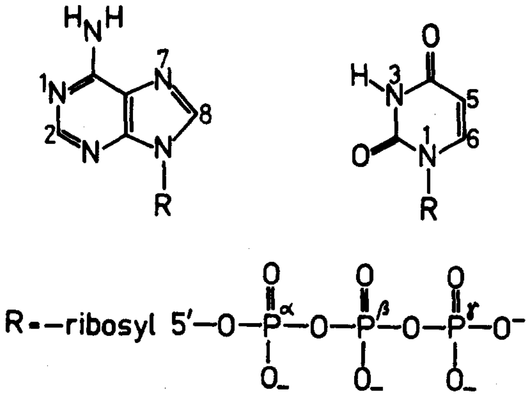
α-(+)-liopic acid is an important co-enzyme, it is widely distributed in animals and plants. A simple relationship between the enthalpies of complexation, stability constants and metal cation radii has been proposed [396].

Several papers deal with the methodology of equilibrium constant determination. A new FORTRAN programme for the calculation of equilibrium parameters of a complex multicomponent system BEST has been described [397]. The accuracy of potentiometric titrations at very high ligand to metal concentrations has been discussed [398]. The copper(II) glycine system has been used to test another new program ACFER; the protonated complex CuglyOH could be detected [399].

The evaluation of conditional equilibrium constants and by anodic stripping voltammetry for copper(II) has been discussed, for the EDTA complex a conditional constant of $10^{7.7}$ was found; this is far below the literature value of $10^{12.8}$ [400]. This has lead over the last year to an interesting exchange of comments [401,402]. There are obviously difficulties in determining equilibrium constants by electrochemical methods not inherrent in more conventional experiments.

The equilibrium properties of labile transition metals have an enormous environmental significance. In this context a number of studies of Fulvic acid have been reported, a novel fluorescence titration technique allows equilibrium constants to be determined [403], dialysis was also used to study such complexation [404] and this area of chemistry reviewed [405]. The complexation of copper(II) by humic acid has been investigated by fluorescence quenching [406]. Solution equilibria have been used to elegantly describe the mode of formation of some rare copper(II) minerals [407].

Ternary complexes have provided the most interesting studies of equilibrium behaviour in recent years. The same is true this year and as usual the majority of studies concern low molecular weight biologically relevant ligands in aqueous solution.



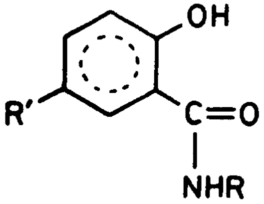
ATP^{4-} UTP^{4-}

15 16

The binary and ternary complexes formed with L-alaninamide and diethylenetriamine in aqueous solutions have been studied potentiometrically [408]. In the $[Cu(dien)(AlaA)]^{2+}$ complex there is evidence that four nitrogens are equatorially co-ordinated and that the carbonyl oxygen of AlaA has a significant apical interaction with the copper ion, as do two nitrogens in $[Cu(dien)_2]^{2+}$. It is concluded that apical co-ordination of copper(II) by amino nitrogen is facile under physiological conditions and that ionized amide groups may only be formed when two equitoriol groups are available at copper(II). Ternary complexes of Cu(II), Zn(II) and Cd(II) have been reported as models for enzyme/metal-ion/substrate interactions [409]. The complexes $[M(ATP)L]^{2-}$ and $[M(UTP)L]^{2-}$ (with ATP and UTP L = NH_3 or imidazole) (15,16) have been studied; only the imidazole complex has appreciable staiblity under physiological conditions.

Copper(II) binary and ternary complexes of dipeptides containing amide carbonyl, alcoholic hydroxy and carboxy groups in their side chains have been investigated. Glycyl-L-serine, glycyl-L-asparagine, glycyl-L-aspartic acid and glycyl-L-glutamic acid were studied [410] as binary and also ternary complexes with, L/D-alanine, β-alanine, L/D aspartic acid, L/D ornithine and 2,2'-bipyridine. Only in the mixed complexes with asparagine and ornithine was stereoselectivity observed. This was ascribed to electrostatic interactions. The copper(II) complexes of a number of dipeptides containing L-histidine investigated [411]. Equilibrium constants have been reported for ternary systems containing histamine [412] or imidazole [413] with various amino acid; ternary species all have very high stabilities.

The mixed complexes containing copper(II) and a range of amino mainly D,L-aminobutyric acids have been investigated [414] tridentate co-ordination is proposed for one of the amino acids. In mixed dipeptide amino acid complexes amide deprotonated peptides have been concluded to be bidentate with both bi and tridentate amino acids [415].



	L^5	L^6	L^7	L^8
R =	H	C_6H_5	H	C_6H_5
R' =	H	H	Br	Br

17

In dioxane/H_2O as a solvent the mixed complexes of 2,2'-bipyridyl or 1,10-phenanthroline and copper(II) with 1,2 diamines, glycine, alanine and malonate have been studied [416,417] (17), the enhanced stability of the ternary species is explained in terms of a lowering of repulsion between metal d electrons and ligand electrons.

Other studies of ternary complexes are summarised in Table 2.

Table 2 Studies of Ternary Complex Formation

ligands	ref.
thiocarboxylates/malonic acids	[418]
glycyl-phenylalanine/amino acids	[419]
dipeptides/amino acids	[420]
nitrilotracetate/amino acids	[421]
thiocyanate/aspartic acid	[422]
arginine or histidine/histamine or imidazole	[423]
2,2'-bipyridine etc/diamine	[425]
2,2'-bipyridine etc./acetoacetonate	[428]
2,2',2''-terpyridine/oxydiacetate	[426]
nitrilotriacetate/purine	[427]
malonic acid/glycine	[428]

Studies of simple copper(II) equilibria have also appeared. Glycine like co-ordination at copper(II) is concluded in a study [429] of L-tyrosine copper(II) complexation (log K_1 = 7.85, 25°C, I=0.1M). The complex equilibria between oxidised glutathione and copper(II) have been investigated [430]. In the aqueous chemistry of 2-oxalopropionic acid, acetoacetic acid and α-ketobutyric acid copper(II) complexes of 1:1 and 2:1 stoichiometries are formed, the existance of a deprotonated and binuclear species was also suggested [431]. The complexation of copper by

The reaction is first order and may occur via intramolecular condensation of a labile ternary complex. The exchange reactions of 2-amino pyridine Schiff's bases are influenced by steric factors [468]. The formation of pyridoxal-5'-phosphate complexes from copper(II) pyridoxamine has been studied in the pH range 2-4 [469]. The rate law k_{obs} = A'+B' [phosphate] is observed; an intermediate carbinolamines proposed to account for the rapid reaction in the pH range 4.0 - 7.0. Ligand substitution reactions for the copper(II) EDTA complex have been investigated [470].

