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Copper 1991–1994

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Contents

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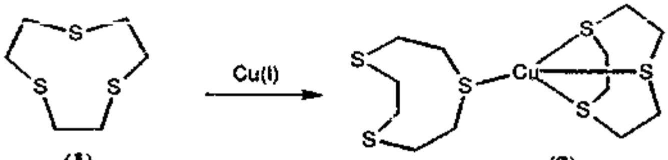
1. Introduction

This review provides an overview of the coordination chemistry of copper published between 1991 and 1994 and is by no means comprehensive. Because of the enormous number of publications arising during this period, it has been necessary to limit the literature reviewed. The method chosen has been to select only those complexes with full structural characterisation and located in the Cambridge Crystallographic Data Base and then further restricted, with a few exceptions, to those published in major journals. In this review, complexes are arranged according to the oxidation of the copper centre and subdivided into the nuclearity of the complexes and the ligand donor atom. Structural figures have been redrawn using crystal coordinates, and with one exception, omitting the hydrogen atoms. Organometallic complexes are not included in this article since they are reviewed elsewhere.

2. Copper(I)

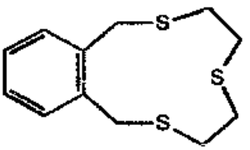
2.1. Mononuclear complexes with macrocyclic ligands

1,4,7-Trithiacyclononane (**1**) as a free ligand is in a fairly rigid endodentate [333]-conformation which arises as a consequence of the angular restraints of the small ring size. This makes (**1**) an ideal ligand for the facial coordination to a metal ion. This has been demonstrated by its coordination to Cu(I) ions [1]. The complex crystallises as $[Cu(\mathbf{1})_2]PF_6$(**2**) and contains two independent formula units having distorted tetrahedral CuS_4 coordination spheres with monodentate and tridentate ligands (**1**). The two units differ mainly in the ligation of the monodentate ligand (**1**) although the ring conformation remains the same. The uncoordinated sulfur atoms on the monodentate ligand are directed outward relative to the coordinated sulfur and are prone to attack by metal ions added to the solution to produce a tridentate ligand with the standard [333]-conformation. The addition of Cu(I) ions to $Cu(\mathbf{1})_2$ results in a transient trinuclear complex which has been detected by spectrophotometric and electrochemical techniques. The electrochemical oxidation of $Cu^I(\mathbf{1})_2$ occurs rapidly with the electron transfer being accompanied by chemical steps, *i.e.* a conformational reorganisation of the ligand (**1**).



(1) **(2)**

In contrast, the enlargement of ligand (**1**) by the introduction of a benzene spacer results in a macrocycle (**3**) which coordinates to a Cu(I) centre to form the mononuclear complex [Cu(CH$_3$CN)(**3**)][ClO$_4$] [2]. In this case the fourth coordination site is occupied by an acetonitrile molecule rather than by a sulfur atom of another ligand moiety. It has been shown that the coordinated acetonitrile molecule can be displaced by ancillary ligands, *e.g.*, benzonitrile, pyr, PPh$_3$ or PPh$_2$Me. The crystal structure of the complex with a coordinated PPh$_2$Me ligand shows two independent cations which are geometrical isomers by virtue of rotation of the PPh$_2$Me ligand. The Cu(I) is in a tetrahedral environment with the ligand coordinated facially. The solid state structure of the free ligand reveals the sulfur atoms are exodentate to the ring. The crystal structure of [Cu(**3**)Cl] has also been reported in which the only difference to that of [Cu(CH$_3$CN)(**3**)][ClO$_4$] is that the axial site is filled by a chloride ion [3].

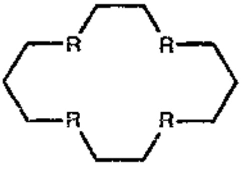


(3)

The coordination of a ferrocenophane ligand with copper(I) ions has been investigated [4]. The copper(I) centre in the resulting mononuclear complex has a distorted tetrahedral geometry which results in a large S-Cu-S angle of 145.4(2)°.

Using macrocyclic polyamino polythioether ligands of the 14-membered tetradentate (**4**) and 15-membered pentadentate (**5**) series a study has been carried out on the influence of the amine nitrogen and thioether sulfur donor atoms on the electrochemistry of the Cu(I/II) couple [5]. The electrochemical potentials show a fairly linear relationship with the value of x in each of the donor sets N_xS_{4-x} and N_xS_{5-x}. The dependence of the Cu(I/II) potential on the relative number of nitrogen atoms and sulfur atoms is attributed to the preference of the Cu(II) ion for the amine donor atoms relative to the thioether sulfur donor atoms.

The allosteric effect (*i.e.* protonation followed by complexation) which often occurs on complexation of a metal ion to a macrocycle is shown on complexation of Cu(I) chloride with the macrocycle 1,5(2,6)dipyridina-3,7(1,4)dipiperazinaoctacyclophane (**6**) [6]. The solid state structure of the free ligand shows the cavity is very crowded and complex formation is sterically hindered. However, on addition of the copper(I) salt one of the piperazine rings undergoes a 180° rotation (instead of the more usual



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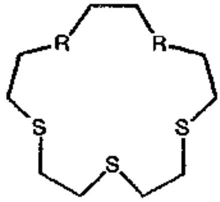
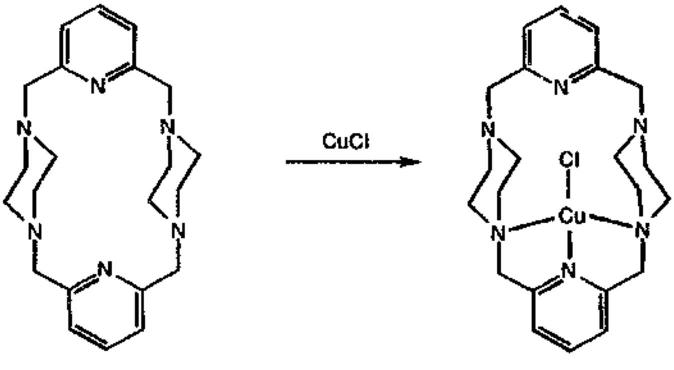


(5) R = S or NH

chair-to-boat conformational change) and alters the spatial orientation of the free electron pairs on the nitrogen atoms. This creates a suitably sized pocket-shaped coordination site accessible to the copper(I) cation. The coordination sphere of the copper centre in (7) consists of three nitrogen atoms (one from a pyridine ring and two from two piperazine units) and one chloride ion. The four coordinated atoms surround the copper ion in an asymmetric manner resulting in the metal centre having the unusual [2+2] coordination geometry.



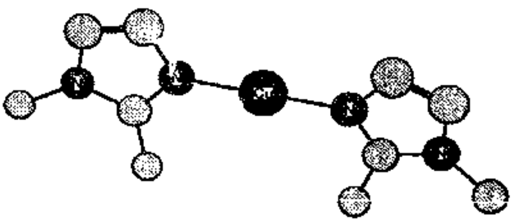
(6)

(7)

2.2. Mononuclear complexes with acyclic ligands

A study of the copper(I) complexes with 1,2-dimethylimidazole (Me_2im) has provided insights into the factors which govern dioxygen binding and activation in imidazole ligated copper complexes and proteins [7]. The 2-coordinate linear complex $[Cu^I(Me_2im)_2][PF_6]$ (**8**) has been shown to be unreactive towards either dioxygen or carbon monoxide, but reaction with one additional molar equivalent of ligand yields a 3-coordinate complex $[Cu^I(Me_2im)_3][PF_6]$ which reacts with dioxygen to give a peroxodicopper(II) complex $[Cu_2(Me_2im)_6(O_2)]^{2+}$. Hence this study suggests that a distorted trigonal (*pseudo*-T-shaped) copper(I) centre may be a prerequisite for dioxygen binding and/or monooxygenase activity.

An investigation has been made into dioxygen reactivity with copper(I) complexes



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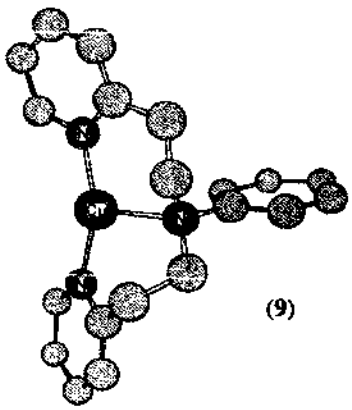


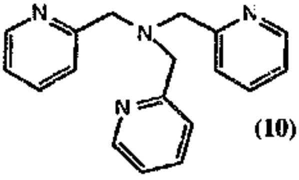
(9)

of dipyridyl tridentate ligands [8]. The solid state structure of one of the precursor complexes (**9**) shows the copper centre to have the distorted trigonal geometry thought to be necessary for dioxygen binding. At temperatures above 0°C, the mononuclear complexes react with dioxygen in a stoichiometry of 4:1 (Cu:O_2) giving an oxo-bridged dicopper(II) product, but at lower temperatures the stoichiometry of the reaction is 2:1.

An investigation has been carried out to assess the effects of steric and electronic properties of the ligand on the ability to stabilize a copper-dioxygen complex [9,10]. The copper(I) complexes of a series of related tetradentate ligands (**10**-**13**) have been studied in reactions with dioxygen. The study demonstrates that steric factors and not electronic effects seem to be important in the stabilization of the copper-dioxygen complex. As the number of quinolyl groups increases in the ligand so the Cu(I)/Cu(II) redox potential becomes significantly more positive.

Reaction of *N*,*N*′-bis{[2-(phenylmethylthia)phenyl]methylene}ethane-1,2-diamine (**14**) with a copper(I) salt enabled the complex [Cu(**14**)]$^+$ to be isolated [11]. The cation is inherently dissymmetric owing to the helical attachment of the ligand to the metal which gives rise to *R* and *S* enantiomeric forms of the complex. In addition, the overall stereochemistry is determined by the chirality at each of the two sulfur atoms which can be either *R* or *S* when coordinated. Thus there are three possible diastereoisomers of [Cu(**14**)]$^+$. The solid state structure of [Cu(**14**)][ClO_4] shows the two sulfur atoms to have opposing chirality and the unit cell to contain equal numbers of right handed [*R*-*R**,*R**,*S**] and left handed [*S*-*R**,*R**,*S**] cations. A variable-temperature ^{13}C NMR spectroscopic study of the complex in nitromethane solution indicates that [Cu(**14**)]$^+$ exits predominantly as an equilibrium mixture of the other two diastereoisomers [(±)-(*R**,*R**,*R**)] and [(±)-(*R**,*S**,*S**)] for which the energy barrier for interconversion is $\Delta G^{\ddagger} = 59.8 \pm 0.6$ kJ mol^{-1}.

Treatment of [Cu(**14**)][ClO_4] with a second molar equivalent of the ligand (**14**) results in the copper(I) ion becoming coordinated to two ligands, each by way of its diimine moiety, giving an orange, air stable complex [12]. Although there is no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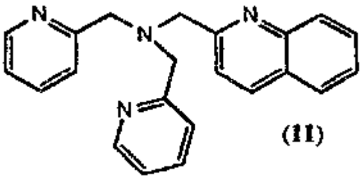
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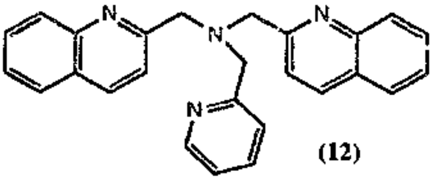
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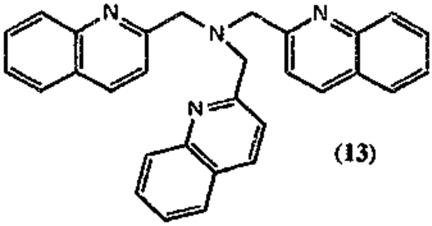
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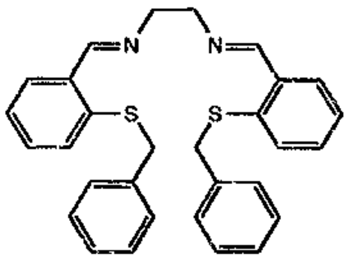
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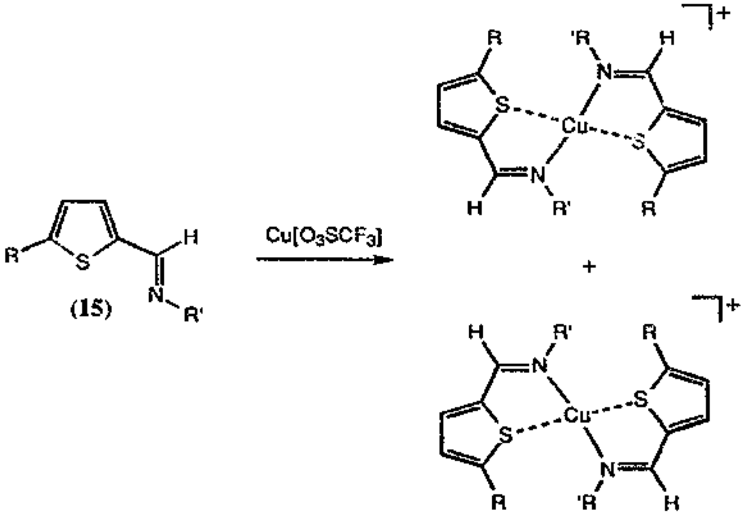
dramatic change in the electronic structures of [Cu(**14**)]$^+$ and [Cu(**14**)$_2$]$^+$, there is a partial loss in the reversibility of the CuI/II couple. This is attributed to the enhanced reactivity of the Cu(II) bound imines which develops on detachment of the thioether units. Hence this suggests that the coordinated thioethers perform a protective role towards the copper centre.

Another example in which the reaction of a ligand with a metal centre results in the formation of an enantiomeric complex is seen in the 1:2 molar reaction of M(O$_3$SCF$_3$), where M = Cu or Ag, with the NS donor system (**15**) [13]. The introduction of a variety of substituents on the ligand has been investigated and the solid state structure of [Cu(**15**)$_2$][O$_3$CF$_3$], R = Me, R′ = ^{i}Pr determined. The unit cell consists of a pair of enantiomeric complexes, *i.e.* one cation having the *Δ* (**16**) and the other the *Δ* (**17**) configuration about the Cu(I) centre. The cation structure consists of a linearly coordinated sp-hybridised metal nucleus with strong imine N-Cu bonds and extremely weak thiophene S-Cu interactions. NMR spectroscopic studies (both ^{1}H and ^{19}F) indicate that the structure of the complexes persists in solution.

The reaction of the highly basic, sterically hindered tertiary phosphine ligand,



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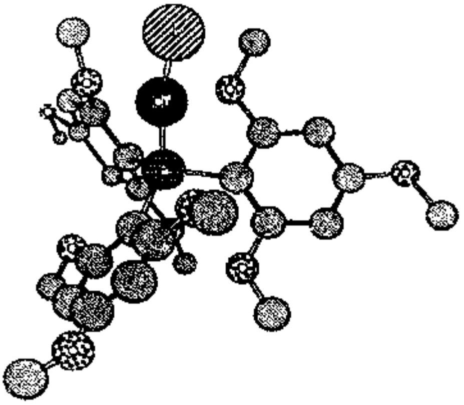
(16)

(17)

tris(2,4,6-trimethoxyphenyl)phosphine with Cu^{I} in acetonitrile yields 1:1 complexes whose structures depend on the molar ratio of the reactants [14]. The crystals which first deposit from the 1:2 ligand: Cu^{I} reaction correspond to the 1:1 molecular adduct (**18**). The complex contains a linearly-coordinated copper centre and is claimed to be the first solid state structure of a compound containing a 2-coordinate P-Cu-P grouping and the first example of a 2-coordination complex of Cu^{I} with a neutral ligand. The structure is isomorphous with the corresponding Cl and Br compounds.

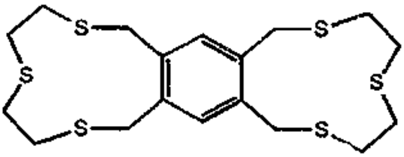


(18)

A study of the coordination behaviour of tetradentate phosphoamines has shown that the ligands stabilize copper(I) complexes either by ligand-exchange reactions from labile [Cu^{I}(MeCN)$_4$]$^+$ or by ligand promoted reduction of a Cu^{II}Cl$_2$.2H$_2$O precursor [15].

2.3. Dinuclear complexes with macrocyclic ligands

Extending the macrocycle (**3**) to contain two crown thioether units resulted in a ditopic ligand (**19**) containing two equivalent S_3 donor sets, separated by a durene spacer group, which can coordinate facially to a metal centre [16,17]. The reaction of (**19**) with a Cu(I) salt followed by the addition of a phosphine ligand resulted in the two Cu(I) centres coordinating in identical distorted tetrahedral geometries with the fourth site filled by the phosphine ligand. The conformation of the complex was shown to be dependent on the nature of the phosphine ligand. Using the monodentate phosphine ligand PPh_2Me gave a complex having an *anti* conformation (**20**) whilst the didentate ligand, $PPh_2CH_2CH_2PPh_2$, gave the *syn* conformation (**21**). The *anti* conformation maximises the separation between the two copper centres with a Cu···Cu distance of 8.5 Å compared with the Cu···Cu distance of 5.9 Å in the *syn* conformation of (**21**).



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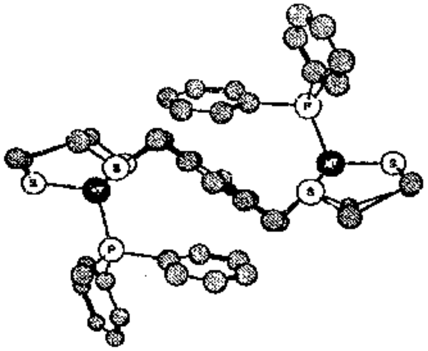

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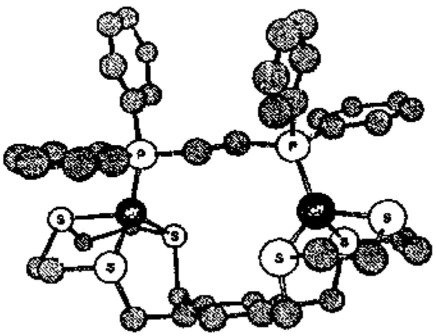
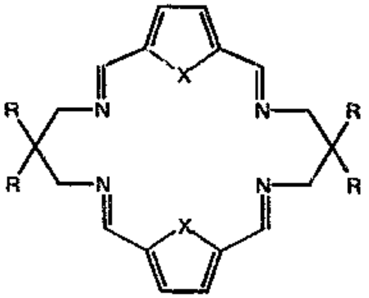


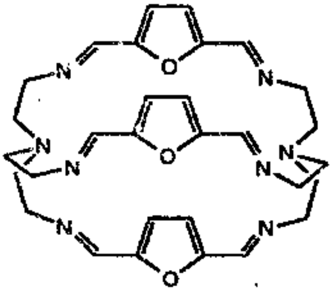
(21)

A study of the coordination of Cu(I) ions in macrocycles having a mixed donor set (**22**)-(**24**) has been carried out [18]. The solid state structures of all three complexes show the Cu(I) centres are 3-coordinate being bound to two nitrogen atoms of the macrocycle and one nitrogen atom of a coordinated acetonitrile molecule in a pyramidal coordination sphere. The Cu···N distances range from 1.86 to 1.99 Å. In (**22**), the Cu···S distances are 3.07 and 2.89 Å, indicating a fairly strong interaction. This has the effect of distorting the planar portion of the macrocycle leading to a large Cu···Cu separation of 4.65 Å. The corresponding values in (**23**) and (**24**) are 3.40 and 3.68 Å, respectively. The slightly larger Cu···Cu distance found in (**24**) compared with (**23**) arises from the repulsion between the additional methyl groups on the macrocycle.