Elegant studies of ligand substitution reactions of bis(N-t-butylsaliicylideneimato)-copper(II) complexes in aprotic solvents continue [471] a two term rate law ($k_{obs} = k_o + k_1$[ligand]) was observed; the ligand independent path is composed of a solvent and water contribution. The solvent polarity parameter $E_t(30)$ has been used [472] to correlate the rate of solvent initiated ligand substitution for such systems. Complex formation with N-(2-hydroxy-5-X-benzyl)-serines (X = H, OCH_3, Cl, NO_2) and related benzyl serines have been investigated [473]. The rate determining is the formation of the Cu-N bond by which the five-membered chelate ring is closed.

The kinetics of dissociation of ethylenedibiguanide copper(II) in acid follows a two term rate law with both $[H]^+$ and $[H]^{+\ 2}$ dependencies [474]. Pulse radiolysis has been used to study the formation of $Cu\text{-}H^+(aq)$: [475] this decomposes via:

$$Cu\text{-}H^+(aq) + H_2O \longrightarrow Cu^{2+}(aq) + H_2 + OH^-(aq)$$

(rate = 4 x $10^3 s^1$). Metal exchange reactions between cobalt(II) and lead(II) complexes of nitrilotriacetic acid and copper(II) [476] follow a rate law:

$$d[Cu(nta^-]/dt = \{k^{M(nta)} + k_H^{M(nta)}[H^+] + k_{Cu}^{M(nta)}[Cu(II)]\}[M(nta)]$$

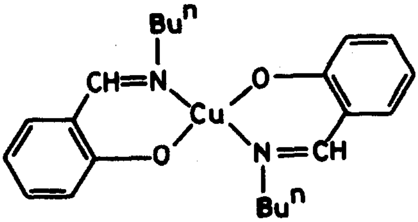
with $k_{Cu}^{M(nta)}$ = 2.6 and 35 $dm^3\ mol^{-1}\ s^{-1}$ for the Co(II) and Pb(II) complexes respectively. The exchange reaction between (1,2-diaminoethane N,N'-di-α-propionato) nickel(II) and copper(II) has been studied [477].

The kinetics of the redox chemistry of copper(II) in 2,9-dimethyl-1,10-phenanthroline complexes has again been investigated [478] and morpholine (perhydro-1,4-oxazine) has been investigated, the work is relevant to water treatment in the secondary systems of nuclear power reactors [432]. A value of $\log_{10}K_3$ of 14.64 was calculated (25°C, I= 1.0M), for the most significant tris complex, dissolution kinetics are discussed on kinetic and thermodynamic grounds.

The binding of copper(II) to the anthracycline containing antibiotic quinizamine (1,4-dihydroxyanthraquinone) has been investigated [433]. The cocaine model N-methyl piperidine forms stable complexes with copper [434]. A study of both copper and proton complexation with the indicator 'Magneson I' has been reported [435]. The boron analogues of glycine and N-methylated glycine (R_3NBH_2COOH) in contrast to glycine (and its derivatives) do not chelate copper (or zinc) [436a]. The 1:1 complexes of furan-2 carboxylate an d tetrahydrofuran-2 carboxylate have been studied in water/dioxane (50/50) solutions [436b]. Other studies of copper(II) complexes in solution are summarised in Table3.

4.2.10 Kinetic and Mechanistic Studies

The mechanism of the formation of the Schiff's base between diethylenetriamine and the salicyaldehydato-ion in the presence of copper(II) [467] has been investigated (18).



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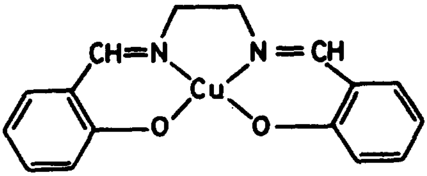


(8)

Table.3 Simple Copper(II) Systems Studied by Equilibrium Methods:

Ligand	Notes	ref.
3,3'[ethane-1,2-dylbis(imino)] bispropamide	$\log K_1=11.89$	[437]
chloride	calorimetry	[438]
acetysalicylate	polarography	[439]
oxalate	polarography	[440]
3,5-xylamino-N,N-diaceticacid	polarography	[441]
triethanolamine	-	[442]
m-phenylenediamine-tetraacetic acid	calorimetry	[443]
N-cylcohexylglycine	-	[444]
amino alcohols	polarography	[445]
hydrolysis	various methods	[446]
sulfadiazene	-	[447]
EDTA	DMSO/H_2O	[448]
hydroxide	$pK_a=7.4$	[449]
triethanolamine	$\log K_1=4.1$	[450]
EDTA	-	[451]
iminodimethylenephosphoric acid	-	[452]
molybdouranic acid	$\log K=5.18$	[453]
p-acetylamino-benzamidoxime	-	[454]
copper acetate/amines	calorimetric	[455]
aromatic-hydroxycarboxylates	-	[456]
1,7-dihydroxy-4-sulphonato napthonic acid	-	[457]
1-benzoyl-2-monothiobiuret	-	[458]
benzoylglycine	-	[459]
diaminocyclohexanetetraaceticacid	-	[460]
benzamidothiosemicarbazide	-	[461]
N-methyl-2-ethylenediamine	-	[462]
Chloride	-	[463]
isovaleric acid	-	[464]
violurate	DMSO	[465]
arzenato	-	[466]

interpreted in terms of the Marcus theory. The water solubilized copper(II) complex of 2,9-dimethyl-4,7-bis[(sulphonyloxy)phenyl]-1,10-phenanthroline has been further studied, significant differences are observed in reactivity with different reducing agents [479], the kinetics is rationalized in terms of four and five co-ordinate copper(II) intermediates. Kinetic studies of mixed bipyridine (and 1,10 phenanthroline) copper(II) complexes have been reported [480].