X = S, R = H (**22**)
X = O, R = H (**23**)
X = O, R = Me (**24**)

The same basic design has been used in the synthesis of the unsaturated cryptand (**25**). This has been shown to accommodate a pair of Cu(I) cations inside the cavity with a separation of 4.2 Å [19].

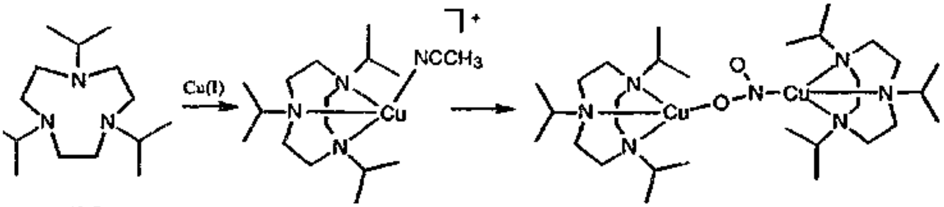


(**25**)

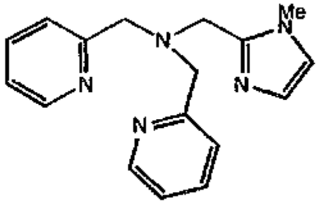
In a study undertaken with the aim of providing more understanding of the interactions of nitrogen oxides with copper-containing sites in biological and heterogeneous catalytic systems the first example of a Cu(I)-NO_2 complex is claimed [20]. Reaction of the macrocycle (**26**) with a copper(I) salt gave a monomeric complex (**27**) which reacted with $NaNO_2$ to form the dinuclear complex (**28**) in which the nitrite ion bridges the two Cu(I) centres. The nitrite ion coordinates to one copper ion via its nitrogen atom and to the other via the *syn* lone pair of one oxygen atom. This results in a coplanar Cu-(μ_2NO_2)-Cu unit. The copper centres adopt a C_{3v} distorted tetrahedral geometry which is characterised by small intraligand NL-Cu-NL angles (av 85.4°) and large NL-Cu-N(O) angles (av 128.2°). The complex is electrochemically active and reveals an electrochemically *quasi*-reversible and chemically reversible oxidation with $E_{1/2} = 0.07$ V vs. SCE.

2.4. *Dinuclear complexes with acyclic ligands*

A study of the stability of the binding of dioxygen with tripodal ligands containing pyridine and imidazoyl rings has been carried out [21]. The solid state structure of



the complex $[Cu_2(\mathbf{29})_2]^{2+}$ shows each copper centre is in a trigonal pyramidal N_4 environment in which the dimeric structure arises from ligation of the imidazoyl group on the ligand to the adjacent copper centre. Conductivity measurements have shown that the dinuclear complexes dissociate in nitrile or dmf solvents. The copper complex of (**29**) forms the stable dioxygen adduct $\{[Cu(\mathbf{29})]_2(O_2)\}^{2+}$, while the introduction of the second imidazoyl group into the ligand (**30**) results in a destabilisation of the dioxygen complex.



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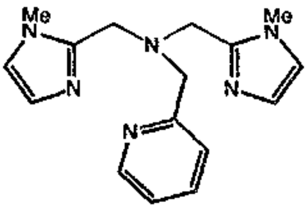

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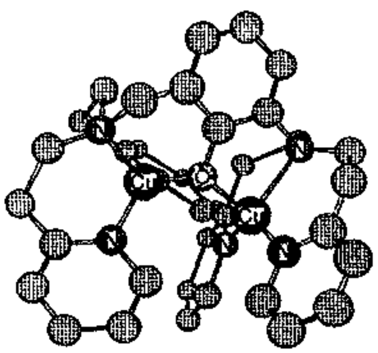
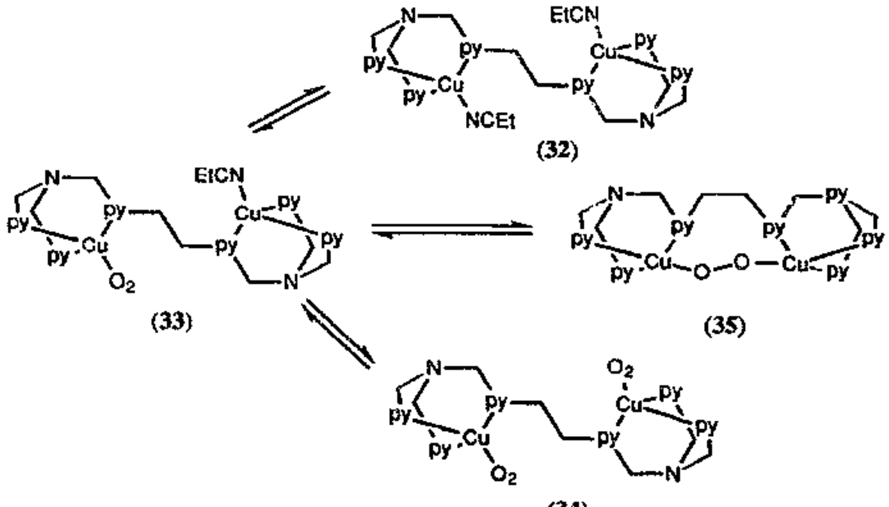
An investigation into the synthesis of peroxo- and hydroperoxo-dicopper(II) species having enhanced solution and solid state thermal stability has resulted in the characterisation of a dicopper(I) precursor (**31**) [22]. The dicopper(I) complex reacts reversibly with dioxygen at -80°C giving an intensely purple solution corresponding to the peroxo-dicopper(II) complex.

A kinetic study of the binding of dioxygen by the dinuclear copper(I) complex



(31)

(**32**) has been undertaken [23]. The study has shown that although the intramolecular binding of dioxygen by the two copper(I) ions in (**32**) significantly increases the kinetic reactivity leading to the μ-peroxo complex (**35**), the increased rate of formation is insufficient for increased thermodynamic stability and hence the system "looks at" the other species (**33**) and (**34**).



(**32**)

(**33**)

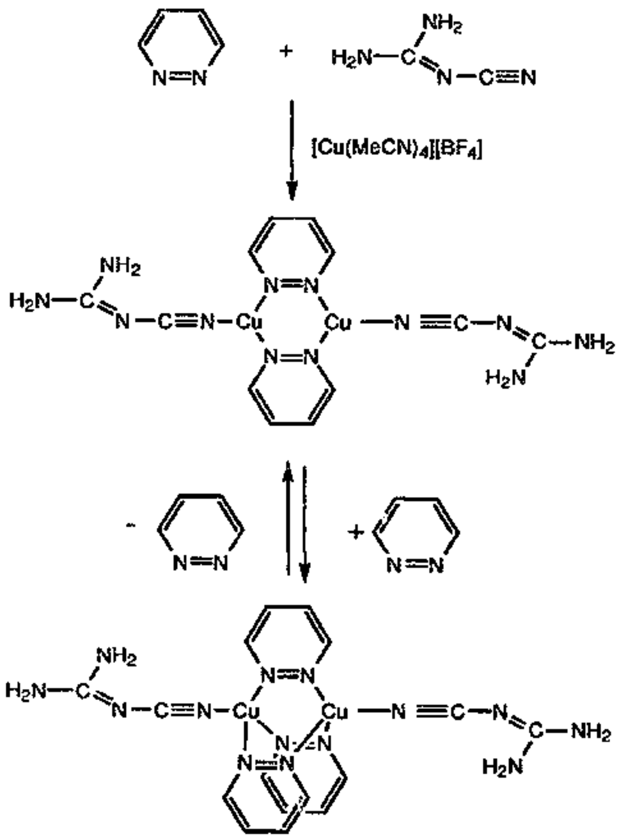
(**35**)

(**34**)

Coordinatively unsaturated Cu(I) cations have been shown to be stabilised by 2-cyanoguanidine (cnge) in the complex bis(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] tetrafluoroborate (**36**) [24]. The solid state structure shows the cation contains two trigonal-planar copper(I) ions bridged by two pyridazine (pydz) molecules and terminally coordinated by a cnge molecule. This complex itself can act as a receptor molecule by binding a further pydz molecule to form tris(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] tetrafluoroborate (**37**). The X-ray structure shows the complex contains two Cu(I) cations with distorted tetrahedral geometries which are bridged by three pydz molecules and with the coordination shell completed by a cnge molecule. TGA studies of (**37**) have shown that heating removes the third bridging pydz unit to regenerate (**36**). This behaviour is attributed to the unusually high stability of the coordinatively unsaturated Cu(I) in (**36**).

Another example of pydz being used as a bridging ligand in a dinuclear Cu(I) complex is $[Cu_2(pydz)_3(MeCN)_2][PF_6]_2$ [25]. The complex (**38**) shows the two copper(I) ions are bridged by three pydz ligands with a Cu···Cu separation of 3.065(2) Å. Each copper centre has a distorted tetrahedral geometry consisting of three nitrogen atoms of three different pydz molecules and one N from an acetonitrile molecule.

Phenazine (phz) can act as either a monodentate or a bridging ligand as well as an electron donor. The reaction of phz with Cu(I) ions has been demonstrated to be solvent dependent, forming the dinuclear complex (**39**) in methanol but a mono-



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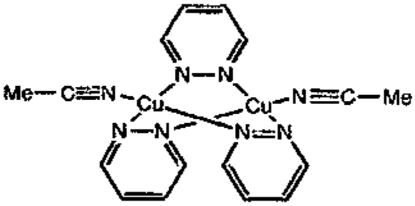

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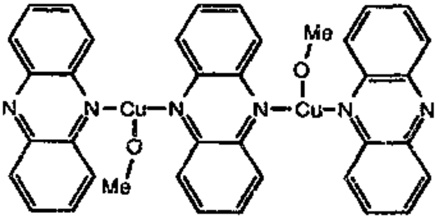
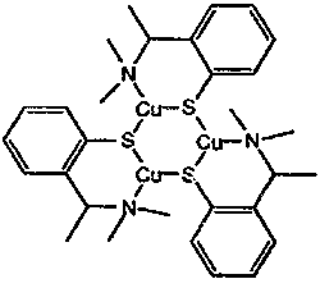


(39)

nuclear complex in acetone [26]. The solid state structure of (39) shows alternate stacks of the metal-free phz molecules and the dicopper complex. The dihedral angle between the two sets of molecular planes is 7.6° and the nearest separation between planes is 3.42 Å. A charge transfer band can be observed in the UV spectrum of the complex. This has been attributed to the transfer of electrons from the metal-free phz molecules to the bridging phz unit of the dinuclear complex which can act as an electron acceptor owing to the coordinated copper ions.

2.5. Trinuclear complexes

Members of a series of neutral (arenethiolate)copper(I) complexes containing an intramolecularly coordinating ligand have been synthesised [27]. The solid state structure of one of the complexes (**40**) has been determined and shows the central Cu_3S_3 6-membered ring to have a chair-like conformation with alternating Cu and S atoms. The presence of the bridging arenethiolate group results in an acute Cu-S-Cu angle of 79.63°, short Cu-S bonds of 2.231 and 2.186 Å and a short Cu···Cu distance of 2.828 Å. These features reflect an electron deficient two electron Cu_2S centre in which there is an interaction between a sulfur sp^2 hybrid orbital with a bonding combination of empty orbitals on the two copper ions. In solution the complexes are found to remain trimeric, but exist as two conformers that are in equilibrium through inversion of the bridging sulfur atom.



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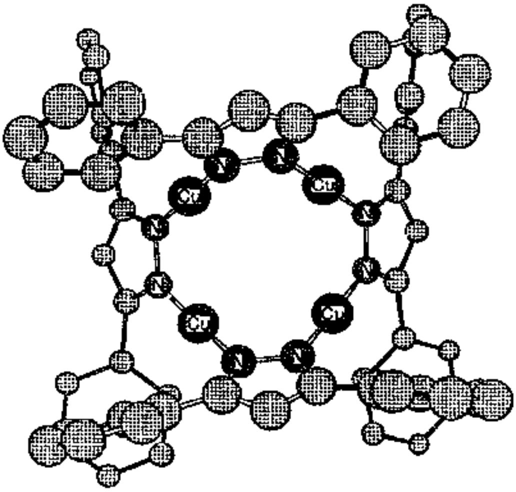
2.6. Tetranuclear complexes

The reaction of $[Cu(CH_3CN)_4][BF_4]$ with 3,5-diphenylpyrazole in the presence of triethylamine has been shown to form the tetrameric complex (**41**) [28]. The Cu(I) centres are separated by the ligands in an *exo*-didentate mode giving a Cu···Cu separation of 3.12 Å (av). The tetranuclear complex is catalytically active in the oxidative coupling of primary aromatic amines in the presence of molecular oxygen leading to the corresponding azobenzene. The reaction proceeds with 100% selectivity.

The reaction of CuBr with a variety of lithium silylamides has been investigated [29]. The solid state structure of $\{Cu[N(SiMe_2Ph)_2]\}_4$ has been determined and reveals an amide-bridged tetrameric structure with an almost square planar arrangement of the four copper centres. The bridging amides are displaced from the Cu_4 plane such that the Cu_4N_4 core possesses a butterfly structure (**42**).



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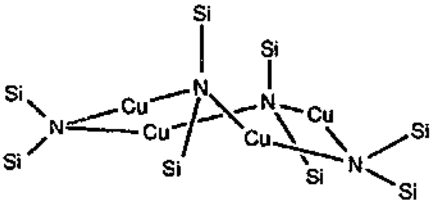
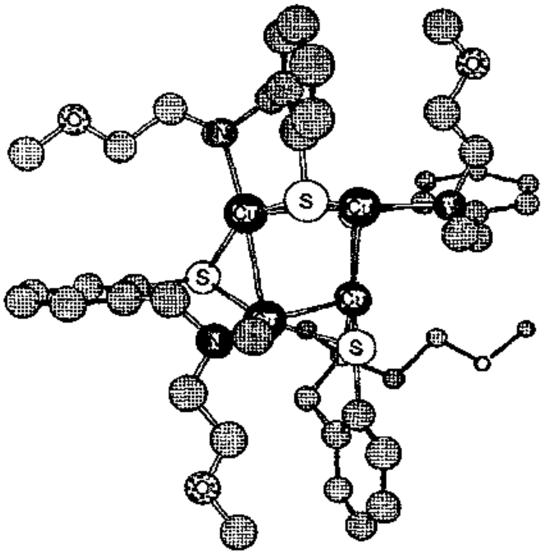


(42)

2.7. *Cluster complexes*

The solid state structure of a tetranuclear copper arenethiolate complex (**43**) has been determined [30]. The four copper centres are in a flattened butterfly arrangement with a thiolate sulfur atom bridging each Cu···Cu edge alternately above and below the copper array. The copper and sulfur atoms form an 8-membered ring in a twist boat conformation with the four aryl groups in equatorial positions. The acute Cu-S-Cu angle of 74.5° (av) and the short Cu···Cu distance of 2.693(9) Å (av) indicate that each sulfur atom forms an electron deficient three-centre bond with its neighbouring copper ions.

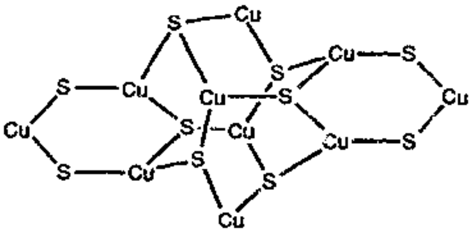
The oxidatively induced reductive coupling of mesityl complexes has been investigated [31]. The dioxygen effected coupling of mesitylcopper(I) has resulted in the formation of an orange-red intermediate structure containing oxide ligands trapped in an unusual coordination mode on the surface of the cluster. The complex has $\sim D_{3h}$ symmetry such that two oxide ligands and a central Cu(I) ion are situated on the approximate 3-fold axis while the remaining nine copper ions form three wings each with three copper(I) centres participating in two electron-three centre bonds with two mesityl groups. The Cu···Cu distances range from 2.376(8) to 2.439(6) Å and the oxide ligands are trigonal pyramidally coordinated to four Cu(I)



(43)

centres at a distance of 1.81-1.90 Å and are slightly displaced (0.1 Å) from the cluster surface.

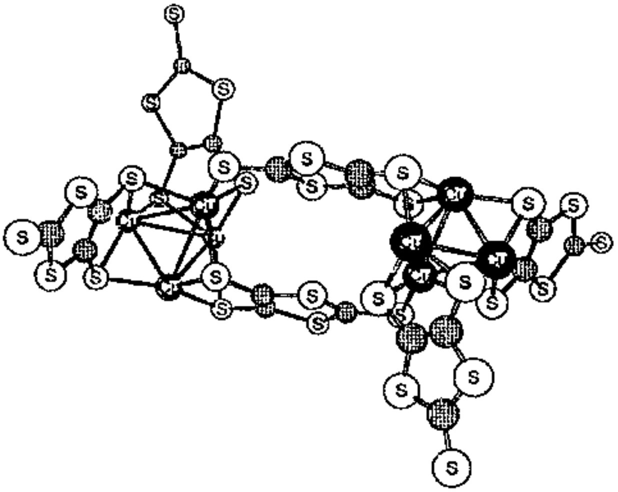
A molecular copper thiolate complex has been characterised and is claimed to be the first example without containing aryl substitution [32]. The cluster framework (**44**) is composed of alternating copper and sulfur atoms in a centrosymmetric arrangement with four different copper environments. The cluster and its solvent surround exist as discrete molecules without close intermolecular contacts in the crystal lattice. There is a close Cu···Cu contact (2.898 Å), but not a significant bonding interaction.



(44)

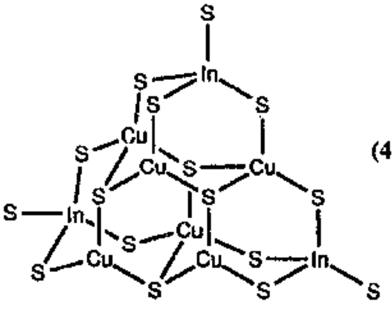
The cluster complex bis(*N*-methylpyridinium)tris[4,5-dimercapto-1,3-dithiole-2-thionato-(2-)]tetracopper(I) has been characterised [33]. The solid state structure (**45**) consists of dimerised anion units with interanionic Cu-S and S-S contacts which further interact with each other through several non-bonded S-S contacts to form a 2-dimensional sheet.

The solid-state structure of a nonanuclear mixed Cu-In thiolate cluster has been



(45)

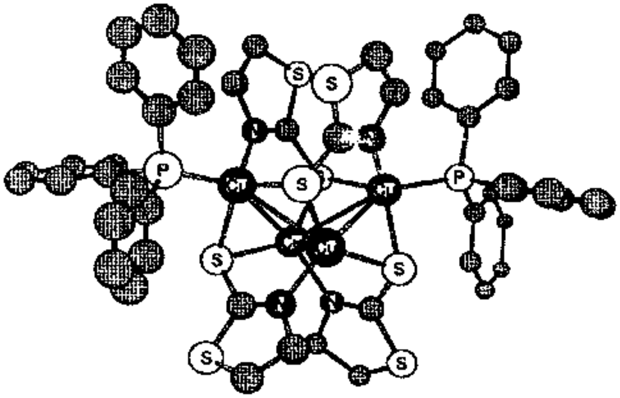
determined [34]. The cluster $(Ph_4P)[Cu_6In_3(SEt)_{16}]$ is stabilised with an overall truncated tetrahedral structure based on adamantane building units. The cluster consists of a $[Cu_6In_3S_{16}]$ core **(46)** in which the Cu-S distances are influenced by the metal coordination type rather than by the binding mode of the sulfur atoms. Thus, the Cu-S bonds around the three trigonal planar copper centres are shorter than those around the three tetrahedral copper centres (2.19-2.26 Å and 2.30-2.48 Å, respectively). The In-S bonds for all of the terminal thiolates are shorter than those of the bridging In-S bonds.



(46)

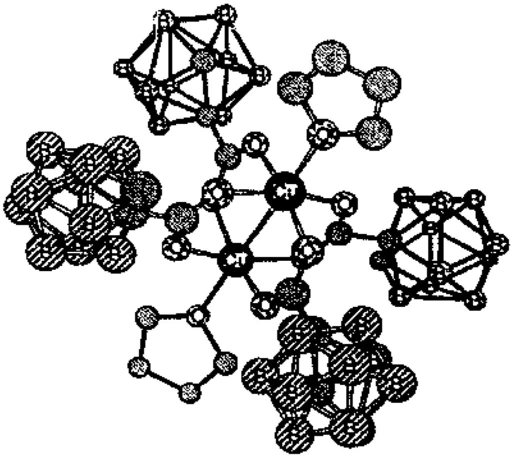
The reaction of 2-mercaptothiazoline with metal ions has been investigated [35]. The cluster **(47)** formed from the reaction of 2-mercaptothiazoline, copper(II) acetate and PPh_3 has been shown to consist of a tetranuclear butterfly-shaped cluster with the ligand bonded to the wing tip metal atoms. A mixed metal (Cu^I-Ag) cluster has also been prepared.

An investigation has been carried out into the thermolysis of molecular solids composed of cluster-substituted metal coordination compounds [36]. This study suggests that the thermolysis will only yield complex, reproducible solids when the



(47)

cluster-central metal link has greater thermal stability than the cluster itself. This is shown to be the situation for the metal cluster-substituted carboxylates $[M^{II}(1,2\text{-}C_2B_{10}H_{11}CO_2)_2]$ (M = Cu, **(48)**) that yield active porous materials, but not so for the analogous carborane-substituted complexes, $M^{II}[1,2\text{-}C_2B_{10}H_{10}(CO_2)_2]$, studied. The high stability of the carborane cage permits substantial cluster loss before temperatures high enough to cause cluster decomposition are reached.



(48)

The cluster $[Cu_{96}P_{30}\{P(SiMe_3)_2\}_6(PEt_3)_{18}]$ has been characterised [37]. The cluster core is sterically shielded by eighteen PEt_3 ligands and six μ_2-$P(SiMe_3)_2$ groups. The phosphorus atoms show high coordination numbers, acting as μ_6, μ_7, μ_9 and μ_{10} ligands.

2.8. *Polymeric complexes*

2.8.1. *Nitrogen coordination*

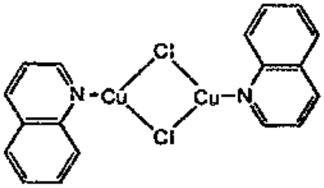
The reactions of copper(I) ions with pyrazine (pz) and its methylated derivatives have been investigated by a number of research groups [38–40]. The reaction of copper(I) ions with pyrazine resulted in the formation of the polymer $[Cu_2(pz)_3SiF_6]_\infty$ [38]. This polymer exists as honeycombed grids arising as a direct consequence of the Cu(I) centres adopting the more unusual 3-coordination trigonal geometry. The pz ligands bridge adjacent trigonal copper centres to form the honeycomb grids with bridged Cu ions at 6.936 and 6.685 Å. The presence of such large hexagons and a distance of 8.405 Å between parallel grids enable the enmeshing of an identical set of parallel sheets in the orthogonal direction to be accommodated. The closest Cu···Cu distance between adjacent grids is 6.0335(3) Å and precludes any possibility of inter-grid bonding. The counter ions are located in channels. In another study, the reaction of copper(I) ions with pyrazine resulted in the formation of a polymeric structure having the formulation $\{[Cu(pz)_{3/2}(CH_3CN)][PF_6].0.5C_3H_6O\}_\infty$ [39]. The solid state structure shows the polymer to have a 2-dimensional sheet structure with the copper centres having a distorted tetrahedral geometry. In contrast, the reaction between, 2,5-dimethylpyrazine and $CuClO_4$ has enabled two polymeric structures to be determined, one yellow in colour with a graphite-related lattice and the other orange-red in colour with a diamond-like lattice [40]. The polymer formed from the analogous reaction with tetramethylpyrazine afforded a colourless cationic linear chain structure $\{[Cu_2(Me_4pz)_3][ClO_4]_2\}_\infty$ [39]. The presence of the methyl substituents prevents formation of the hexagonal structure. The reaction of 4,4′-bipyridine with $[Cu(CH_3CN)_4][PF_6]$ has been shown to produce a polymeric structure composed of four independent concatenated diamondoid networks [38]. The copper centres have a tetragonal geometry with a Cu···Cu separation of 11.16 Å and with the counter ions occupying the channels.

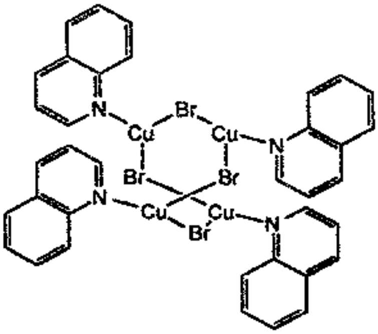
A study has been carried out to compare the structures of the 1:1 adducts formed between quinoline and Cu(I) chloride, bromide and thiocyanate salts [41]. The resulting structure of the product is found to be dependent on the copper salt used. With Cu(I) chloride, a "stair polymer" is formed (**49**) while the thiocyanate salt yields an "expanded stair polymer" similar to (**49**) but with the halide ion replaced by the SCN unit. In contrast, the reaction with CuBr resulted in a tetrameric structure (**50**) rather than a polymer.

Three copper(I) complexes having the formulation $[Cu_2(\mu\text{-}X)_2(\mu\text{-}phz)]_\infty$, where phz = phenazine and X = halide, have been synthesised and their solid state structures determined [42]. In the case where the iodide salt was used, the polymer contains Cu_2I_2 rhomboids which are bridged by phz molecules to give an infinite linear chain structure (**51**). The phz molecules in adjacent chains are aligned with an interplanar separation of 3.46 Å. With chloride or bromide anions a 2-dimensional polymeric sheet is obtained with phz molecules hanging between the polymeric stair frameworks of CuBr (**52**) or CuCl.

The reaction of the acyclic ligand (**53**) with $[Cu(MeCN)_4]^+$ in acetonitrile has been investigated [43]. On reaction with a copper(I) salt a dinuclear structure (**54**)

(49)





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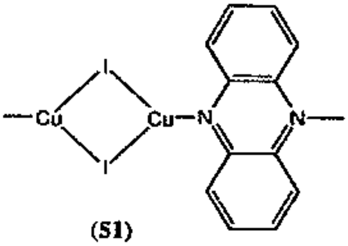

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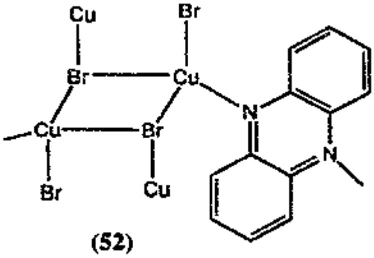
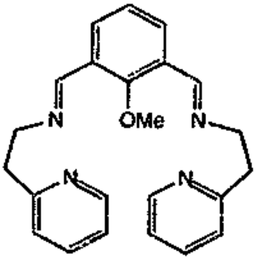


(52)

is formed initially in which the geometry of the metal centres is determined by the amount of acetonitrile used in the reaction. On standing in acetonitrile, an oxygen sensitive orange crystalline solid was formed. Analysis by X-ray crystallography showed this to be a linear coordination polymer containing two ligand strands twisted around each other and coordinated to copper centres resulting in a helical structure. The Cu···Cu distance of 7.650 Å is strongly influenced by the presence of the methoxy substituent.



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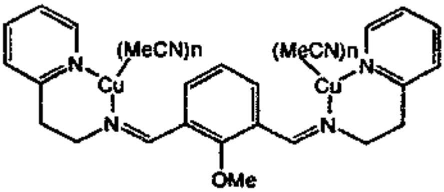

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A study of the architecture of new 2-dimensional polynuclear complexes has been carried out on systems consisting of 6-membered rings of Cu(I) ions interconnected by benzothiadiazole (btd) molecules [44]. The solid state structures of the complexes

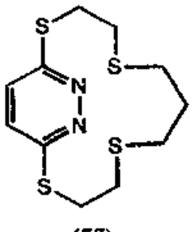
$\{[Cu_2(btd)_3(ClO_4)][ClO_6].2thf\}_\infty$ and $[Cu(btd)(HPO_3F)]_\infty$ show they are planar polymers while in $[Cu(btd)(NO_3)]_\infty$ the copper ions are no longer in the same plane but occupy a chair arrangement. This makes it possible for the btd molecules to stack both within and between the 2-dimensional sheets and results in the formation of a layer structure similar to graphite.

The coordination of cyanoguanidine (cnge) with copper(I) halides has been investigated [45]. The air and moisture stable Cu(I) complexes Cu_2X_2.cnge and CuX.cnge.H_2O ($X = Cl,Br,I$) have been prepared. The solid state structures of Cu_2Cl_2.cnge and Cu_2Br_2.cnge have been determined and are shown to be isostructural consisting of mutually perpendicular chains of $[XCu(cnge)]_n$ and $[CuX_2^-]_n$ joined at a common halogen atom. The cyanoguanidine uses both its nitrile and imine nitrogen atoms to bridge the copper centres, which complete their coordinatively unsaturated trigonal planar geometry with the common halogen atom. In contrast CuBr.cnge.H_2O has been shown to consist of a zigzag CuBr chain and a buckled $[BrCu(cnge)]_n$ chain joined at a common copper atom. The $BrCu(cnge)]_n$ chain is similar to that in $[XCu(cnge)]_n$, but the buckling results in a dihedral angle between adjacent cnge molecules of 8.9°.

2.8.2. *Sulfur coordination*

Whereas *ortho*- and to a lesser extent *meta*-aromatic spacers in a cyclophane ring encourage endodentate coordination, the inclusion of a *para*-aromatic fragment has been shown to lead to preferential exodentate coordination with the formation of polymeric chains [46]. The macrocyclic ligands (**55**) bind in an *exo*-didentate fashion with each ligand bonded by two adjacent aliphatic thioether sulfur atoms linking the Cu_2Br_2 units into an interlocked 2-dimensional "zig-zag" latticework (**56**). The ligands alternate in a *pseudo-trans* arrangement. The pyridazine nitrogen atoms are not involved in the coordination to the copper centres.

The solid state structure of the polymer formed from the reaction of the thione



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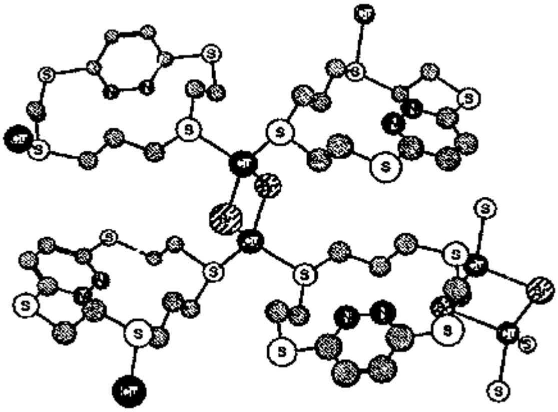
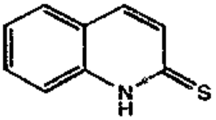


(56)

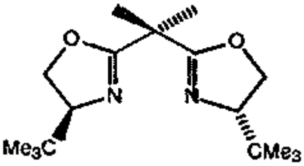
(**57**) with $[Cu(MeCN)_4]^+$ shows it to be an infinite 3-dimensional structure [47]. Only the sulfur atoms of the thione molecules are involved in coordinating to the copper(I) centres and do so in a bridging fashion resulting in an infinite linear chain framework of CuS_2. Two types of chain-chain interactions can be observed which lead to the 3-dimensional structure, (i) stacking between the planar thione molecules and (ii) hydrogen bonding between the counter anion and the NH groups of the thione.



(57)

2.8.3. *Nitrogen and oxygen coordination*

The polymeric Cu(I) complex of the chiral ligand (**58**) has been shown to be an effective catalyst for the enantioselective cyclopropanation of olefins with diazoacetic acid esters with 97 to >99% ee [48]. In the solid state the catalyst has a chiral non-racemic helical structure with the bis(oxazoline) ligand occupying bridging positions between nearly linear 2-coordinate Cu(I) ions. The ligand adopts a conformation with the ᵗbutyl group directed away from the centre of the helix. The Cu(I) ions are sterically protected from oxidation by the ᵗbutyl groups and the complex is stable in air for several months.

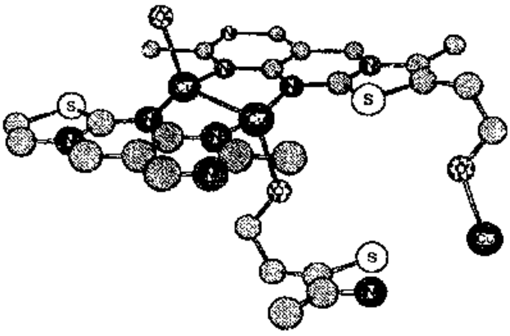


(58)

The complex formed between copper(I) and thiochrome (tc = 2-(2,7-dimethyl-5H-pyrimido[4,5-d]thiazolo[3,2-a]-pyrimidin-8-yl)ethanol) has been shown to exist as a polymer in the solid state but as a dimeric species in solution [49]. The solid state structure consists of an infinite stair-type chain in which dimeric units are mutually linked by the 2-hydroxyl group of the coordinated ligand (**59**). Each Cu(I) ion has a T-shaped geometry and the Cu···Cu separation is only 2.476 Å. In solution, the hydroxyl groups do not coordinate to the copper centre resulting in a low molecular weight dicopper complex persisting.

2.9. *Supramolecular complexes*

An air sensitive copper(I) complex of 2,2′:6′,2″-terpyridine has been stabilised independently by two research groups [50,51]. This has been achieved by the



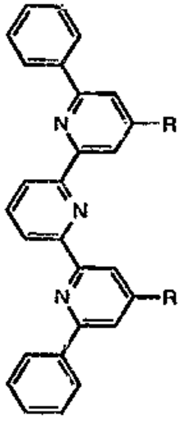
(59)

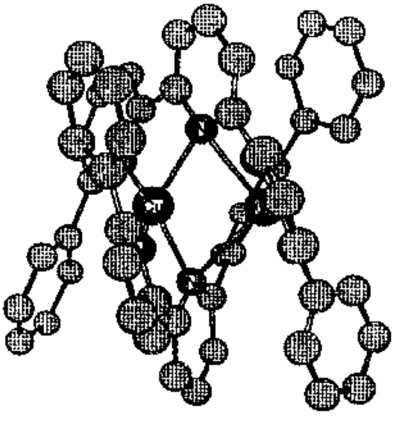
introduction of phenyl substituents at the 6-position of the two terminal rings of the tpy unit. Both the unsubstituted ligand (**60**) and the bisthiomethyl substituted ligand (**61**) form dinuclear double helical structures and the thiomethyl substituents serve only to affect the pitch of the helix. This is demonstrated by the slightly larger Cu···Cu separation of 2.631(2) Å in $[Cu_2(\mathbf{61})_2]^{2+}$ compared to 2.570(2) Å in $[Cu_2(\mathbf{60})_2]^{2+}$. The solid state structures of both complexes show the two copper centres to have different coordination numbers, with one Cu(I) ion being in a distorted tetrahedral environment while the other is almost linear (**62**). However, the approximate linearly coordinated copper centre does show longer ranging interactions with the nitrogen atom of the "bridging" pyridine rings. In solution the complexes exist in a more symmetrical form with the copper centres becoming equivalent. The cyclic voltammogram of $[Cu_2(\mathbf{61})_2]^{2+}$ shows a significant degree of metal-metal interaction to exist. This is evident from the large difference in potentials ($\Delta E^{\circ\prime} = 860$ mV) of the two one electron oxidations.

The same two research groups have also investigated the coordination of quater-

R = H (60)

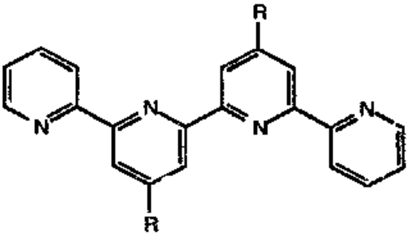
R = SMe (61)





(62)

pyridine systems with copper(I) ions [52,53]. Comparison of the solid state structures of the two complexes, $[Cu_2(\mathbf{63})_2]^{2+}$ and $[Cu_2(\mathbf{64})_2]^{2+}$ shows them to be dinuclear double helical structures with the copper centres having distorted tetrahedral geometries. The effect of the substituents in increasing the pitch of the helix is once again demonstrated by the Cu···Cu distance being 3.17 Å and 3.32 Å in $[Cu_2(\mathbf{63})_2]^{2+}$ and $[Cu_2(\mathbf{64})_2]^{2+}$, respectively.

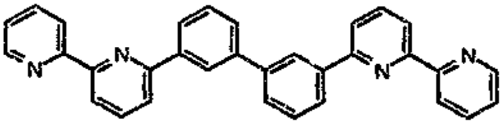


R = H (**63**)

R = SMe (**64**)

Much investigation has been carried out on synthesising ligands with the metal-binding domains separated by spacer groups and studying their complexation with metal ions. The reaction of copper(I) ions with a ligand containing two bipyridine (bpy) units separated by a biphenyl-3,3'-diyl spacer group (**65**) has resulted in the isolation of a dinuclear double helical structure [54]. The complex shows an increased intermetallic separation (Cu···Cu = 6.26 Å) compared with ligands (**63**) and (**64**) in which the metal binding domains are directly linked. The effect of incorporating the more flexible ethane bridge between bpy centres (**66**) has also been investigated [55]. The solid state structure once again shows the complex to have a dinuclear double helical structure with the copper cations having a distorted tetrahedral geometry separated by a distance of 5.926 Å. The complexation of copper(I) ions with the analogous ligand incorporating phen units instead of bpy groups (**67**) has also been studied [55,56]. The introduction of the phen units has resulted in a slightly shorter Cu···Cu distance in the dinuclear double helical structure at 5.729 Å. These studies have demonstrated that the formation of helical complexes can be controlled by the careful design of the ligands.