An interesting study of the kinetics of the reaction of iodide with copper(II) has appeared [481]. The use of a huge excess of chloride ions keeps copper(I) in solution and readily avoids the inherrent problems of heterogeneous systems , a rate law rate = $k[Cu^{2+}][I^-]^2$ was obtained. A study of the copper catalysed oxidation of ascorbic acid by dioxygen established the rate law, $-d[O_2]/dt = k_{obs}[O_2]$ the effect of chloride ion investigated and the involvement of Cu(I) and or Cu(III) discussed;[482] in related study the oxidation of L-ascorbic acid by peroxodisulphate catalysed by copper(II) is reported [483].

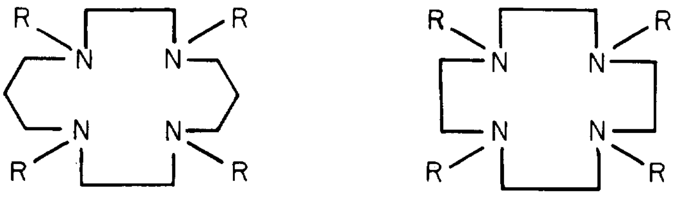
The ester hydrolysis of O-ethyl-2-pyridine carboxaldoxime is catalysed by copper(II) [484]; apparent rates for water and hydroxide paths are enhanced by 2.2×10^7 and 1.1×10^4 respectively. The dynamics and equilibria of the α-alanine, β-alanine, and 1,2diamine [485], mixed bipyridyl glycine [486] and glycyglycine [487] copper(II) systems have been investigated in NMR relaxation studies. In related work several amino acids [488] and dipeptides have been studied [489].

The kinetics of the dissolution of copper into sodium hydroxide in the presence of halides has been interpreted in terms of absorbed anions [490]. The dissolution of Cu_2S into aqueous EDTA follows a two step process with the intermediate formation of CuS [491]. The kinetics of precipitate flotation of copper hydroxide has been investigated [492]. The effect of substitution on the reduction rate of copper(II) diphosphate studied [493].

4.2.11 Macrocyclic Complexes

Crystallographic papers are summarized at the end of the structural section. A dinuclear copper(II) cryptate [494] has been investigated by structural and spectroscopic methods. The magnetic orbitals on the metal ions are accidentally orthogonal leading to antiferromagnetic coupling. The complexion kinetics of cryptand (2,2,1) in DMSO have been studied; both formation and dissociation rate constants have now been measured [495]. The results agree well with thermodynamic measurements of the equilibrium constant. The bis-tren cryptates of copper(II) have been studied potentiometrically [496]. Macrocyclic complexes with tetraketones [497] synthesised. Flow micro-calorimetry has been used to investigate the co-ordination of 1,4,7,10-tetra-azacyclotetradecane [498] which forms a seven membered chelate ring. The macrocycle is more stable than the corresponding polyamine $[Cu(tien)]^{2+}$ due to a favourable entropy contribution; the enthalpy term being slightly unfavourable. The Irving/Williams order was found in a study of various complexes of one fourteen and one sixteen membered macrocycle; alternate five and six membered rings enhanced stability [499]. The electrochemistry of various fourteen membered tetra-aza macrocycles, has been studied [500] complicated mechanisms are involved, at high scan rates Cu(III)/Cu(II) and Cu(II)/Cu(I) $E_{0.5}$ values could be estimated using cyclic voltammetry. In a related study [501] and effects on the Cu(II)/Cu(I) redox potentials of macrocyclic complexes were investigated. A variety of physical techniques have been used to investigate a imidazolate bridge dinuclear macrocycle [502].

Kinetic studies of macrocyclic complexes include: the acid an base catalysed dissociation of the macrocyclic complexes; $[Cu(trans-Me_6[18]diene\ N_4]^{2+}$ and $[Cu(cis-Me_6[18]diene\ N_4)]^{2+}$ have been studied, [503] complexation of copper(II) by 1,4,8,11-tetraazacyclotetradecane-*N*,*N*',*N*'',*N*'''-tetraacetate (19):



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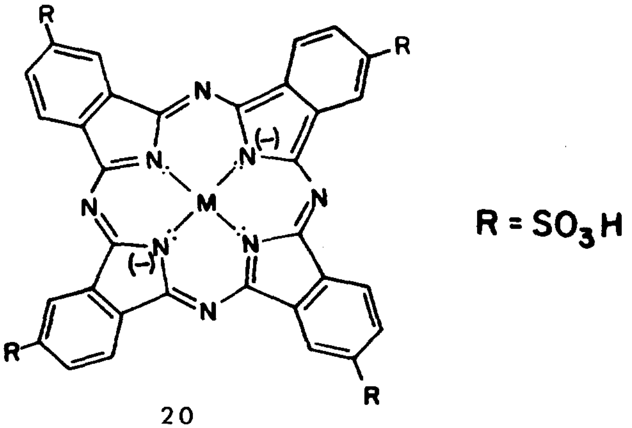
[504] follows a rate law $k_{obs} = (A[M^{2+}])(1+1K[M^{2+}])^{-1}$.

Studies of various mechanisms in the decomposition of tetra-aza macrocycles have been repeated [505], and of an unusual (possible pentagonol pyramidol) N-substituted labile tetradecane [506]. In the presence of oxygen a polycyclic Schiff's base undergoes oxidative dehydrogenation to form a macrocycle [507].

Synthetic papers include work on the new ligand 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane, and its copper(II) complex as the perchlorate salt [508]. An "openfaced" macrobicycle ligand has been described [509] and the design and synthesis of dinuclear copper(II) complexes discussed. The reaction of 2,6-diacetylpyridine with 1,3-diaminopropane in the presence of Sr(II) or Ba(II) produces a twenty membered macrocycle [510]. The barium or strontium may be displaced by copper(II) to produce a binuclear complex, this complex has been characterized by crytallographic and spectroscopic methods. The copper(II) complex of the cyclic ligand 5,8,11-trioxa-2,14-dithia[15](2,6)-pyridinophane has been described [511]. A tetra-aza macrocycle derived from pulegone has been synthesised [512] complexes with dibenzo(f,n)2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca[16]1,3,9,11 tetraene prepared [513] the oxidative coupling of phenylacetylene studied [514], and various dioxine macrocyclic complexes investigated [515].

A number of porphyrin complexes have been studied. The reduction of (tetracyanotetraphenylporphinato)copper(II) in DMF has been studied [516];



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[$(CN)_4$TPP Cu] is reduced by seven electrons in five steps. A wave at E=-1.95V is attributed to the reduction of the Cu(II) dianion to a Cu(I) complex. The reaction of copper(II) with mesotetraphenyl porphyrin in a water/oil microemulsion at pH 3 is catalized by surfactant anions such as chloride or bromide [517]. A dimeric form of the copper(II) mesoporphyrin IX ester complex was studied at 77K by luminesence and EPR [518].

Phthalocyanines have also been investigated. The monomeric tetrakis (N-octadecylsulfamoyl)pthalocyanine copper(II) complex (20), has been investigated by flash photolysis [519]. Mechanism involving short lived n^* states and two photon photochemistry involving a long-lived π^* triplet-doublet are discussed. The conductivity of copper(II) phthalocyanin under pressure [520] and molecular orientation defects in crystal films [521] have been studied. A spectral study of protonated phthalocyanin copper(II) complexes [522] has been undertaken.

4.2.12 Biological Studies

Both the division of this section from the rest of the review and internally has been difficult. Obviously many papers have a biological relevance, this section contains papers where the specific intention of the authors was to mimic a biological system or to present biologically relevant and useful results. The more chemical papers are dealt with first and this section includes some fairly physically orientated model studies. The following papers are then collected on the basis of the system (usually enzymatic) studied or modelled. A number of more general studies are collected at the end of this section.

Copper amino acid complexes have been studied by EXAFS [523]; results on simple systems of this kind are needed if the great potential of such methods is to be realized. A number of copper(II) amino acidate/acetate systems have been investigated in water [524]. The complexes of salicylaldehyde-benzoyl-hydrazone (sbh) exhibit diverse biological properties [525] [CuCl(sbh))].H_2O inhibiting tumor growth in mice, crystallographic and other results have been obtained. The conformations of the epimeric amino acids, L-threonine and L-allothreonine and L-leucine and L-isoleucine complexed to copper(II) have been investigated by the consistent force field model [526a]. Thermodynamic results were in accord with these calculations. The copper(II) complexes of the neurotoxic oxalyldiaminopropionic acids found in L. Sativus have been synthesised [526b]. The vitamin d-biotin complexes copper(II) $\log_{10}$ K= 0.03 (96%DMF, I = 0.5, 25 C); in chiral situations co-ordination at the sulphur of biotin is stereoselective [527]. Mixed ligand pyridoxamine complexes of divalent metal ions with amino acids have been studied potentiometrically [528]. The structures of pyridoxal-amino acid Schiff's base complexes have been determined [529]. Heterobinuclear complexes are formed by carnosine copper(II) and cadmium or zinc [530]. The related dimeric copper(II) carnosine complex has been studied [353]. At subsaturated concentrations the dimer dissociates into two identical monomers, however at temperatures as high as 80 C no dissociation was observed in saturated solutions. Variable temperature (4.2-300 K) magnetic susceptibility measurements on imidazolate bridged copper(II) complexes confirm such a bridge to exist in the copper(II) substituted form of bovine erythrocyte superoxide dismutase [531].

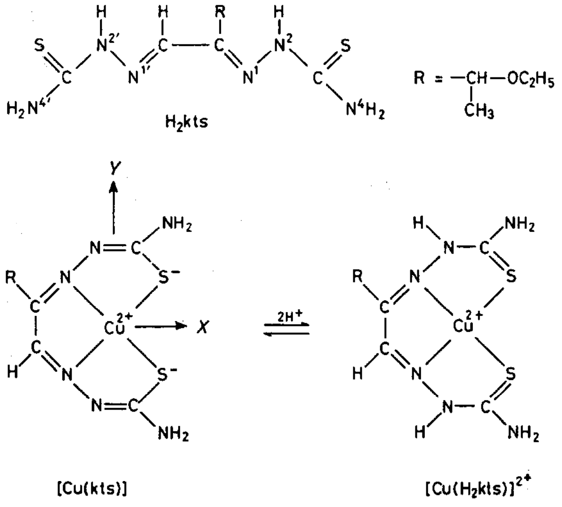
A number of peptide complexes have been studied including those of: N,N'-diglycyl-1,2-diaminoethane [532], histidine dipeptides [533], the human serum tripeptide glycyl-L-histidyl-L-lycine [534] and triglycine [535]. The copper complexes of clupeine YII(a monoprotamine found in herring sperm nuclei and associated with DNA synthesis) have been studied [536], together with peptides that model N-terminal clupeine.

The complexation of copper(II) by [5-leucine] and [5-methionine] enkephalin has been studied under physiological conditions [537]. The major species formed involves the tyrosine amino group, two glycine peptide linkages and the carboxylate function of the C-terminal residue. Enkephalin-metal complexation may be used to determine the structure of biologically active conformations [538, 539]. Stability constants for histamine/copper(II) and L-histidine, L-glutamine or L-threonine have been measured (37°C, I = 0.15 M) [540] such complexes may be important in the pathological activty of copper(II). The interaction of thiomolybdates with copper(II) has been investigated with a view to a better understanding of copper molybdenum antagonism in ruminants [541].