The complexation of copper(I) ions with imidazole-containing ligands has been investigated. The ligand (**68**) has been shown to bind in a bismonodentate coordination mode and form the strands of a helix that twist around the helical axis on which the Cu(I) ions lie [57]. Each copper centre is essentially linearly coordinated by two imidazole units. The solid state structure shows two crystallographically distinct $[Cu_2(\mathbf{68})_2]^{2+}$ units stacked on top of each other, with the second rotated by 90° with respect to the first. This allows for a strong stacking interaction between the imidazole planes of superimposed complexes. The rotation by 90° allows the units to mesh together so that the structure appears as an infinite double helix. The importance of the spacer group between the imidazole units in the formation of helical complexes has been determined from the complex formed between (**69**) and $Cu(ClO_4)$ [58]. The solid state structure shows that the complex is dinuclear with each copper centre linearly coordinated to a benzimidazole group of two ligands,



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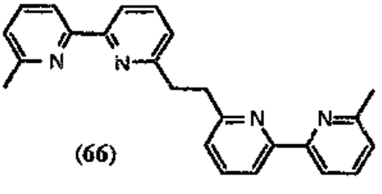

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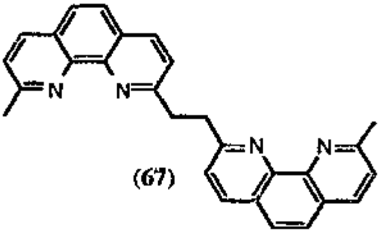
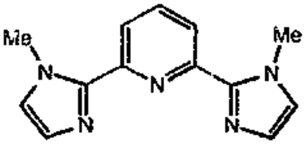


(67)

but that the ligands are not wrapped around the copper centres and hence the complex does not have a helical structure (**70**).



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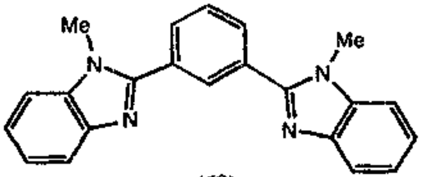

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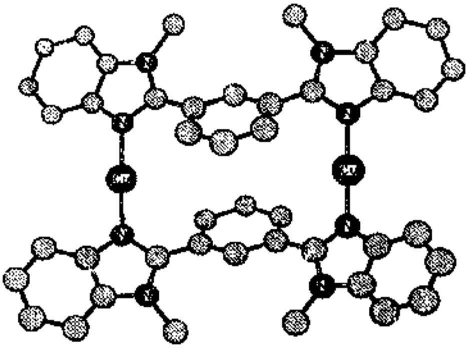
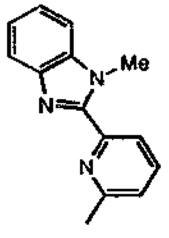


(70)

Solid state characterisation of the complex formed between 6-methyl-2-(1-methylbenzimidazol-2-yl)pyridine (**71**) and Cu(I) ions has shown it to be mononuclear in which the Cu(I) centre is *pseudo*-tetrahedrally coordinated to two didentate α,α′-diimine donor groups [59]. The linking together of two molecules of (**71**) by a methylene bridge has been shown to result in the formation of ligand (**72**) which is constrained into acting as a bis(didentate) ligand rather than a mononuclear tetradentate ligand.

A study has been carried out on the coordination of copper(I) ions with ligands



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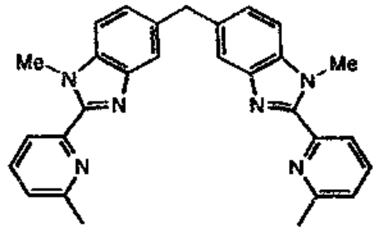
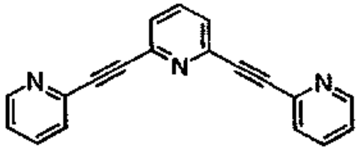


(72)

containing ethyne-spaced pyridine rings [60]. The reaction of 2,6-bis(2-pyridylethynyl)pyridine (**73**) with a copper(I) salt has resulted in the formation of the complex $[Cu_3(\mathbf{73})_3]^{3+}$ in which the copper(I) ions coordinate to three pyridine rings of three different ligand strands (**74**). The ligands wrap around the copper centres in a helical manner with the Cu···Cu being ~4.5 Å. The formation of this triple helical structure arises as a consequence of the spacer group making adjacent pyridine groups too far apart for the ligand to act in a didentate mode.



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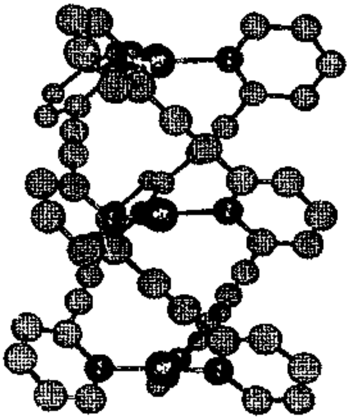
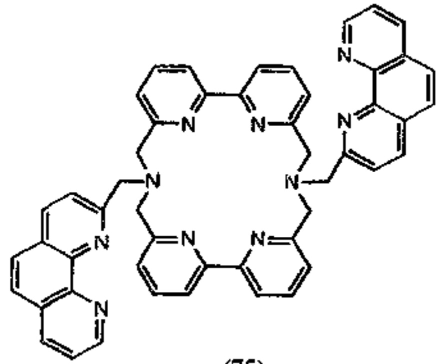


(74)

The reaction of the macrocyclic ligand (**75**) with $[Cu(CH_3CN)_4][ClO_4]$ has resulted in the formation of a deep red, air stable tetranuclear complex (**76**) [61]. The copper(I) ions are coplanar in distorted tetrahedral environments and form a rhombus with sides of 7.133 Å long. The phen units arranged in a *cis* fashion and the two bpy units of each macrocycle form a cross which results in a double stranded helicate. Varying the amount of the copper salt used (from 0.5 to 2.0 equivalents) resulted in only the tetranuclear complex being formed. This illustrates there is a positive cooperativity in the complexation of the copper ions.

The reaction of 3,6-bis(2-pyridyl)pyridizine with $[Cu(CF_3SO_3)]_2.C_6H_6$ has enabled a tetranuclear structure to be characterised [62]. The complex (**77**) consists of four ligand strands and four copper ions. The copper centres each have a distorted tetrahedral geometry each bound to two different ligand strands through a pyridine



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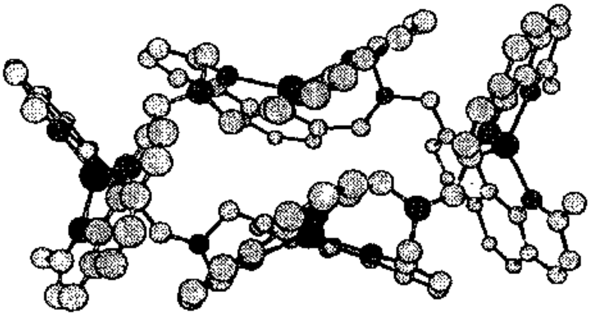
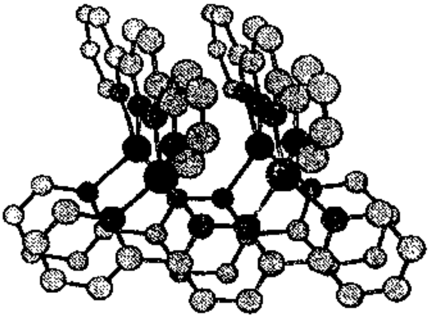


(76)

and a pyridizine nitrogen atom. The ligand is slightly twisted around the exocyclic C-C bond with dihedral angles of 9°. This demonstrates that the ligand is sufficiently flexible to adjust to the stereochemical requirements of the Cu_4 unit. Pairs of ligands are almost parallel and separated by 3.47 Å which leads to significant π-π stacking interactions.

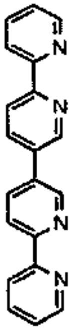
A multi-ligand, multi-metal self-assembly process involving two types of ligands

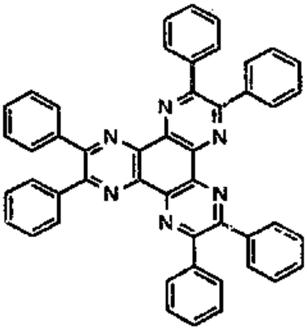


(77)

and several copper(I) ions has been investigated [63]. The addition of six equivalents of $[Cu(CH_3CN)_4][BF_4]$ to a solution of three equivalents of (**78**) and two equivalents of (**79**) resulted in all eleven particles coming together to form a dark purple hexanuclear cylindrical complex (**80**). The complex has an internal cavity with a height of 7.4 Å and a radius of 5.5 Å.

(78)





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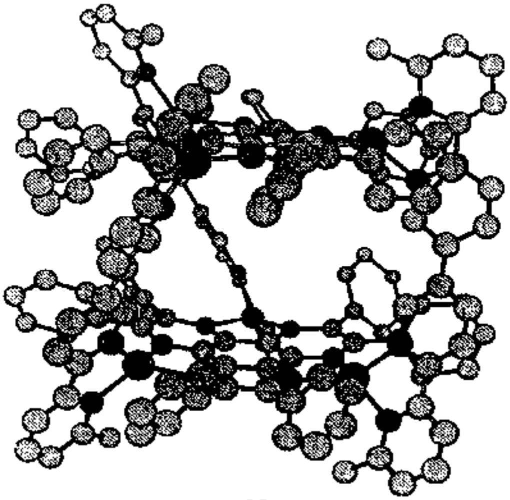
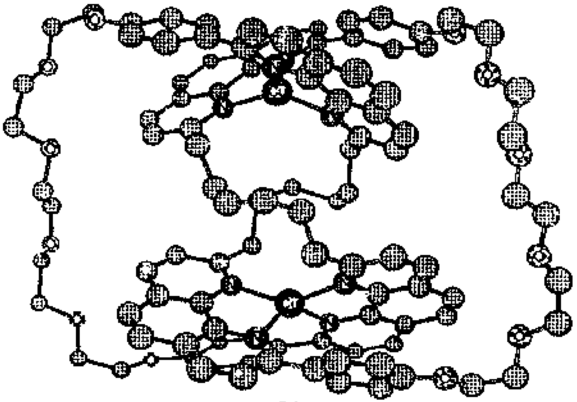


(80)

A demetallation kinetic study of various knots and related unknotted complexes has been reported [64]. The compounds studied were either dicopper(I) knots or face-to-face complexes and as expected the knotted complexes are much slower to demetallate than the unknotted analogues. The crystal structure of the trefoil knot (**81**) formed from a 3-dimensional template effect of two copper(I) ions has been reported. This has enabled the distance between the two copper centres to be determined as 7.03 Å.



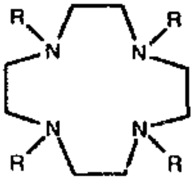
(81)

3. Copper(II)

3.1. *Mononuclear complexes with macrocyclic ligands*

3.1.1. *Nitrogen coordination*

An investigation into the stability of the copper(II) complexes of the 12-membered macrocycle 1,4,7,10-tetraazacyclododecane (**82**) and its derivatives has been carried out [64]. This study has shown that these complexes are easier to reduce than Cu(II) complexes of larger tetraaza macrocyclic ligands and that the Cu(II) complexes containing the 12-membered macrocycle with tertiary nitrogens (**83**,**84**) are easier to reduce than the similar complex containing secondary nitrogen atoms (**82**). The X-ray structure of the complex $[Cu(83)(H_2O)](NO_3)_2.H_2O$ shows the cavity of the macrocycle is too small to accommodate the metal ion which is raised above the N_4 plane by 0.5 Å in a square pyramidal geometry.



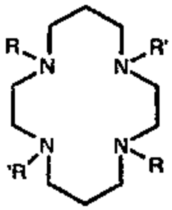
R = H (**82**)

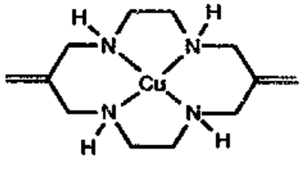
R = CH_3 (**83**)

R = $CH_2C_6H_5$ (**84**)

The formation of Cu(II) complexes with cyclam derivatives has been investigated by a number of research groups. A variety of 1,8-disubstituted derivatives of cyclam have been synthesised (**85**) and their coordination with Cu(II) ions studied [65]. The solid state structure of a Cu(II) cyclam derivative containing exocyclic olefinic bonds (**86**) has been reported [66]. The X-ray structures of the protonated and deprotonated complex of Cu(II) with 1,4,5,11-tetraaza-5-oxocyclotetradecane (**87**) have shown that the carbonyl oxygen atom is the protonation site and has enabled the mechanism of acid dissociation to be discussed [67].

(85)





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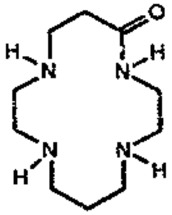

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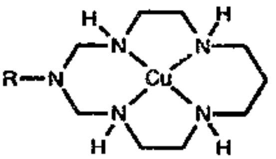

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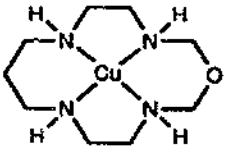


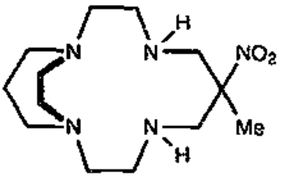
(89)

The formation of cyclam derivatives has also been accomplished by using a template synthesis. In the formation of **(88)**, a number of amines have been used as the locking fragment and a kinetic study of the rate of the template reaction shows the rate seems to be related to the strength of the diprotic acid used as the capping unit [68]. The crystal structure of one of the complexes has shown the Cu(II) centre to have an elongated octahedral geometry where the four secondary nitrogen atoms of the macrocycle are bound in a regular square stereochemistry. The axial sites are occupied by the oxygen atoms of nitrate ions. The synthesis of oxatetraazacycloalkanecopper(II) **(89)** has also been achieved using Cu(II) as the template in the condensation of tetraamine copper(II) complexes with paraformaldehyde in acetonitrile or dioxane [69].

Increasing the rigidity of the small saturated macrocycles containing the N_4 donor set leads to the so called "reinforced" macrocycles. 6-Methyl-6-nitro-1,4,8,11-tetraazabicyclo-[9.3.2]hexadecane **(90)** occurs in both the *syn* and *anti* forms with respect to the relationship of the ethylene bridge and the nitro group. The reaction of this ligand with Cu(II) ions affords two complexes, one red and the other blue [70]. The red complex, [Cu(**90**)(NO_3)][ClO_4], has the *anti* geometry while the blue complex, [Cu(**90**)(H_2O)][ClO_4]$_2$, has the *syn* arrangement. The difference in the colour of the two complexes arises from a difference in the coordination geometry.

The slightly larger reinforced macrocycle **(91)** demonstrates the benefit of the extra rigidity of the macrocycle [71]. In the Cu(II) complex, the metal centre lies in an approximately square planar geometry, displaced from the N_4 plane by 0.36 Å. The Cu-N distances of 2.09 Å are longer than in their unreinforced analogues. A similar reinforced macrocycle Cu(II) complex **(92)** has been synthesised using a metal directed condensation reaction [72].

The effect of the attachment of a 2,2'-bipyridine unit to a cyclam unit on the formation of a Cu(II) complex has been investigated [73]. The solid-state structure



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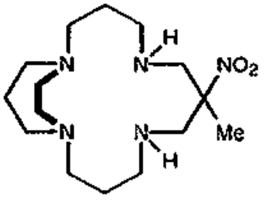

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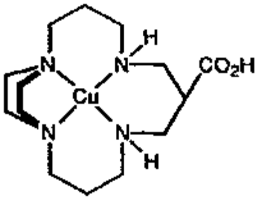
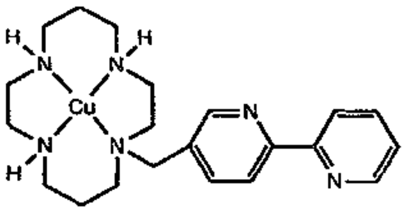


(92)

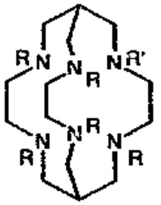
of the complex **(93)** shows the cyclam to have the unrestrained *RRSS*-configuration and that the bpy unit takes no part in the coordination to the copper centre; the axial sites are occupied by perchlorate ions. The UV-VIS spectrum of the complex formed from the reaction of **(93)** with *cis*-$[(bpy)_2RuCl_2]$ was characteristic of $[Ru(bpy)_3]^{2+}$ and its cyclic voltammogram was consistent with there being no interaction between the $[Ru(bpy)_3]^{2+}$ and $[Cu(cyclam)]^{2+}$ units.



(93)

A study has been carried out on the penta-, hexa-, and hepta-*N*-methylated derivatives of the macrobicyclic hexamine 3,6,10,13,16,19-hexaazabicyclo-[6.6.6]icosane **(94)** [74]. The unsubstituted ligand **(94)** acts as a hexadentate ligand while **(95)**, **(96)** and **(97)** all coordinate as tetradentate ligands both in the solid state and in solution. This difference in coordination behaviour is attributed to an unfavourable steric strain arising when the methyl substituents are introduced.

A study of the complexation of the sterically crowded porphyrin 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin **(98)** with a range of transition metal ions has shown that the metal ion alters the degree of planarity of the macrocycle, with a larger metal ion favouring a more planar conformation [75]. The solid state structure of the Cu(II) complex reveals the porphyrin to be in a



R' = R = H (**94**)

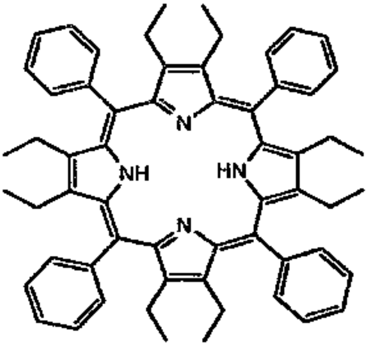
R' = R = Me (**95**)

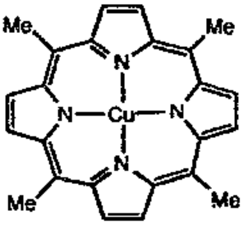
R' = Me, R = H (**96**)

R' = Me, R = Me$_2$ (**97**)

non-planar saddle conformation. In another study the consequences of oxidising the multiple-substituted porphyrin (**98**) to its π-cation radical [Cu(**98**)$^{\cdot +}$[ClO$_4$] have been investigated [76]. The oxidation of the non-planar porphyrin results in further conformational changes with an increased ruffling imposed on the original saddle shape effecting a twisting of the pyrrole rings, the *meso* carbon atoms move alternately up and down out of the plane of the porphyrin plane by ~0.2 Å and the phenyl rings rotate further into that plane by more than 10°. The radical cation is found to be EPR silent and the ^{1}H NMR spectrum is indicative of a diamagnetic species which arises from the Cu(II) ion and the nonplanar π-radical spins being antiferromagnetically coupled. This result shows that the conformations of the radicals control the magnetic coupling with metals, with this being especially important in Cu(II) cation radicals in which the $d_{x^2-y^2}$ orbital is directed into the plane of the porphyrin.