A binuclear dissymmetric Schiff's base formed from copper(II), salicylaldehyde and (1S-2S)-$(+)_D$-1-phely-2-amino-1,3-propanediol has been synthesised [542]. The complex reacts in solution with various ligands to produce a series of adducts in which the Schiff's base remains intact. The bis(imidazole) adduct exhibits catalase activity, in the presence of H_2O_2 a band at 400nm is observed, this is probably an O_2^{2-}-Cu(II) charge transfer transition. Various binuclear complexes including a 2,6-diformyl-4-methylphenol with the amino acid "mixed" dimeric copper species have been investigated for catecholase activity [543, 544].

The quenching of electronically excited tris(2,2'-bipyridine)ruthenium,(II) by reduced "blue copper" proteins has been studied and interpreted using Marcus theory reported [545]. Schiff's base complexes formed by pyridoxal, salicylaldehyde, and pyruvic acid with histidine and histidine methyl ester [546] have been investigated by EPR and CD.

The copper dependence of hydroxyl radical damage to ascorbic acid has been discussed in terms of a mechanism in which ascobate behaves as both a reductant for copper and substrate for radical damage [547]. The degradation of DNA in the presence of a copper(II) 1,10-phenanthroline complex and superoxide ($O_2^{\bullet -}$) radicals has been investigated, various mechanisms are discussed [548].



Structural formulae of H_2kts, [Cu(kts)], and [Cu(H_2kts)]$^{2+}$ showing the number of atoms for the former

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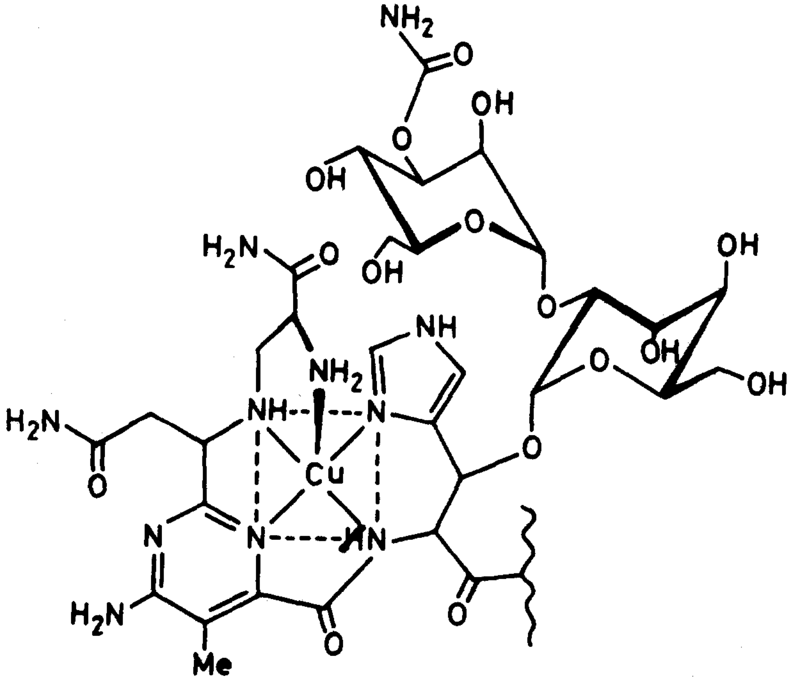
Stereoselective aldol condensations on mixed amino acid complexes have been studied [549], as has the reactivity towards O_2 of novel dinuclear complexes [550]. The antimicrobial effects of copper(II) carboxylates have been investigated [551]; the activity increases in the order $Cu(FCH_2COO_2)<Cu(ClCH_2COO_2)<Cu(BrCH_2COO_2)_2<Cu(ICH_2COO_2)$, aryl carboxylates were also studied. The stability constants of β-thiosemicarbazones [552] (including Cu(I), Cu(II) and Zn(II)) suggest that complexation is not important in the antiviral activity of such agents. The copper(II) complex of the anti-tumour agent H_2Kts has been studied, Raman spectra of protonated and deprotonated complexes recorded [553]. The species involved are outlined below above.

A simple analogue of the metal-complexing pseudopeptide bleomycin(22) was synthesised [554] spectral parameters of the copper(II) complex correspond to those of the copper(II)/bleomycin (Blm) system.



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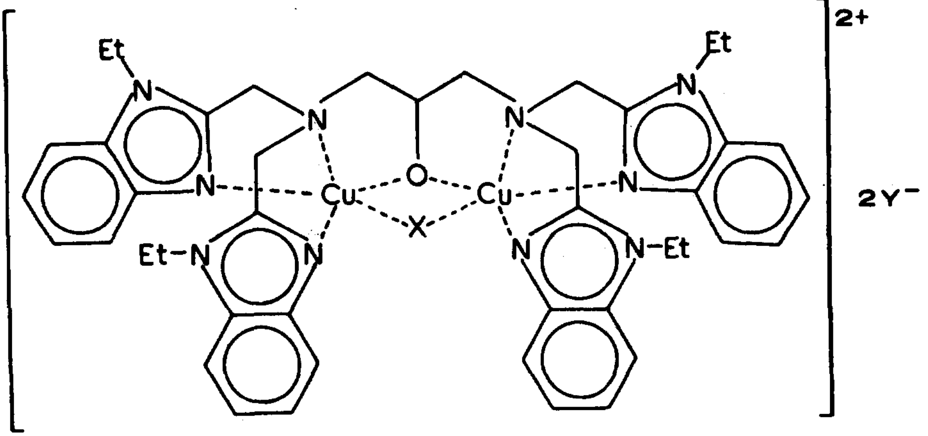
The chemical reactivity of copper bleomycin has been studied [555]; the rate constant for reduction by mercaptoethanol is $9.5 \times 10^{-3}\ M^{-1}\ s^{-1}$ (pH = 7.4, 25°C); and the [CuBlm] complex is stable in human plasma. The binding of copper to the antitumour antibiotics daunomycin and adriamycin leads to 2:1 and 1:1 complexes [556]. However at pH>8 insoluble polymeric species are formed.