(**98**)

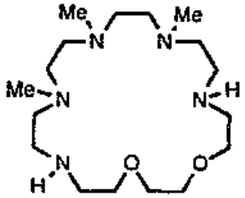


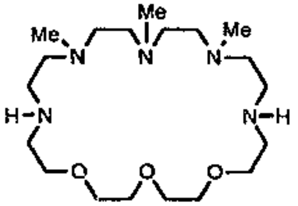


(**99**)

The electrochemical oxidation of (5,10,15,20-tetramethylporphyrinato)Cu(II) in the presence of the perrhenate ion has been shown to result in a new molecular conductor [77]. The complex is composed of partially oxidised cations (**99**) stacked metal-over-metal and surrounded by chains of ReO$_4$ anions. Magnetic studies have shown that the local Cu(II) moments and the itinerant π-carrier electrons participate in strong spin exchange. The conductivity is weak but thermally activated. A study of the basicity behaviour of the two new oxa-aza macrocycles (**100**) and (**101**) has been performed using potentiometric and NMR spectroscopic techniques [78]. Both are found to behave as tetraprotic bases under the conditions used. Both ligands give rise to a weak overall interaction with Cu(II) ions with respect to other polyazacycloalkanes. The solid state structures of [Cu(**100**)]$^{2+}$ and [Cu(**101**)Cl$_2$](ClO$_4$)$_2$.2H$_2$O show only the nitrogen atoms coordinate to the copper centres while the oxygen atoms remain unbound. Thermodynamic data have determined a low enthalpic effect for the formation of the complexes which is attributed in part to the methylation reducing the overall interaction between the ligand and the metal ion.

(100)

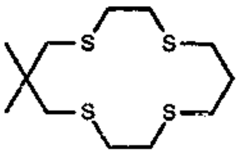




(101)

3.1.2. *Sulfur coordination*

The reaction of sulfur derivatives of cyclam with metal ions has been investigated [79]. Whereas the reaction of (**102**) with copper(II) ions afforded only one isomer, the reaction of the tetramethyl derivative (**103**) resulted in the formation of two isomeric complexes, *syn* and *anti*, with the *syn* isomer being the major product. Both the *syn* (**104**) and *anti* (**105**) conformations of the 14-membered thioether macrocycle are observed within a single crystal lattice.



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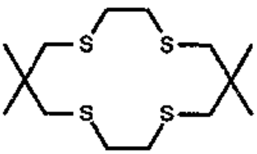

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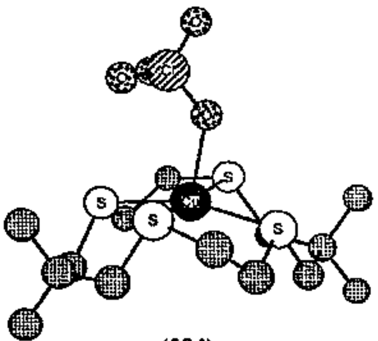

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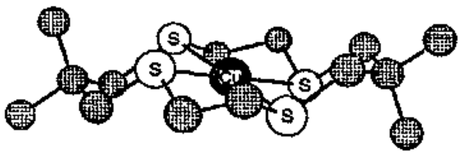
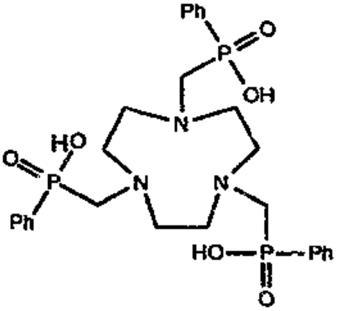


(105)

3.1.3. Nitrogen and oxygen coordination

A study has been carried out on the coordination of 1,4,7-triazacyclononane-1,4,7-trimethylenetris(phenylphosphine) (**106**) with a range of divalent and trivalent metal ions [80,81]. The complexes formed with the divalent ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, all have C_3 symmetry and the complexes formed with the trivalent ions Fe^{3+}, Co^{3+}, Ga^{3+} and In^{3+} are structurally similar. The solid state structures of eight complexes have been determined and, in all, the ligand adopts the same rigid conformation and a single chiral diastereoisomer is formed at each stereogenic phosphorus centre, giving a racemic mixture of *RRR* or *SSS* enantiomers. The metal centres have a slightly distorted octahedral geometry and the Cu(II) complex (**107**) only exhibits a Jahn-Teller distortion below 100 K. Since the divalent complexes are isostructural the study demonstrates that the coordination environment around the metal centre is determined essentially by the minimisation of the intramolecular ligand interactions involving the PPh groups. The rigid ligand imposes its preferred geometry on the metal ion and overrides any effects of complex geometry of either crystal field stabilisation energies or π-bonding effects.



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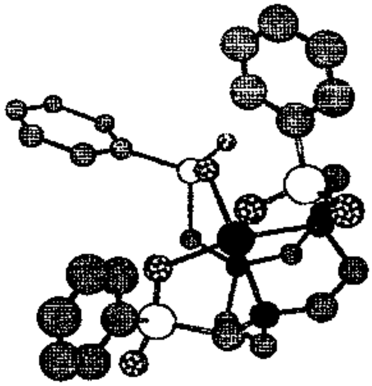
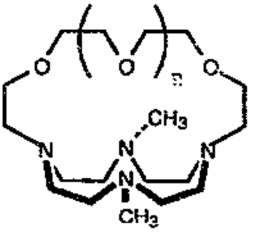


(107)

The two aza-oxo cryptands (**108**) and (**109**) have been shown to bind Li^+ and Na^+ as well as Cu^{2+}, Zn^{2+} or Cd^{2+} in aqueous solutions [82]. Potentiometric and spectroscopic techniques indicate that the divalent ions coordinate to the tetraaza portion of the receptor, with the coordination sphere being completed by an oxygen atom from the polyoxa chain or by a water molecule. The same situation is found in the solid state as shown by the crystal structures of [Cu(**108**)][ClO_4] and [Cu(**109**)(H_2O)][ClO_4]. The stability constants for the copper complexes are low: for [Cu(**108**)], log $K=12$ and for [Cu(**109**)], log $K=14$. This is a consequence of the rigidity imposed by the short ethylenic chains and the methyl substituents in the *trans* arrangement leading to crowding which prevents the donor atoms from adapting themselves to the stereochemical requirements of the metal ion.

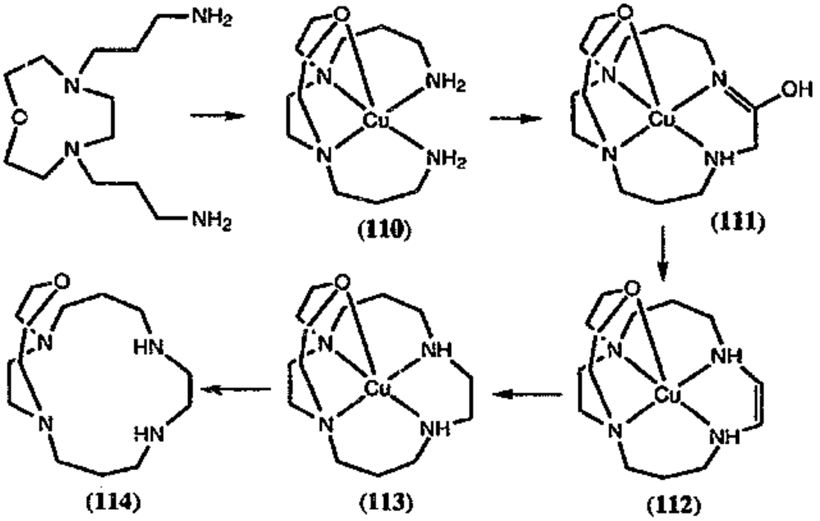
The macrobicyclic ligand 17-oxa-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane



n = 1, **(108)**

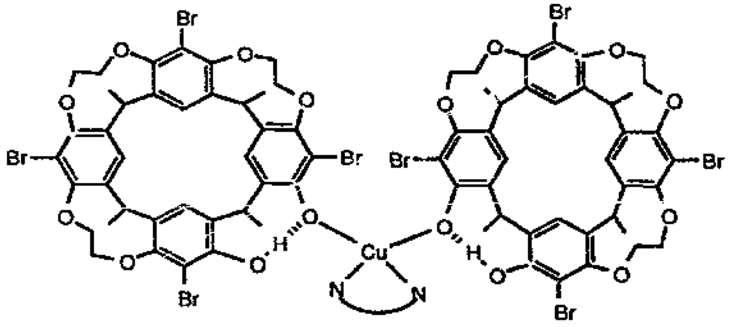
n = 2, **(109)**

(114) has been synthesised using a Cu(II) template reaction [83]. All of the intermediates **(110-113)** have been characterised by X-ray crystallographic analysis.



The copper(II) complex of a partially-unlinked cavitand derived from the condensation of resorcinol and acetaldehyde has been characterised [84]. The cavitand derivative functions as a monodentate ligand towards transition ions and has led to the isolation of the complexes with the formula [$(\text{cavitand})_2\text{ML}$] (M = Co, Cu(**115**), Zn) and [$(\text{cavitand})_2\text{NiL}_2$], where L is a didentate ligand.

A study has been carried out to synthesise 5-coordinate Schiff base copper complexes (**116**) which can serve as direct precursors to the host cobalt(II) complexes [85]. The study has shown that by varying the bridging groups the size of the hydrophobic pockets above the copper centres can be controlled. Moreover the presence of the bridging group has been shown to have a substantial effect on the metal coordination geometry forcing the ligand to adopt a more planar environment than that found in the unbridged complexes. ESR spectroscopic data suggest that the complexes are 5-coordinate with a geometry intermediate between trigonal bipyramidal and square planar.



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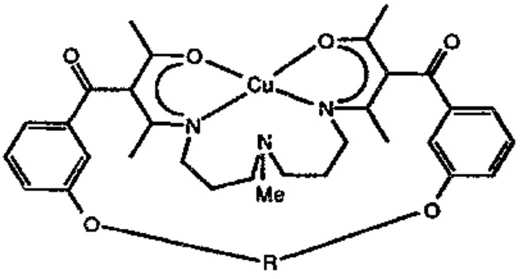
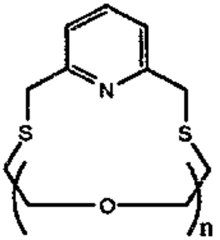


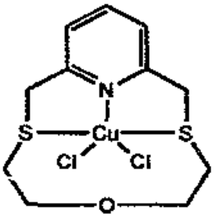
(116)

3.1.4. Nitrogen and sulfur coordination

A study has been performed on pyridine-based macrocyclic ligands containing nitrogen, oxygen and sulfur donor atoms [86]. The macrocycle (**117**) has been incorporated as a sensor into a neutral mobile-carrier based liquid membrane electrode. The macrocycle, however, showed only a small selectivity of Cu(II) over Co(II) and Ni(II). The solid state structure of the copper(II) complex (**118**) has been determined and shows that the metal centre binds to the nitrogen and sulfur donor atoms, but with the oxygen atom remaining uncoordinated.



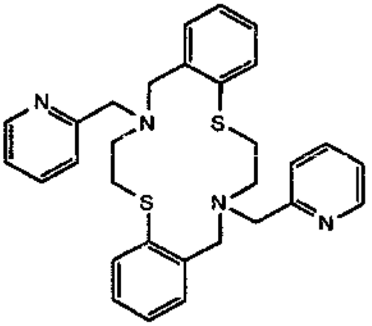
n = 1, (**117**)



(118)

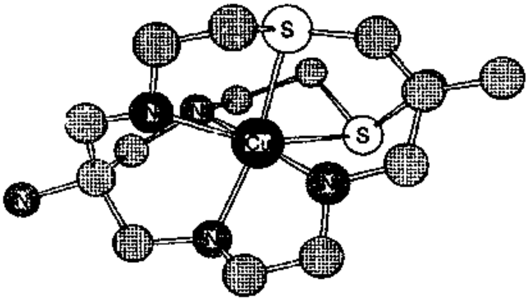
The coordination of copper(II) ions with a macrocycle possessing a nitrogen and sulfur donor set (**119**) has been investigated [87]. In the free ligand none of the donor atoms are oriented towards the ring cavity but on reaction with a copper(II) salt a conformational change occurs leading to the formation of the complex

[Cu(**119**)][ClO_4]. The copper centre has a highly distorted trigonal prismatic coordination geometry with all six donor atoms of the ligand coordinated and lies outside the macrocyclic cavity being situated 1 Å above the mean plane through the donor atoms of the folded macrocycle.



(119)

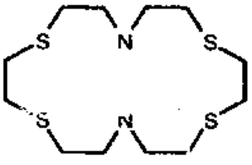
The Cu(II) complex of the N_4S_2 encapsulating ligand 1-methyl-8-ammino-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]icosane (**120**) is reported [88]. The copper ion is in a distorted form of a [4+2] elongated octahedron with a pronounced tetragonal distortion arising from long Cu-N and Cu-S axial bonds (2.447(5) and 2.600(2) Å respectively). The presence of the longer Cu-S bonds *cis* to shorter Cu-N bonds results in a tilting of the capping group in relation to the *pseudo*-3-fold axis of the metal complex. The solid state structure also shows the two capping units to be eclipsed.

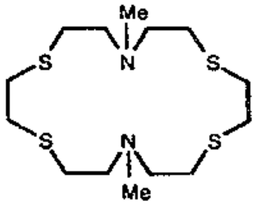


(120)

The complexation of copper(II) ions with 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (**121**) and its dimethyl derivative (**122**) has been investigated [89]. In the complex [Cu(**121**)][ClO_4] the Cu(II) ion is bound to all six macrocyclic donor atoms to give a tetragonally compressed octahedral complex with the ligand in a *fac* configuration. The introduction of the methyl substituents in (**122**) has resulted in the formation of a tetragonally elongated octahedral complex in a *meso* configuration. The effect of the methyl substituents is also seen in the electrochemical behaviour of the complexes. While $[Cu(\mathbf{121})]^{2+}$ shows a reversible Cu^{II}/Cu^{I} couple at $E_{1/2} = -0.31$ V *vs* the Fc/Fc$^+$ couple, that for [Cu(**122**)]$^{2+}$ occurs at a more anodic potential of $E_{1/2}$ at +0.06 V.

(121)



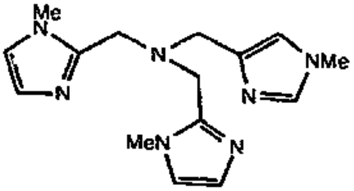


(122)

3.2. Mononuclear complexes with acyclic ligands

3.2.1. Nitrogen coordination

A study has been performed on new polyimidazole tripodal ligands as synthetic analogues of metalloprotein active sites known to contain multiple imidazole donor groups [90]. Both of the mixed imidazole ligands (**123**) and (**124**) stabilise the Cu(II) centres in complexes having distorted bipyramidal structures in which the imidazoles occupy the equatorial sites. In comparison to the Cu(II) complex of the analogous ligand containing only 2-substituted pendant groups (TMIMA) the visible-near-IR spectra of the Cu(II) complexes of the mixed imidazole complexes are shifted towards the blue region of the spectrum. This suggests that the ligand field strength of the tripods increase as the 2-substituted pendants are replaced by the 4-substituted pendants. Electrochemical analyses of the complexes show a cathodic shift in the Cu^{II}/Cu^{I} potentials relative to the complex of TMIMA which indicates that the tripodal ligands (**123**) and (**124**) are less able to stabilise the Cu(I) oxidation state.



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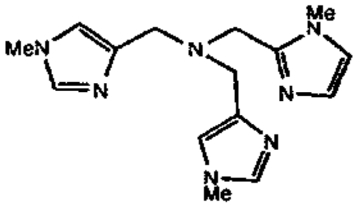
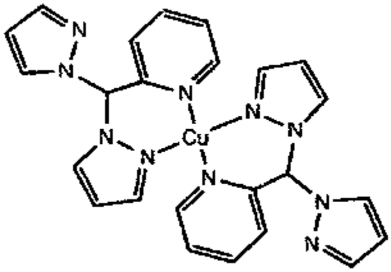


(124)

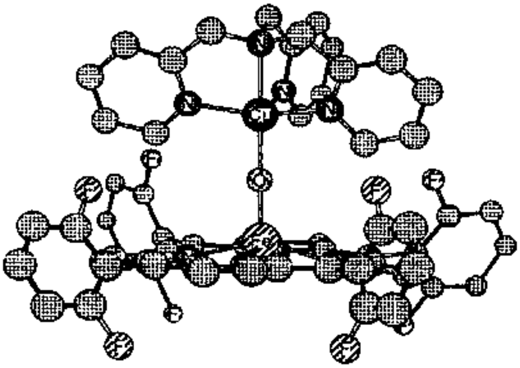
A series of metal complexes has been synthesised using the unsymmetrical tripodal *N*-donor ligand bis(pyrazol-1-yl)(pyridin-2-yl)methane [91]. The ligand produces a relatively strong ligand field consistent with the relatively short Cu-N bond lengths in (**125**). The study shows the pyridine group to be a slightly stronger σ donor than the pyrazine groups and with both acting as weak π donors.

A model compound for the Fe/Cu heterodinuclear centre in cytochrome *c* oxidase has been synthesised [92]. The solid state structure (**126**) shows an almost linear μ-oxo-bridging ligand with an Fe-O-Cu angle of 178.2(4)°. The metal-oxygen dis-



(125)

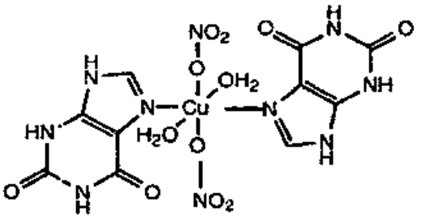
tances are unusually short with Fe-O = 1.740(5) Å and Cu-O = 1.856(5) Å resulting in the Cu···Fe separation being 3.596(2) Å. Mössbauer spectroscopy shows the structure has a high spin ferric ion and the observed magnetic properties demonstrate that the ferric ion is coupled to the cupric ion to form an overall integer spin system. Another study has demonstrated the importance of the tripodal ligand and bridging ligand in these systems [93]. In this case there is a tetradentate tripodal ligand (as opposed to the tridentate one in (**126**)) which results in a trigonal bipyramidal geometry compared to the square based pyramidal arrangement in (**126**). There is an almost linear Fe^{III}-C-N-Cu^{II} bridge and the iron centre remains low spin.



(126)

An investigation has been performed to determine the preferred site of coordination of the enzyme xanthine oxidase [94,95]. The copper(II) complexes of both xanthine and alloxanthine (an inhibitor of xanthine oxidase) show that the preferred coordination site is through N(9). Very similar crystal structures are obtained for the complexes (**127**) and (**128**) with the copper(II) ions in [4+2] elongated octahedral geometries with the equatorial sites occupied by two N(9) coordinated monodentate xanthine ligands and two water molecules in (**127**), and by two N(9) coordinated monodentate alloxanthine ligands and two water molecules in (**128**). In both structures the apical sites are occupied by oxygen atoms of nitrate ions.

The crystal structure of the copper(II) complex of 4,5-diazafluoren-9-one (**129**) has been reported [96]. This structure is claimed to be the first crystallographic example of $[Cu(NN)_2X_2]$ chromophores (where NN is a rigid didentate ligand and



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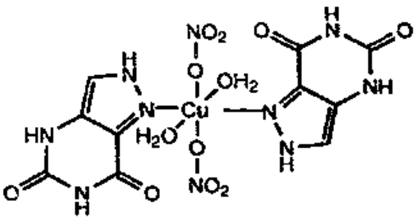
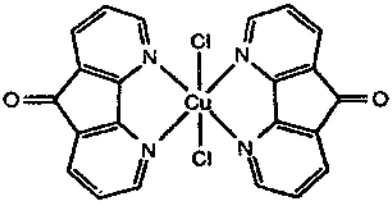
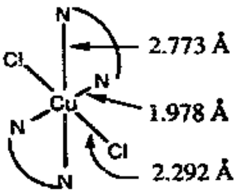


(128)

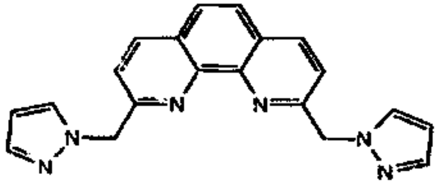
X is an ion) that has retained its octahedral coordination through *trans* ligation in spite of steric effects. Unlike all other reported [Cu(NN)$_2$X$_2$] complexes, (**129**) has a coplanar CuN$_4$ coordination in which the strain caused by the crowding of the hydrogen atoms adjacent to the nitrogen atoms is relieved by the lengthening of one pair of Cu-N bonds.



(**129**)

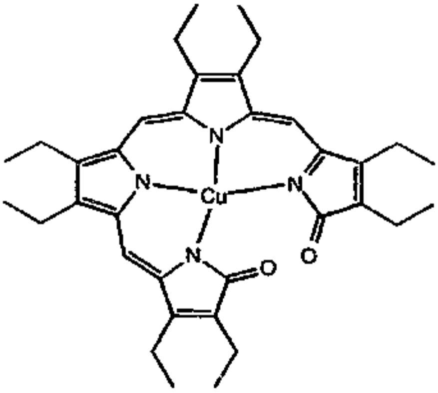


The novel ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (**130**) has been synthesised and its complexation behaviour with both Cu(I) and Cu(II) ions investigated [97]. The solid state structure of the Cu(II) complex shows the cation is 5-coordinate in a trigonal bipyramidal structure. The coordination sphere is comprised of two phen nitrogen atoms, two pyrazole nitrogen atoms and a water molecule. The complex shows a reversible CuII/CuI couple in its cyclic voltammogram with a potential of 0.037 V *vs* the Ag/AgCl couple.

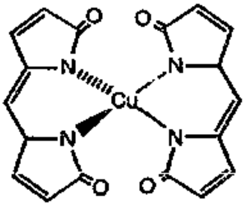


(**130**)

An analogue of the blue-green intermediate in heme catabolism *Biliverdin* has been synthesised [98]. In the copper(II) complex (**131**), the billindione ligand has a helical geometry which avoids any contact between the two keto groups, O···O = 3.154(4) Å. The IR spectrum shows two carbonyl stretches at 1665 and 1660 cm^{-1}. From spectroscopic evidence, the complex (**131**) is best formulated as containing a copper(II) centre and a tetrapyrrole radical anion. The complex is air sensitive and readily oxidises to (**132**).

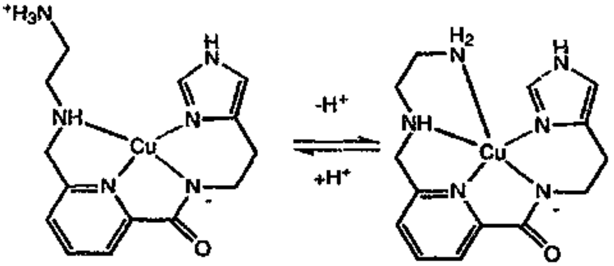


(131)



(132)

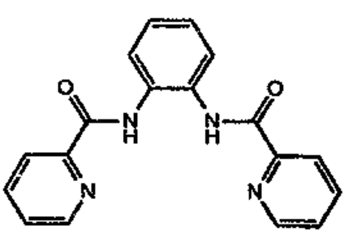
A study has been carried out on simplified mimic ligands for the anti-tumour drug bleomycin [99]. The structures of the copper(II) complexes have been shown to be acid dependent. At $pH < 5$, the complex has a 4-coordinate square planar geometry (**133**) in which one of the amide groups in the ligand is deprotonated and the terminal NH_2 group is protonated. At $pH > 6$, the copper(II) centre is 5-coordinate in a square pyramidal geometry (**134**) in which the terminal NH_3^+ group has been deprotonated and the NH_2 group binds axially to the copper centre.



(133) **(134)**

A study has been carried out to reveal the stereochemical changes around the Cu(II) centre caused by ligand-structure modification [100]. The ligands chosen for the study (**135**, **136**, **137**) all possessed two types of nitrogen donor atoms, i.e. pyridine and peptide units, and with the phenyl group in (**136**) and the trichloro-substituted phenyl ring in (**137**) expected to impose steric hindrance in their copper(II) complexes. The absorption spectra of $[Cu(\mathbf{136})]^{2+}$ and $[Cu(\mathbf{137})]^{2+}$ show the absorptions arising from the d-d transitions to be considerably red shifted compared to those of $[Cu(\mathbf{135})]^{2+}$. Also electrochemical studies have shown the

CuII/CuI couple to be substantially shifted to more positive values in $[Cu(\mathbf{136})]^{2+}$ and $[Cu(\mathbf{137})]^{2+}$. These spectroscopic data are explained in terms of the distortion of the $Cu\text{-}N_4$ unit caused by the imposed steric effects from the phenyl substituents.



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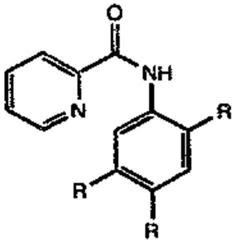
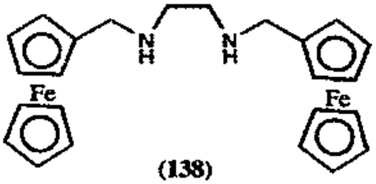


R = H, **(136)**; R = Cl, **(137)**

The copper(II) complex of a didentate ligand containing electroactive ferrocene units has been characterised [101]. The reaction of the ligand **(138)** with copper(II) ions resulted in the formation of the neutral complex $[Cu(\mathbf{138})_2(NO_3)_2].2CH_3OH$ in which the copper centre is in a distorted octahedral environment. The four equatorial sites are occupied by the nitrogen atoms of two ligand molecules and the apical sites filled with the oxygen atoms of weakly coordinating nitrate anions. Cyclic voltammetry has shown that the ferrocene groups all oxidise at the same potential. Hence this complex can be considered as a four electron reservoir with the potential capability of acting as a multi-electron mediator in redox catalytic reactions.

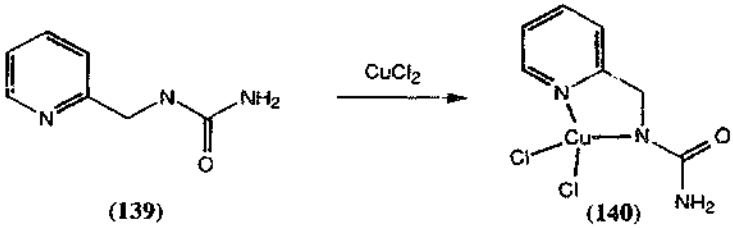


(138)

The crystal structures of Cu(II) complexes with urea derivatives have been reported wherein the metal coordinates through the nitrogen atom of the ligand rather than the more usual coordination through the oxygen atom [102]. The reaction of copper(II) chloride to **(139)** afforded a mononuclear complex with the metal centre in a distorted square geometry **(140)**. The ligand acts as a chelating ligand with the remaining two sites filled by chloride ions. The coordination of the ligand via the nitrogen atom has been shown not to be a consequence of an enforced geometry since the analogous zinc(II) complex shows the standard mode of complexation through the oxygen atom.

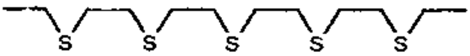
3.2.2. Sulfur coordination

An investigation has been carried out on the coordination of 3,6,9,12,15-pentathiaheptadecane **(141)** with copper(II) ions [103]. The coordination



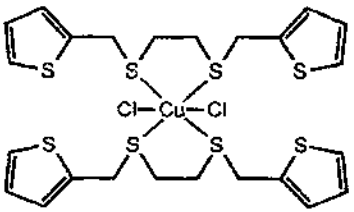
(139) **(140)**

sphere about the copper centre is a slightly distorted square based pyramid with all the sulfur atoms coordinating to the metal ion. The distortion is caused by the terminal sulfur atoms drooping ~20° below the plane of the pyramid. The cyclic voltammogram of the complex has revealed $E_{1/2}$ of 1.08 V *vs* NHE for the Cu^{II}/Cu^{I} couple which is reported to be the highest redox potential for the couple with exclusively thioether donors.



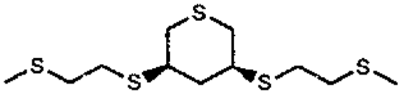
(141)

In a related study of the coordination of polythioether ligands with copper(II) ions, the effect of the introduction of thiophene units has been investigated [104]. The solid state structure of one of the complexes (**142**) shows an elongated octahedral coordination geometry, although 5-coordinate species are obtained when the ligand is extended to incorporate three thioether atoms or an oxygen atom. The complexes are shown to undergo significant structural changes upon being dissolved. The nature and extent of these changes depend on the solvent and the concentration of the solution. In poorly coordinating solvents (e.g. CH_2Cl_2) the ligand donor atoms may be displaced, but only if they are weakly bound, dimers may be cleaved and 5-coordinate species may become 6-coordinate. In more nucleophilic solvents (e.g. acetonitrile, DMF) dissociation of the Cu-Cl bond may occur, as may dissociation of the Cu-S and Cu-O bonds leading ultimately in dilute solutions of [CuCl.n(solvent)]$^-$ and free ligand.



(142)

A study has been performed on the formation of Cu(II) complexes with the non-macrocyclic pentathioethers (**143**) and (**144**) [105]. Both of the *cis*-disubstituted ligands function as pentadentate ligands and the solid state structures of the complexes $[Cu(\mathbf{143})(ClO_4)]^+$ and $[Cu(\mathbf{144})(BF_4)]^-$ have been determined. In $[Cu(\mathbf{143})(ClO_4)]^+$, the thiane ring adopts a chair conformation with the substituents axially disposed as expected. The Cu-S(thiane) bond (2.581(2) Å) is distinctly longer than the other Cu-S bonds (2.32-2.35 Å). The coordination sphere of the copper centre is completed by a weakly bound perchlorate ion. The situation in $[Cu(\mathbf{144})(BF_4)]^+$ is similar to that found in $[Cu(\mathbf{143})(ClO_4)]^-$, except that in this case there is a weakly bound tetrafluoroborate ion. Once again the ring-sulfur atom forms a longer bond to the Cu centre (2.510(2) Å) than the other four bonds (av 2.34 Å). The stability constants of the complexes show that (**144**) has a slightly greater affinity for Cu(II) ions than (**143**), but the value is still an order of magnitude less than that observed for pentathia[15]crown-5.



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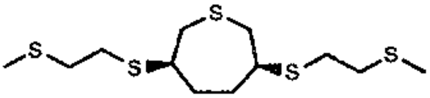
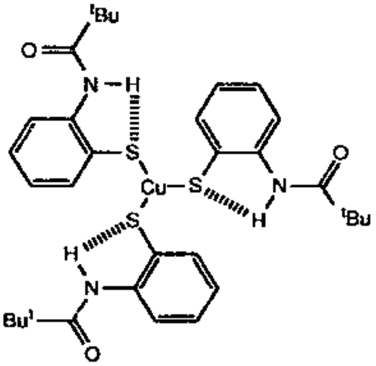


(144)

A model complex of the active site in blue copper proteins has been synthesised to incorporate NH···S hydrogen bonding interactions which have been suggested to occur between the S(cysteinate) units and an amide nitrogen atom of a peptide chain [106]. The crystal structure of the model complex (**145**) shows the copper(II) ion to lie in the plane of the three donor sulfur atoms with a mean distance of 1.227 Å and with the phenyl rings rotated at an angle of 33° relative to the trigonal plane. The IR spectrum shows significant S-H interaction to occur as evident from the NH stretching frequency at 3226 cm^{-1} compared to 3389 cm^{-1} for a free NH group.

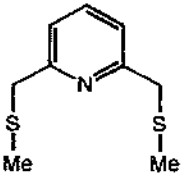


(145)

3.2.3. *Nitrogen and sulfur coordination*

A comparison has been made between the complexation behaviour of *S*-alkyl and *S*-aryl ligands [107]. The substitution of the *S*-methyl groups in

2,6-bis(thiomethyl)pyridine (**146**) by *S*-aryl groups, *e.g.* (**147**), has been found to markedly affect the physical and geometrical properties of the resulting copper complexes. Whereas the copper complexes of the *S*-alkyl ligands tend to be blue-green in colour, those of the *S*-aryl ligands tend to be red in colour. The CuII/CuI redox couple is found at higher voltages in the *S*-aryl complexes than for the *S*-alkyl complexes. This implies that the presence of the softer and more π-acidic *S*-aryl groups have an enhanced capacity for stabilising the low oxidation state.



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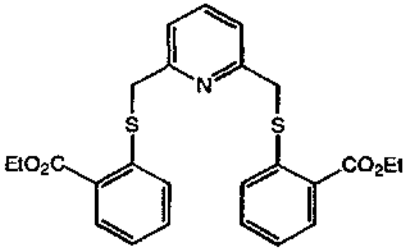

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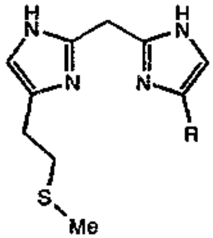


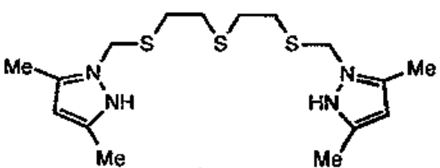
(148)

A study has been carried out aimed at modelling the active site of blue copper proteins [108]. The solid state structures of the copper(II) complexes of the polyimidazole-thioether ligands (**148**) have been characterised and all show the sulfur atom occupies one of the equatorial sites around the copper centre. This is in contrast to the situation in the blue copper proteins which have the sulfur atom in the apical position.

The acyclic pentadentate N_2S_3 donor ligands (**149**), (**150**) and (**151**) have been synthesised and their Cu(II) complexes characterised as the perchlorate, tetrafluoroborate and triflate salts [109,110]. The solid state structures of the perchlorate and triflate salts of (**151**), i.e. $[Cu(\mathbf{151})][ClO_4]_2$ and $[Cu(\mathbf{151})][CF_3SO_3]_2$, show only minor differences with the greatest difference in bond length being 0.053 Å and the greatest difference in angle being 5°. However, the electronic structures of the two complexes show significant differences which are indicated by their difference in colour. The perchlorate salt is deep blue while the triflate salt is bright green in colour. In weakly coordinating solvents the triflate salt becomes deep blue in colour. This investigation also demonstrates the sensitivity of the Cu^{II}/Cu^{I} redox to the subtle steric effects of the ligand.

3.2.4. *Nitrogen and oxygen coordination*

An investigation has been carried out to establish the structure and spectroscopic effects of phenolate donors in the enzyme galactose oxidase using monomeric copper(II) complexes containing phenolate and imidazole donor groups [111]. The mononuclear complexes of tri- and tetradentate tripodal ligands containing phenolic hydroxyl, benzimadozole and pyridine groups have been prepared. The EPR spectra of the complexes indicate that all the complexes have square pyramidal geometries and this was confirmed for the complex $[Cu(\mathbf{152})Cl].H_2O$ with the equatorial sites occupied by a tertiary amine, two pyridine nitrogens and a chloride ion. The axial site



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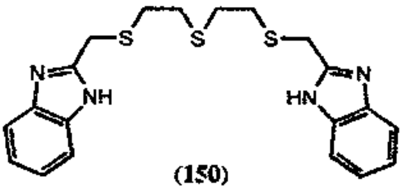

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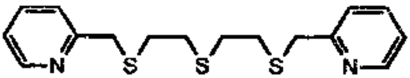
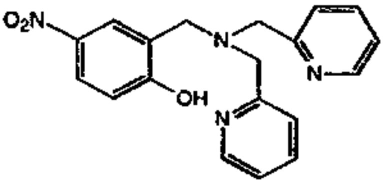


(151)

is occupied, unusually, by the phenolate ion. The spectral and electrochemical results of the study indicate the order of donor strength to be nitrophenolate < pyridine < benzimidazole in the tridentate complexes and nitrophenolate < benzimidazole < pyridine in the tetradentate ligand complexes.

A study has been undertaken to prepare copper monooxygenase models, particularly of dopamine β-hydroxylase [112]. These models have been used to achieve hydroxylation of aliphatic C-H bonds by dioxygen activation.



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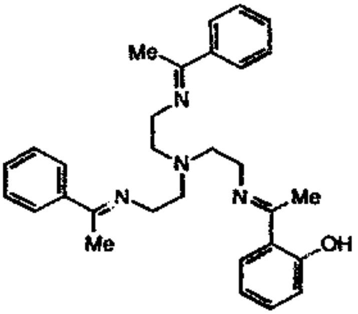
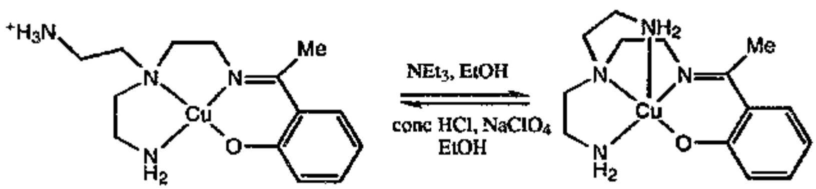


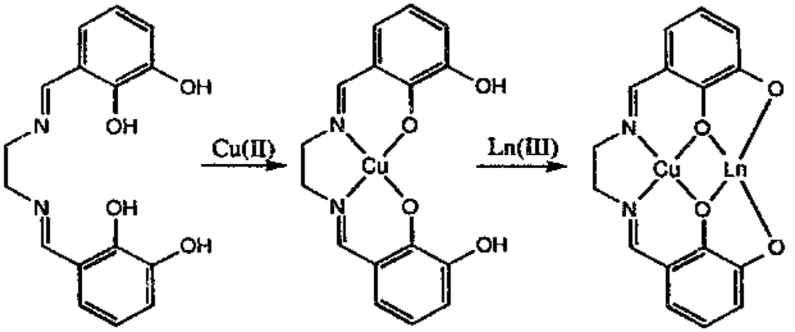
(153)

The complexation behaviour of the potentially heptadentate Schiff-base tripodal ligand (**153**), derived from tris(2-aminoethyl)amine and 2-hydroxyacetophenone, with Cu(II) ions has been carried out [113]. The reaction of (**153**) with $Cu(ClO_4)_2$ gave an intense green coloured solution from which red crystals of (**154**) deposited on cooling. The crystal structure of (**154**) showed that the ligand (**153**) had hydrolysed on complexation and its hydrolysed form existed in a Zwitter-ionic form with a near square planar environment for the Cu(II) ion. Under basic conditions, the pendant arm of (**154**) deprotonates to yield a green 5-coordinate complex (**155**) in which all the nitrogen atoms interact with the copper centre. This deprotonation is reversible and the addition of a molar equivalent of hydrochloric acid in the presence of perchlorate anions generates the red crystals of (**154**).



(154) **(155)**

The potentially hexadentate compartmental ligand (**156**), formed from the condensation of 2,3-dihydroxybenzaldehyde with ethylenediamine, has been used to form mononuclear complexes with Cu(II) (**157**) and Ni(II) ions [114]. The mononuclear complexes can, themselves, act as ligands leading to heterodinuclear complexes on reaction with a lanthanide salt (**158**).

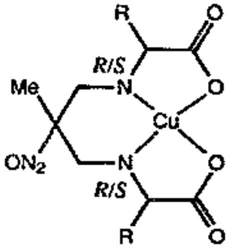


(156) **(157)** **(158)**

The Cu(II) directed condensation of amino acids with formaldehyde and nitromethane has resulted in the high yielding and stereoselective formation of the copper(II) complexes of open chain tetradentate ligands (**159**) [115,116]. With optically pure L-amino acids, full retention of configuration is achieved while a racemic mixture of amino acids gives only one of the three possible diastereoisomers (the *SR* isomer).