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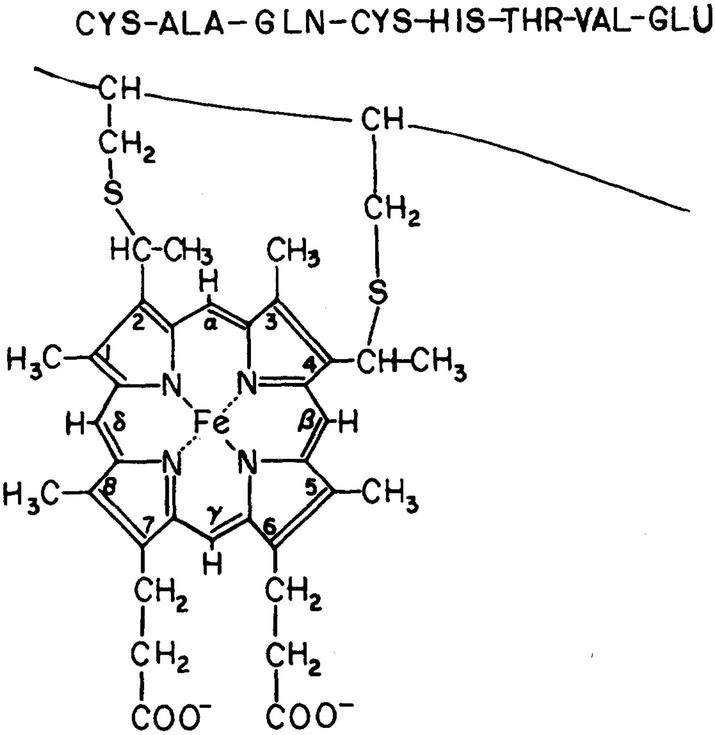
The active site of haemocyanin is similar to that shown in the model complex illustrated above (23) [557]. The nature of the bridging ligand X changes the ground state of the copper form $d_{x^2-y^2}$ (imidazole) to d_{z^2} acetate; the physical properties of such models are very close to those of haemocyanin. The observed stoichiometry of carbon monoxide binding to haemocyanin has been explained in terms of [558] a linear two co-ordinate copper(I) centre which is unreactive to CO. The anti-tumour agent (2-formylpyridine monothiosemicarbazonato)copper(II) forms adducts [559] with the sulphur and nitrogen donors of cat haemoglobin, EPR studies are reported. The haem iron of the chains of mammalian haemoglobins are rapidly and selectively oxidised in the presence of excess copper(II) by a reaction requiring the presence of free -SH groups in the globin chain [560]. Vibrational studies of the binding of CO to haemocyanin suggest C-co-ordination [561].

Many papers deal with either models for or co-ordination in cytochrome-c oxidase. A trimeric iron(III) haem-copper(II) complex [562] provides support for an alternate explanation of the "EPR silent" iron-copper pair in cytochrome-c oxidase. Fe/Cu are bridged by a cysteine-like thiolate. A μ-oxo mixed metal complex of copper(II) and an iron(III)-porphyrin has been reported [563] as a resting state model for the cytochrome-c oxidase active site. Imidazolate bridged binuclear metalloporphyrin complexes of Fe(III) and Cu(II) or Zn(II) have been synthesised, isolated and characterised in the solid state [564]. Yet



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another model involves the copper(II)-protoporphyrin-iron(III) complex; copper(II) binds to the propionate groups, some evidence for interaction between the two metal nuclei was presented [565]. Outer-sphere electron-transfer reactions of the isolated active-site heme octapeptide (24) from, cytochrome-c [567]; provide an estimate of the self exchange rate for the heme peptide $k > 10^6$ M^{-1} s^{-1} ($I = 0.1M$). The haem peptide self-exchange rate exceeds the self exchange rate for cytochrome c; these results show that incorporation of a prosthetic group into a metalloprotein need not increase the basic reactivity of the metal. A synthetic analogue of cytochrome P-450 involving a "mercaptan tail" porphyrin has been reported [568].

The EPR spectra of copper-transferrin-bicarbonate complexes show well resolved nitrogen super hyperfine splittings, only a single nitrogen is coupled to the copper [569]. There have been suggestions that the binding site of this protein involves two histidine imidazole residues; these results would indicate one planar ($d_{x^2-y^2}$) site and one apical (d_{z^2}) nitrogen. The kinetics of the interaction of copper(II) with apo-transferrin have been studied [570], an initial rapid step is first order in both copper and the protein. As model for transferrin ethylenebis((o-hydroxyphenyl)glycine) has been investigated [571], copper(II) complexes were prepared, meso and racemic forms of the ligand separated and spectroscopic studies undetaken. The oxidation of cysteine by caeruloplasmin and non-enzymatic copper(II) has been studied [572], and a model of haemocyanin based on 1,3-bis[*N*,*N*'bis(2-benoimidazolylmethyl)-amino-methyl] cyclohexane reported [573]. An assignment of the resonance Raman spectra of azurin has been made on the basis of a normal co-ordinate analysis [574]. Tetrahedral and trigonal structures give the best fit between theory and experiment; considerable mixing of Cu-S (Cys) and Cu-N (His) modes occurs. The trigonal model was preferred. The binding site of copper(II) in Stellacyanin has been investigated by EXAFS [575]. The results suggest that there are two nitrogens in the first co-ordination sphere of the oxidised protein (copper(II)) r(Cu-N) (1.95 -2.05 A) and one in the reduced (copper(I)) form, together with either one or two sulphur atoms. The structure of the copper(II) complex [576], [*N*,*N*'-ethylenebis(methyl-2-amino-1-cyclopenteneditiocarboxylato)]-copper(II), a model for a type I centre has been reported. Schiff's base models of azurin prepared from salicylaldehyde and t-butylamine or other bulky amines have been investigated [577].

Tripod ligands containing three and four donor atoms have been used [578] to model type I and II copper centres. Spectroscopic results are used to classify the complexes as four co-ordinate, trigonal bipyramidal and square pyramidal; some are held to be good models for type I and type II proteins. Tetragonal versus trigonal co-ordination at copper(II) in type I copper protein has been discussed by comparison to two model complexes [579]. Kinetic studies of the reaction of azurin with various Co(III) and Fe(II) complexes have been reported [580].