A study has been carried out to develop models for the metal site of phenylalanine hydroxylase based on pterin and pteridine derivatives [117]. The complex (**160**) shows the copper(II) centre to have an elongated octahedral coordination geometry in which the axial sites are filled by oxygen atoms of the 2-(ethylthio)-4-oxopteridine units and with the equatorial sites defined by four nitrogen atoms (two from two pteridine derivatives and two from the phen ligand).

A study of the cytotoxicity and antiviral properties of the ternary complexes of Cu(II) with substituted phenanthroline and salicylates has been carried out [118]. The most potently cytotoxic complexes were the ternary complexes [Cu(phen)X], where X = a salicylate derivative, which had cytotoxicities comparable with the anticancer drug cisplatin.



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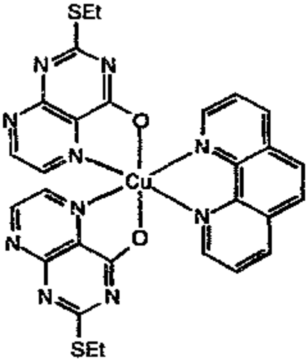

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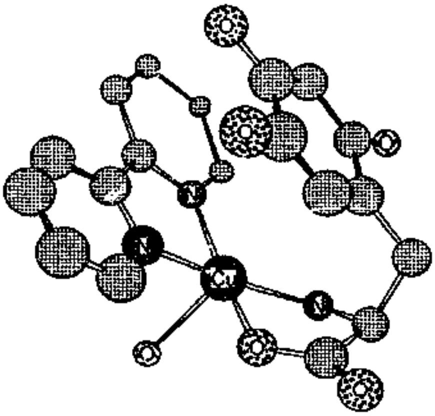
An investigation has been made to provide information about the functional relationships between non-blue copper proteins and the organic cofactor in copper-containing amine oxidases [119]. The solid state structure of [Cu(DL-topa)(bpy)(H_2O)][BF_4].3H_2O (**161**) (topa = 2-hydroxydopa) is claimed to be the first example of a topa-containing ternary copper(II) complex. The aromatic ring of the topa unit is intramolecularly stacked with the bpy unit, with the shortest distance being 3.308 Å. Extensive hydrogen bonding occurs between the three hydroxyl groups of the topa system and the water molecules in the crystal lattice. This complex (**161**) has been shown to catalyse the oxidation of benzylamine to benzaldehyde at room temperature in aqueous solution under aerobic conditions.

The effects of substitution on the complex formation have been studied for systems of the type [Cu(dmc)$_2$L] where Hdmc = 2,5-dimethoxycinnamic acid and L = phen, 2,9-dimephen or 4,7-dimephen [120]. The steric hindrance caused by the methyl groups in the 2 and 9 positions on the phen ring close to the site of coordination plays a fundamental role in the coordination behaviour of the ligands. This is shown by the complexes [Cu(dmc)$_2$(phen)] and [Cu(dmc)$_2$(4,7-dimephen)] having tetragonal geometries while [Cu(dmc)$_2$(2,9-dimephen)] (**162**) is 5-coordinate.

The reaction of [Cu(OMe)$_2$]$_n$ with a fluorinated alcohol in the presence of an



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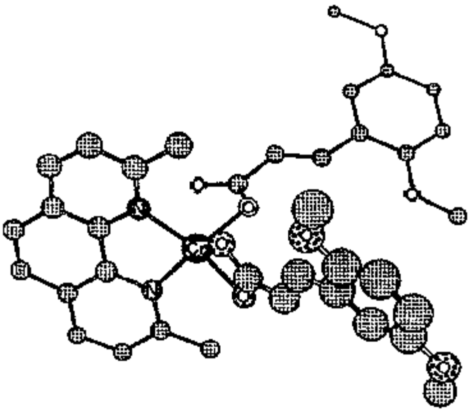
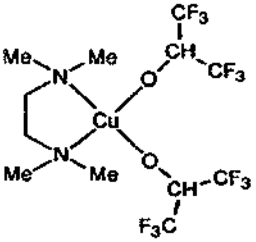


(162)

amine has been shown to produce copper(II) fluoroalkoxides, e.g. (**163**) [121]. These complexes are slow to hydrolyse and some are sufficiently volatile that they can serve as metal-organic chemical vapour decomposition (MOCVD) precursors to copper metal films at 300°C and 10^{-5} Torr. The deposited copper metal is non-crystalline and consists of granules having diameters of 0.1-0.4 μm.

An investigation has been carried out to consider the use of chelating sub-units in the synthesis of diradicals to provide a new type of molecular-based magnetic materials [122]. The system investigated has two *N*-oxyl radical units on either side of either a bpy or a phen unit. The solid state structure of the copper(II) complex (**164**) shows an octahedral copper centre with an almost coplanar bpy unit. This complex shows a strong antiferromagnetic coupling at low temperature.

The reaction of 1,2-dimethylimidazole and *N*-methylimidazole with tetrakis(ferrocenecarboxylato)dicopper(**II**) gives the *cis* (**165**) and *trans* (**166**) monomeric species respectively [123]. In both complexes the copper centres are in a square



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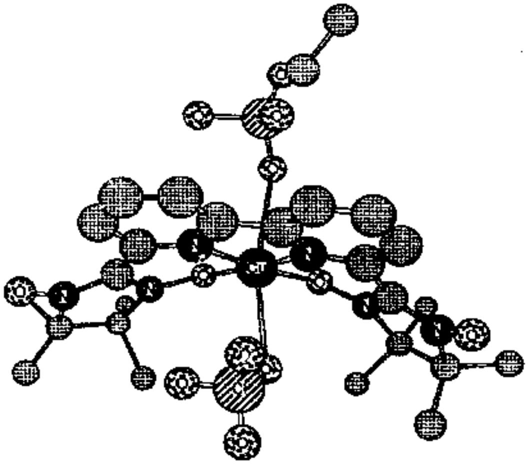


(164)

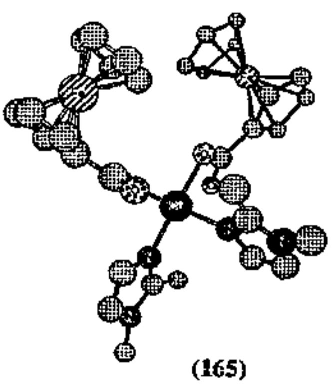
planar environment consisting of two imidazole nitrogen atoms and a carboxylate oxygen atom from each ferrocenecarboxylate ligand. The second oxygen atom of the carboxylate functionalities are involved in weak interactions with the copper centres. The η^5-C_5H_4 and η^5-C_5H_5 rings of the ferrocenyl moieties are nearly eclipsed in both complexes.

The solid state structures of (4(5)-methylimidazole)(7-amino-4-methyl-5-aza-3-hepten-2-onato(-1))metal(II) complexes where M = Cu and Zn have been reported [124]. Both structures correspond to the remote isomers, i.e. with the methyl substituent directed away from the metal ion. Very little of the adjacent isomer, i.e. where the methyl group is near the metal ion, is observed in the reaction.

3.3. Dinuclear complexes with macrocyclic ligands

3.3.1. Nitrogen coordination

The oxidation of the dinuclear Cu(I) complex of the cryptand (**167**) by silver ions has been investigated [125]. The silver ions not only oxidise the copper centres but also deprotonate the pyrrole NH groups. This is evident by the absence of any NH absorption bands in the IR spectrum. The solid state structure shows the two



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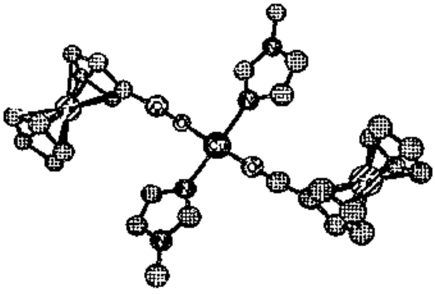

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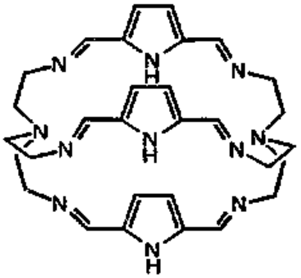
copper(II) centres to be non-equivalent, with one in a 4-coordinate distorted square planar environment and the other approximates towards a square pyramidal coordination mode. The Cu···Cu distance of 3.006 Å is claimed to be the shortest $Cu^{II}\cdots Cu^{II}$ contact unsupported by a bridge. The reaction of the macrobicyclic ligand (**168**) with $Cu(CF_3SO_3)_2$ has been shown to result in a dicopper(II) μ-hydroxo cryptate with the copper centres in identical trigonal bipyramidal environments with a linear Cu-O(H)-Cu bridge [126]. The complex exhibits virtual diamagnetism which arises from efficient antiferromagnetic exchange between the d_z^2 magnetic orbitals mediated via the $2p_z$ orbital of the bridge.



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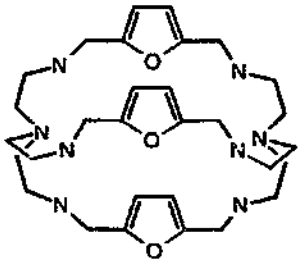

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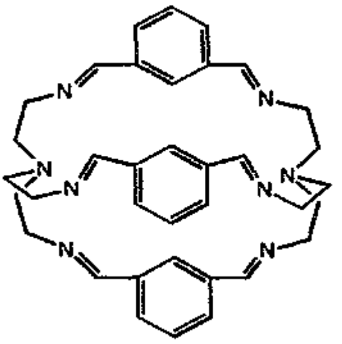
The dicopper(II) complex of the octaazamacrobicyclic ligand (**169**) containing two tris(2-aminoethyl)amine moieties bridged by three *m*-xylyl groups has been synthesised in a copper(II) templated reaction [127].

An investigation into the synthesis of mimics of the hydrolytic enzyme urease has been carried out [128]. Four new dinuclear macrocyclic complexes have been synthesised by a novel template reaction and the structure of the dicopper(II) complex with a bridging imidazolate group (**170**) determined. The synthesis takes advantage of the propensity for Cu(II) (and Ni(II)) to form complexes with imidazolates. The Cu···Cu separation in (**170**) is 5.92 Å. ESR and magnetic measurements show the complex to have antiferromagnetic coupling between the copper centres.



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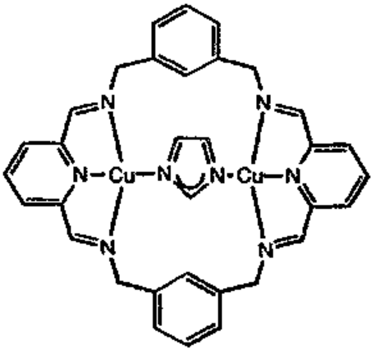

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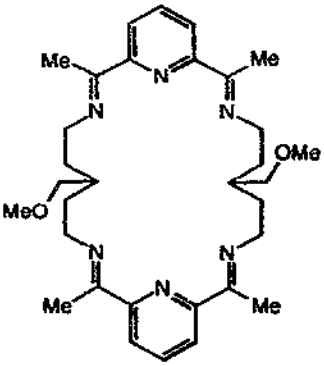

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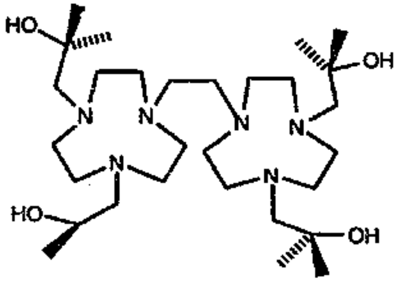
Transmetallation of the barium complex of the bibracchial tetraimine Schiff base macrocycle (**171**) derived from the condensation of 2,6-diacetylpyridine with *N*,*N*-bis(2-aminoethyl)-2-methoxyethylamine with copper(II) ions has been carried out [129]. The resulting homodinuclear complex has the copper(II) ions held by the "head" units of the macrocycle at a separation of 5.56 Å. Compared to the folded cleft-like structure of the mononuclear barium complex, an opening of the cleft has occurred to accommodate the two copper centres.

The coordination of the ligand (**172**) with copper(II) ions has been shown to occur with the deprotonation of two of the pendant hydroxyl groups on each macrocyclic ring to form O···H···O bridges between the two halves of the dinucleating ligand [130]. The complex adopts a *syn*-configuration in which the two encapsulated copper(II) centres lie on the same side of the ligand in distorted square based pyramidal geometries (**173**).

A study has been carried out to synthesise model systems of the photosynthetic reaction centre [131,132]. The low valent titanium induced reductive coupling of Cu(II) 5-formyl-octaethylporphyrin (**174**) has led to the formation of ethene-bridged



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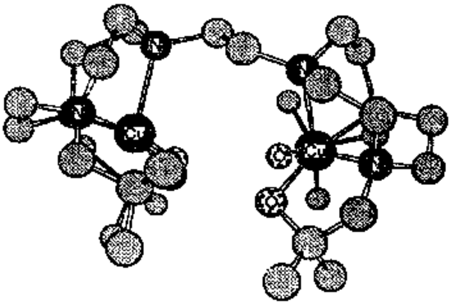
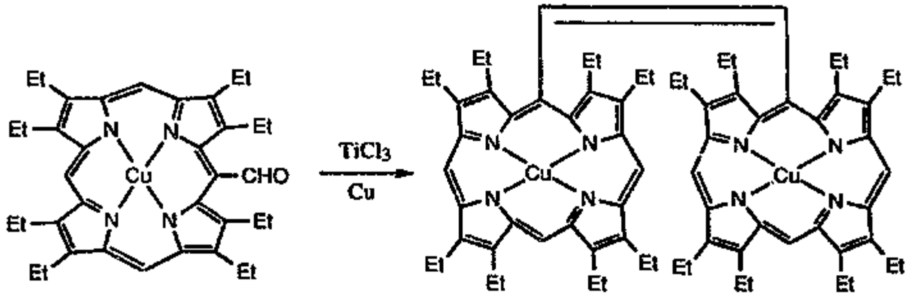


(173)

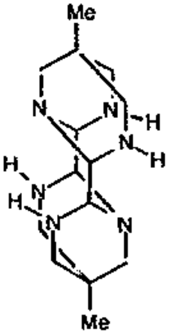
bisporphyrins. The main product from the coupling reaction is the *cis* isomer **(175)** which is in contrast to other reported couplings of aldehydes and ketones which usually lead to the *trans* product. The *cis* isomer can undergo an acid catalysed isomerisation to the *trans* isomer, which is also formed as a minor product in the coupling reaction. The preferential formation of the *cis* ethene-bridged bisporphyrins **(175)** is attributed to the strong aggregation properties of metalloporphyrins. This is evident in the solid state structure of **(175)** which shows a cofacial macrocyclic arrangement with almost coplanar macrocycles separated by 3.36 Å which results in considerable overlap of the π-systems.



(174) **(175)**

The reaction of the hinged macrocycle **(176)** with $CuCl_2$ has been investigated [133]. The dinuclear copper(II) complex **(177)** has a cage-like structure in a staggered arrangement in which the two trigonal bipyramidal copper centres are non-equivalent.

The biscopper(II) complex **(178)** of the naturally occurring cyclic peptide ascidiacyclamide isolated from the *ascidian Lissoclinium patella* has been characterised by X-ray crystallography [134]. The geometry around one copper centre is a distorted square pyramid being coordinated to three nitrogen atoms (one each from an oxazoline, thiazole and deprotonated amide) and with a water molecule and the oxygen of a bridging carbonate anion completing the coordination sphere. The other Cu(II) ion exhibits a similar coordination geometry but with an added distant Cu-O



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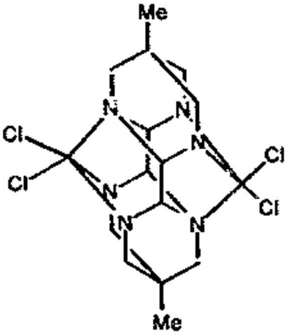
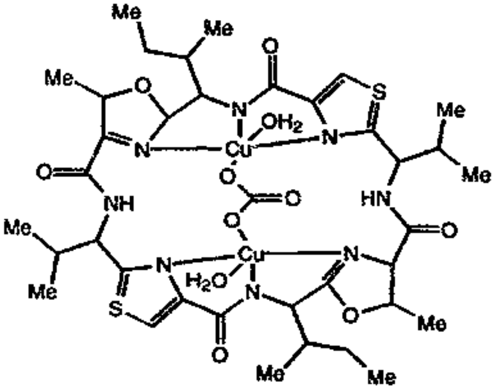


(177)

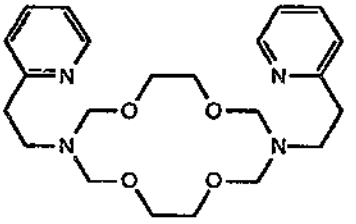
interaction making up a distorted octahedral environment. The Cu···Cu separation is 4.43 Å and magnetic susceptibility measurements show a weak ferromagnetic coupling to exist ($2J = +1.6 \pm 0.4$ cm^{-1}).



(178)

3.3.2. Nitrogen and oxygen coordination

The synthesis of pyridine-crown ether ligands and their complexation with metal ions have been studied [135]. The ligand **(179)** was synthesised by the high pressure addition of vinyl pyridine to diaza-18-crown-6. The addition of $Cu(ClO_4)_2$ to a solution of the ligand resulted in the co-precipitation of $[Cu_2(OH)(\mathbf{179})]^{3+}$ and the bisprotonated ligand. Protonation of the ligand has been shown to occur at the amine nitrogen of the crown with each proton forming a trifurcated hydrogen bond with two crown ether oxygen atoms and a pyridine nitrogen atom. In the dinuclear copper(II) complex the two copper centres are bridged by a hydroxide bridge resulting in the Cu(II) ions having 5-coordinate trigonal bipyramidal geometries.



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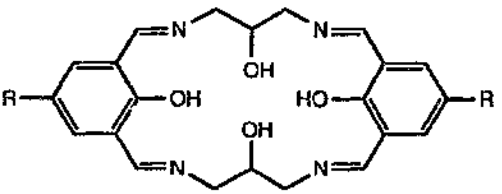
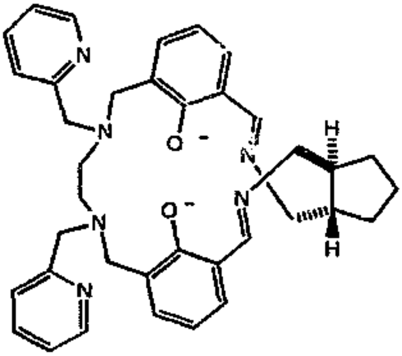


(180)

The template condensation of 2,6-diformyl-4-R-phenols with 1,3-diamino-2-hydroxypropane in the presence of Cu(II) salts has been investigated [136]. This has led to the isolation of six dinuclear complexes of the general formula $[Cu_2(\mathbf{180})]^{2+}$. It has been demonstrated that the template reaction produces only dinuclear phenoxide-bridged macrocyclic complexes in which the secondary alcohol groups do not coordinate to the copper centres. The inability to form tetranuclear complexes is viewed as a consequence of the small macrocyclic ring size.