A review of the inactivation of tyrosinase, a copper containing monooxygenase which catalyses the oxidation of o-diphenols and o-quinones has appeared [581]. The accumulation of Cd by the fungus Agaricus bisporous leads to the absence of tyrosinase [582]. The primary structure of tyrosinase from Neurospora Crassa has been reported [583, 584], histidyl 306 is suggested to be important in binding one of the two coppers in this type III protein. The thermostability of tyrosinases from three wild strains of Neurospora crassa were studied [585]. The kinetics of copper incorporation [586] and the flurorescence [587, 588] of this protein were studied.

A study of the temperature dependance of the reductions potential of the blue copper in fungal laccase [589], lead to $\Delta S^o = -13.9(+2)$ cal mol^{-1} k^{-1} and $\Delta H^o = -22.1(+0.5)$k cal mol^{-1} with $E^o(25^o) = 780(+3)$ mV vs the normal hydrogen electrode. A comparison of ΔS^o and ΔH^o values with single-site proteins suggest the high potential may be attributed to stabilization of the copper(I) centre by enhanced ligand binding; protein solution effects playing a lesser role. The anation of laccase typeII copper by azide follows on Eigen-Wilkins type mechanism involving initial outersphere complexation [590].

Super oxide dismutases are perhaps the most studied of the copper(II) containing enzymes. Spectroscopic studies of copper(II) bound at the active copper site, or substituted at the native zinc site, of bovine erythrocuprein(superoxide dismutase), [591] result in the assignment of a broad band at 300nm (ε_m ~2000) in the copper(II) enzyme as a COO^- or imidazole to Cu(II) LMCT transition. EPR and electronic spectra suggest that Cu(II) in this site is distorted towards tetrahedral or in a distorted-pentacoordinate geometry. An EPR study of the same enzyme [592] reveals that thiocyanate may displace the bridging imidazole group. The succinylation of bovine erthrocyte superoxide dismutase leads to an enzyme with only 10% of the original activity [593]. Spectroscopic studies show that the co-ordination of copper(II) is unaffected, dissociation of the native enzyme into sub-units is suggested to explain these results. An EPR study of a single monoclinic crystal of bovine superoxide dismutase is in accord with earlier crystallographic measurements [594]. The cyanide derivative has also been investigated [595]. The simultaneous addition of zinc and copper to apo-superoxide dismuase results in an unusual metal-deficient form of the enzyme [596]. Studies of the primary structure of human erythrocyte superoxide dismutase have been reported [597, 598].

Copper was found to have a protective effect against whole body (rat) X-irradiation [599], superoxide dimutase activity was important in this effect. Copper deficient rats had up to a 30% decrease in cupro-zinc superoxide dismutase activity [600]. The effect of copper(II) as the sulphate and bis-glycinato complex on indirect assays of superoxide dismutase activity has been studied [601]. Cuprizone (biscyclohexanone, oxaldihydrazone) decreases rat liver copper by 32% [602].

The inactiviation of superoxide dismutase at pH <3.5 exhibits biphasic kinetics and is directly related to the loss of copper from the enzyme [603]. Dimeric complexes of the ligands tris(N-methyl-benzimidazol-2-ylmethyl) amine and azolate are models of superoxide dismutase [604].

Copper substituted human carbonic anhydrase [605] has been used to investigate the inereaction of the enzyme with sulphonamides. The system copper(II) carbonic anhydrase and HCO_3^-/CO_2 has been studied [606]. EXAFS and Raman evidence has been presented [607] for the binding of histidine at the active site of protocatechuate3,4-Dioxygenase. The luminescence properties of neurospora copper metallothionine [608] and copper transfer rates for the above protein have been measured [609].

Other biological studies involving copper(II) include work on lipid peroxidation in copper deficient rats [610], copper(II) induced lipid peroxidation in rat liver mitochondria [611], the effect of tetrathiotungstate dithiotungstate [612] and trithiomolybdates [613] on copper metabolism in rats, the association of retinyl palmitathydrolase on rates with copper metalloproteins [614] and a copper(II) induced decrease in the level of -SH groups in isolated rat liver mitochondria [615].

4.2.13 Copper Catalysed Organic Reactions

Many copper complexes are routinely used to catalyse organic reactions; this work lies between, co-ordination chemistry/organometallic chemistry/organic chemistry. The general kinds of reaction available have been reviewed [616].

A catalytic species $Cu_2Cl_2(C_5H_5N_2)(OCH_3)_2$ related to the copper(II) oxidation of phenols [617, 616] has been investigated. The dimers within this complex are antiferromagnetically coupled with a singlet triplet splitting of 1030 K. The kinetics and mechanism of the oxidation of phenol by copper(II) in acetonitrile have been studied [618] and the synthesis of catecholates from phenols by a copper-catalysed activation of molecular oxygen reported [619,620]. In aprotic media di-μ-hydroxo-bridged copper(II) complexes catalyse the aerobic oxidation of aldehydes and some cabonyls [621]. In aqueous alkaline solutions copper phenanthroline complexes catalyse the oxidation of primary alcohols and cyclohexane to carboxylic acids at 333-373 K [622]; secondary and acyclic alcohols are not oxidised.

Various coupling reactions are catalysed by copper(II). A mild and simple method for the synthesis of some 1-(arylamino)pyrole derivatives [623] by the reaction of (arylazo)alkenes and β-dicarbonyl compounds has been reported. Other synthetic reactions studied include conjugate additions of 2-pyridylcopper [624], the reaction of methylcopper with 1-nitro-2-phenylethene [625], the C-C of alkyl and N-N coupling of dialkylamino groups [626], the synthesis of dihydrofurans from α-diazocarbonyls [627], the oxidative coupling of chiral vinyl and cyclopropyl copper reagents [628] and catalysis of the reaction of phenylisocyanate with methanol [629].

A series of new heterocuprate reagents have been reported. These all have greatly improved thermal stability [630, 631], electronic, steric and co-ordination effects are important in these phosphinato and amido complexes. Novel reagents involving secondary and tertiary aldehyde to sylhydrazones have also been studied [632]. Substitution reactions at unactivated seconary centres have, for the first time been achieved using organocuprates [633].

Copper catalysed decomposition reaction studies include the decarboxylation of 2-oxalopropionic acid [634], the hydrolysis of esters of 2-(hydroxymethyl)picolinic acid [635] and the dehalogenation of halogenarenes during copper-quinoline decarboxylation [636]. Intermediate reaction with molecular oxygen is often important in copper(II) catalysed reactions including those of dinuclear species of N,N,N',N'-tetramethyl-p-phenylenediamine [637] and the catalytic activity of copper(II) complexes in the chemiluminescence of luminol [638]. The isomerization of pentane at room temperature is catalysed by [$Cu(AlCl_4)_2$] [639]. Copper(II) chloride or bromide cleaves the carbon-silicon bond in organopentafluorosilicates [640]. Stereoselective methylcyclopropanations [641] and the reaction of dl-camphorquinone with monoamines [642] in the presence of copper(II) have been reported.

The copper catalized coupling of an ω-bromo-acid with a Grignard reagent has been used to synthesise isotopically labelled saturated fatty acids [643]. On complexation with copper(II) 2-hydrazino-1,10-phenanthroline undergoes oxidation with loss of nitrogen [644]. Copper(II) chloro complexes in a mixture of acetic acid and water catalyse the oxidation of Anthracene [645]. The polyformylation of copper(II) complexes of oct-alkylporphrins has been reinvestigated [646]. The anaerobic cleavage of the disulphide bond of a pyridine containing disulphide by copper(II) has been studied, the crystal structure of the product is reported [647]. The use of thioacetamide to decompose amino acid complexes used for protection of basic amino during peptide synthesis has been suggested [648].

4.2.14 Surface Chemistry

The location and co-ordination of metal ions on catalytic surfaces is important in optimizing catalytic activity. A variety of physical techniques have been used to study copper(I) and copper(II) complexes absorbed on surfaces. The formation of ternary copper(II) complexes at the surface of silica gel has been studied by EPR spectroscopy [649]. Chelating SiO^- groups on the surface are involved, π-conjugated ligands (2,2'bipy etc.) enhance absorption. EPR methods have also been used in an investigation of copper(II) sorbed on to Kaolinite[650]. Electron spin echo modulation results for copper(II) interactions on silica surfaces have been reported [651]. In methanol and acetone, two solvent molecules are associated with the copper and a distorted octahedral environment involving four lattice oxygens is suggested.

The reactions of hexadecyl chloride on copper chromite and copper-on-silica hydrogenation catalysts have been investigated [652]. A novel silica supported copper catalyst prepared from copper(II) acetate showed a high activity for CO oxidation with N_2O at 150°C [653]. The influence of both silica and alumina supports on the temperature programmed reduction [654] of CuO has been studied. On silica dispersed copper oxide and copper silicate species are important.

Catalysts for low-temperature methanol synthesis have been studied. The reduction of CuO in the ternary oxide (Cu:Zn:Al; 62:14:25) occurs in two stages [655]. X-ray photoelectron spectroscopic results on reduced ZnO/Cu catalysts reveal both Cu(I) and two distinct Cu(0) sites [656]. The partial oxidation of n-butane can be performed at low temperature on aerogel CuO/Al_2O_3 catalysts [657].

The kinetics and activity for CO oxidation of sintered and unsintered Pt-Cu/ Al_2O_3 catalysts has been investigated [658]. A detailed study of copper(II) and copper(II)ammines absorbed on α-zirconium phosphate by EPR and reflectance spectroscopy has been reported [659]. Other studies of copper surface chemistry include, absortion of carbon monoxide on Ni/Cu catalysts at 296K [660], the EPR spectra of SO_2 and CO on CuO/alumina [661], a UHV-EPR study of NO absorbed on copper [662] and the stablization of a CuO photocathode by aliphatic alcohols [663, 664].

4.2.15 Analytical

The simultaneous determination of copper, nickel, cobalt and chromium by reversed phase HPLC with electrochemical detection has been reported [665]. A method of determining copper as the dithiocarbamate has been reported [666]. Microparticulate silica has been used in the separation of complexed copper, nickel and palladium by HPLC [667].

Stereoselective co-ordination of amino acids by copper(II) N,N-dialkyl amino acid complexes enables the resolution of L and D amino acids [668] by reversed phase HPLC. An ion exchanger with imine (dimethanephosphoric) groups in amino-copper form has also been used to resolve several amino acids [669].

4.3 COPPER(III)

A blue copper(II) [670] complex has been prepared by the oxidation of the product of the reaction between copper(II) acetate and N.N'-ethylenebis-(iosnitrosoacetylacetoeimine), the similarity of the intense blue (ε_{581nm} ~ 6 x 10^3) to copper protein absorptions was noted. A double ring octa-aza macrocycle incorporates two copper(II) ions in aqueous solution and is easily oxidised by two one electron steps to a dicopper(III) complex [671]. Copper(III) species have been shown to be important [672] in the reaction of aldehydes or ketones with oxalodihydrazide and copper(II) in the presence of molecular oxygen, the structure of the complex based on 1,2,4,5,8,9,11,12-octa-aza-3,10-dimethyl-tetradecane-6,7,13,14-tetrone reported.

Electron transfer reactions of copper(III) peptide complexes with hexacyanoferrate(II) [673] proceed at rates from 2.6 x 10^5 M^{-1} s^{-1} to greater than 8 x 10^7 $M^{-1}s^{-1}$. Inner sphere reactions via bridging cyanides are believed to be involved in these reactions.

4.4 MIXED VALENCE SPECIES

Trinuclear complexes have been studied electrochemically [674] the $Cu(II)_2Cu(III)/Cu(III)_3$ and $Cu(II)_3/Cu(I)Cu(II)$ couples; $E_{0.5}$ values in the range 0.3 to 0.6 and -0.3 to -0.45 V vs. SCE respectively have been measured, for complexes of pyridine-2-carbaldoxime and isonitrosoketimine ligand. A mixed valence one-dimensional metal $Na_3Cu_4S_4$ has been subjected to conductivity measurements from 15 to 300K, [675] conductivity is highly anisotropic and enhanced parallel to the crystal needle axis. The synthesis of a mixed valence copper complexes has been achieved by free radical additions to a copper(II) dimer [676].

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