An investigation has been carried out to discover a way of controlling the stereochemistry in a dimetallic complex [137]. The incorporation of the chiral diamine in the ligand **(181)** enforces the formation of a single diastereomer of the metal complexes. Complexes of formulation $[M(\mathbf{181})(H^+)_2]^{2+}$ and $[M(\mathbf{181})Cu]^{3+}$ have been studied.

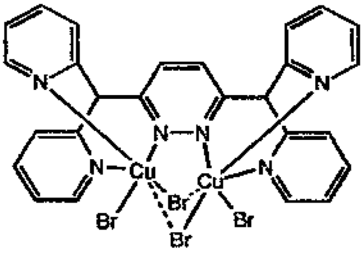


(181)

3.4. Dinuclear complexes with acyclic ligands

3.4.1. Nitrogen coordination

The dinuclear copper(II) complex of the hexadentate ligand 3,6-bis(di-2-pyridylmethyl)pyridazine has been characterised [138]. The solid state structure shows the two copper centres are in distorted octahedral environments with each linked to two pyridine nitrogen atoms, a nitrogen atom of the diazine bridge and with the coordination sphere completed by two halide ions (**182**). This complex shows only a small coupling interaction between the copper centre which suggests that the diazine bridge is not an efficient transmitter of magnetic interaction in this ligand.



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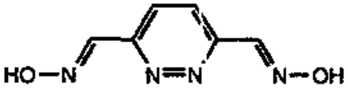

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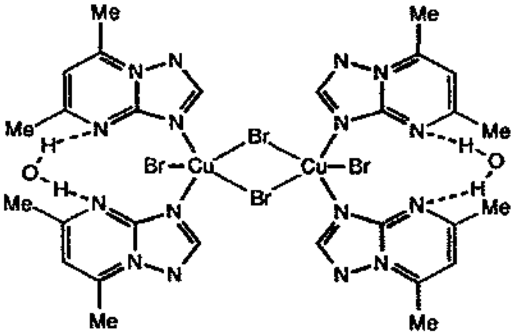
Another study of the complexation of copper(II) ions with a ligand containing a diazine unit has been carried out in which it is incorporated into an essentially planar tetradentate ligand (**183**) [139]. The two copper ions are each coordinated to a diazine nitrogen of two ligands and to an oxime nitrogen atom of two ligands. Two intra-complex hydrogen bonds link the terminal oximator moieties to give dinucleating macrocyclic complexes. An antiferromagnetic coupling of $J = -536\ \mathrm{cm}^{-1}$ is observed in the complex.

The solid state structure of the dimeric copper(II) complex of 5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine (dmtp) has been determined [140]. The structure consists of dimeric molecules of $[\mathrm{Cu(dmtp)_2Br_2}]_2$ in which the copper centres are bridged by bromine ligands (**184**) at a separation of 3.603(3) Å. Magnetic susceptibility measurements indicate an antiferromagnetic coupling with a singlet-triplet separation of $\sim 20\ \mathrm{cm}^{-1}$.



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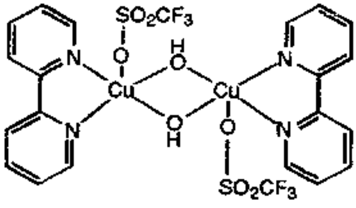
The complexation of copper(I) ions with bipyridine and bipyrimidine has been studied [141,142]. Both complexes are di-μ-hydroxo copper(II) dimers (**185**) and (**186**) and show ferromagnetic coupling between the copper centres.



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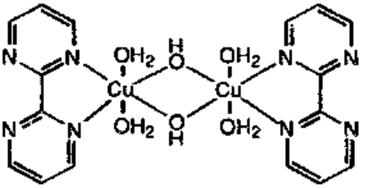

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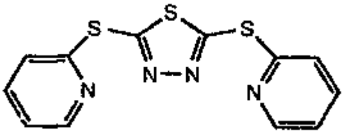
A series of dinuclear μ_2-1,1-azido bridged Cu(II) complexes have been characterised [143–146]. The tetradentate ligands (**187**) and (**188**) react with copper(II) ions to form the complexes $[Cu_2(\mathbf{187})(\mu\text{-}X)_2X_2]$, where X = Br or Cl and $\{[Cu_2(\mathbf{188})(\mu\text{-}Cl)_2Cl_2].2CH_3OH.0.5CH_3CN\}$. The tetrahalide dinuclear Cu(II) complexes of (**187**) involve a triple-bridge arrangement between the copper centres which are only weakly antiferromagnetically coupled ($-2J = 34\text{-}60\ cm^{-1}$). The main superexchange pathway is the diazine bridge. The complex formed with (**188**) is relatively unstable. The coordination of copper(II) ions with the tetradentate phthalazine derivative (**189**) has also been investigated. The ligand acts as in a typical tetradentate N_4 diazine mode forming the complexes $[Cu_2(\mathbf{189})X_4]$ where X = Br, Cl and $[Cu_2(\mathbf{189})(\mu_2\text{-}OH)(NO_3)_2(H_2O)_2][NO_3]$. The two copper centres are antiferromagnetic coupled. In contrast, the dinuclear, triply bridged Cu(II) complex of (**190**) involving end-on μ_2-1,1-azido, μ_2-bromo and μ_2-1,2-thiadazole bridges shows a strong ferromagnetic coupling between the adjacent copper centres (Cu···Cu = 3.138 Å). This feature is present only in a very limited number of copper(II) complexes.



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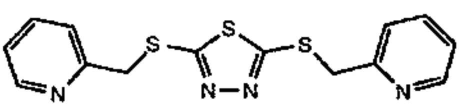

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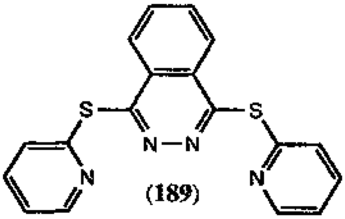

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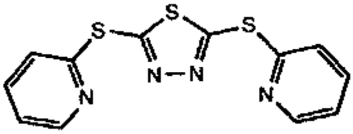
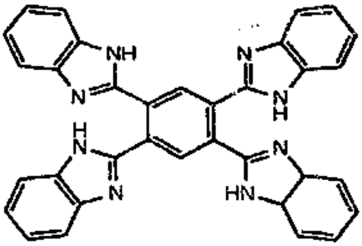
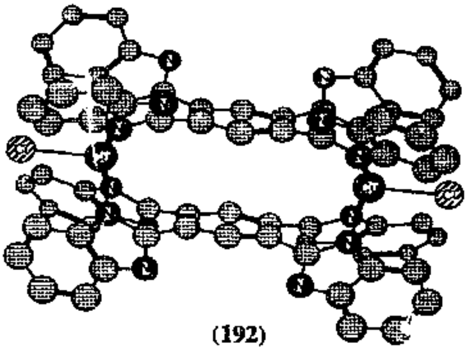


(190)

A study has shown that 1,2,4,5-tetrakis(benzimidazol-2-yl)benzene (**191**) acts as a tetradentate dinucleating ligand and reacts with copper(II) salts to form either a 2:1 or a 2:2 (Cu:(**191**)) derivative depending on the reaction conditions [147]. The reaction of (**191**) with a large excess of Cu(II) ions produced "open" 2:1 derivatives which rearranged and disproportionated on recrystallisation to form the 2:2 "closed" metallocyclic complexes. When a copper halide salt was used a mixture of both the 2:1 and 2:2 complexes was formed. The solid state structure of the 2:2 complex $[Cu_2(\mathbf{191})_2Cl_2]^{2+}$ (**192**) shows the two metals and two ligands create a large empty cavity with the central benzene rings eclipsed and coplanar, separated by a distance of 3.529(9) Å. The metal centres are slightly closer in (**192**) than in the 2:1 complex, 8.082(3) Å compared with 8.805(3) Å.

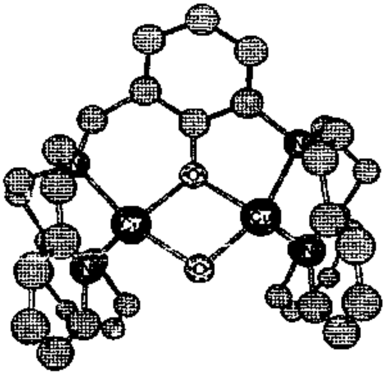


(**191**)



(**192**)

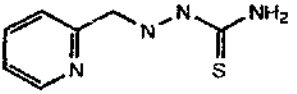
A study has been undertaken to synthesise a species containing unsymmetrically disposed dicopper ion centres as a model of a metalloenzyme [148]. The dicopper(II) species is formed by the room temperature oxidation of the corresponding dicopper(I) species. In the dicopper(II) complex (**193**) the two copper centres are bridged by a phenoxide and a hydroxo group.



(**193**)

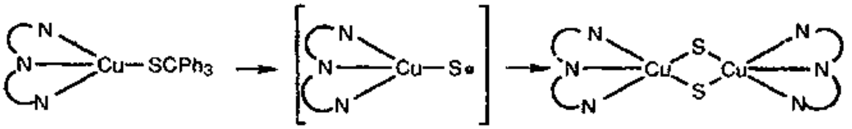
3.4.2. *Nitrogen and sulfur coordination*

A study of the reaction of pyridine-2-carbaldehyde thiosemicarbazole (**194**) with copper(II) halides has led to the isolation of the complexes $[Cu(\mathbf{194})X_2]$ where X = Cl or Br [149]. The copper centres have square pyramidal environments with each ligand acting in a tridentate fashion and the halide ions occupying the equatorial sites. The sulfur atom of (**194**) is in a bridging site occupying the apical position in the coordination sphere of the second copper centre. Magnetic susceptibility measurements show an antiferromagnetic coupling between the copper ions mediated through the sulfur bridges.



(**194**)

In the search for a model of the active site of blue copper proteins the mononuclear copper complex $[Cu(SCPh_3)\{HB(3,5\text{-}Pr^ipz)_3\}]$ (**195**), where $\{HB(3,5\text{-}Pr^ipz)_3\}$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate, was synthesised [150]. However the blue thiolatocopper(II) complex was observed to undergo a spontaneous decomposition by the homolytic fission of the copper sulfur bond to form a deep red-brown μ-η^2:η^2 disulfide dinuclear Cu(II) complex (**196**). The driving force for the formation of (**196**) is attributed to the preference for Cu(II) to adopt a 5-coordinate geometry relative to a tetrahedral geometry.



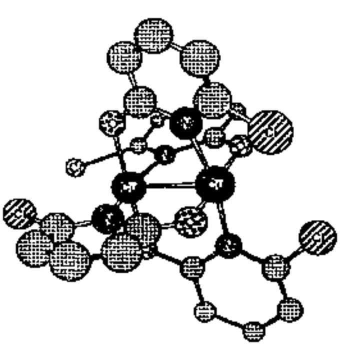
(**195**) (**196**)

3.4.3. Nitrogen and oxygen coordination

The reaction of the anion of 6-chloro-2-pyridone with copper(II) ions has been investigated [151]. A dichloromethane solution of the resulting dinuclear complex (**197**) was found to be EPR silent indicating that there is a strong interaction between the metal centres. The addition of donor solvents to the solution of (**197**) resulted in a dissociation of the dimeric complex which was evident by a colour change from red to green. The reaction of (**197**) with bpy afforded the dinuclear complex (**198**) in which a bpy unit replaces two pyridone molecules [152]. Despite the fact that the pyridone unit remains deprotonated, the ring nitrogen atoms are not involved in the coordination to the copper centres, nor are they involved in hydrogen bonding.

A study of the reaction of copper(II) chloride with 2,2-dipyridine-*N*,*N'*-dioxide has demonstrated that the reaction product is dependent upon the reaction conditions [153]. Two of the products, one green (**199**) and the other yellow-orange (**200**) in colour, have been characterised by X-ray crystallography. The two complexes are isomeric and differ in the bridging units between the two copper centres: in the green complex two chlorine atoms bridge the copper centres while in the other complex the bridging atoms are oxygen atoms of the ligands.

The solid state structure of the copper(II) complex of 2-(2-hydroxyphenyl)-1,10-phenanthroline (HL) has been determined [154]. The structure (**201**) consists of two [CuL] units in which the ligands are near planar. The two



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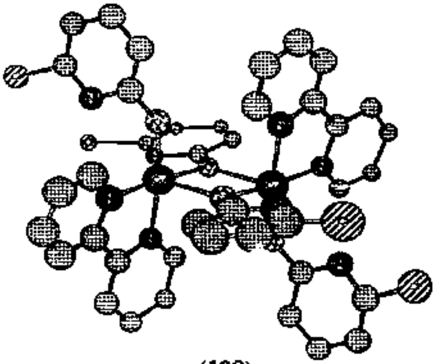

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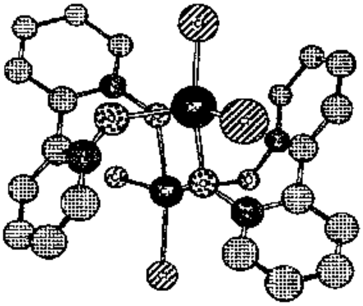

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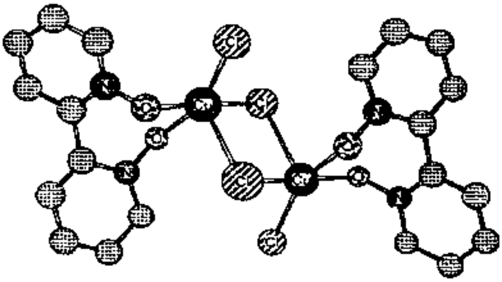
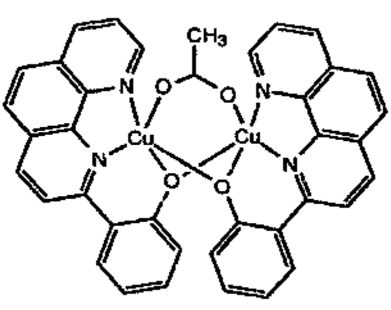


(200)

ligand units are stacked side-by-side such that the phenolate groups can coordinate to both copper centres resulting in $Cu_2(\mu\text{-}O)_2$ cores, with an additional bridging μ-acetato ligand. The rather long apical Cu-O (bridging phenolate) bonds (2.449 Å) arise from Jahn-Teller distortions.



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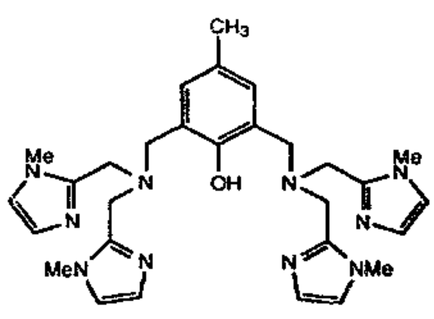
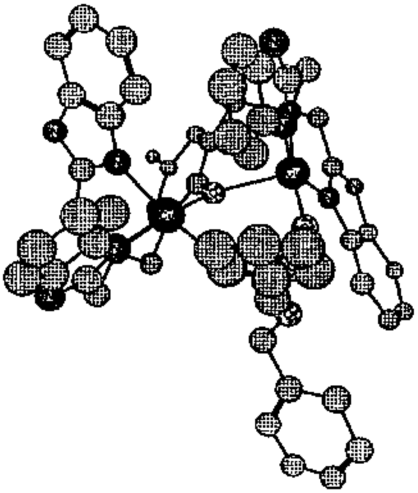


(202)

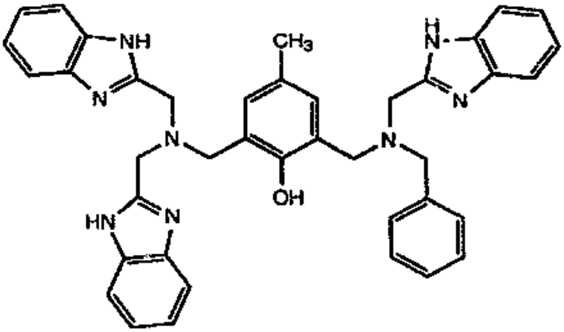
An investigation has been carried out into the synthesis of dinuclear complexes containing histidyl imidazole functionalities as analogues of the ligating sites of complex metalloproteins [155]. The complexation of the dinucleating polyimidazole ligand (**202**) with copper(II) ions was found to form both "open" and "closed" dinuclear complexes. The solid state structure of the "open" type complex, $[Cu_2(\mathbf{202}\text{-H})(CH_3OH)_2][ClO_4]_3$, shows the Cu(II) ions are pentaacoordinate, coordinated to two imidazole nitrogen atoms, a tertiary amine nitrogen atom, a methanol oxygen atom and the bridging phenolate ion. The Cu-O-Cu angle is 142.9° and the Cu···Cu distance is 4.090 Å. In contrast, the Cu-O-Cu angle and the Cu···Cu distance in the "closed" type structure $[Cu_2(\mathbf{202}\text{-H})(OCH_3)][ClO_4]$ were determined as 98.7° and 3.026 Å, respectively. An analogue of a dimetallic enzyme capable of hydrolysing phosphate diester groups has been investigated [156]. The dinuclear complex (**203**) has been found to be more reactive in cleaving a simple RNA/DNA model than its mononuclear analogue. The crystal structure of the complex shows a Cu···Cu separation of 3.67 Å which is comparable to that found in 3′,5′-exonuclease (3.8 Å) and in HIV RNaseH (4 Å).



(**203**)

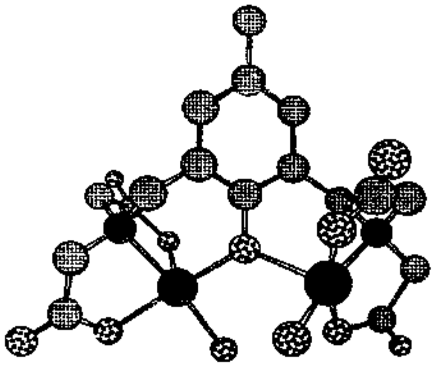
The dinuclear copper(II) complex of the asymmetrical dinucleating ligand (**204**) has been synthesised as a model for metalloproteins that contain asymmetry at their active sites [157]. The solid state structure of the complex shows the presence of bridging chloro and phenolate ligands which are located unsymmetrically between the two copper centres.

A model system for metalloproteins having carboxylate-rich coordination sites has been characterised [158]. The dinucleating ligand *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylene)bis(*N*-carboxymethylglycine) has been used to synthesise the dinuclear Cu(II) diaqua complex (**205**). The two square pyramidal copper centres are each coordinated to two carboxylate oxygen atoms, one amine nitrogen atom,



(204)

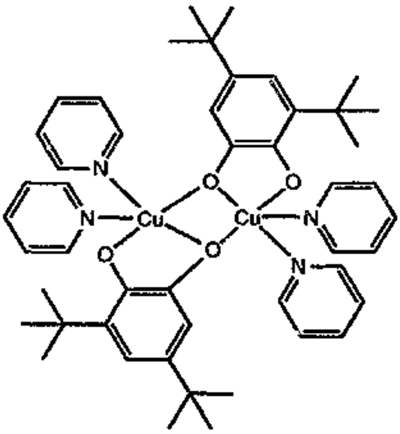
the bridging phenoxylate ion and a water molecule. Magnetic susceptibility data show very little coupling between the two metal centres.



(205)

A study of the reactions of 3,5-di-*tert*-butyl-1,2-benzoquinone with copper metal has been carried out with the aim of synthesising complexes that combine the redox activity of a transition metal with that of an electroactive organic ligand [159]. The reaction of the ligand with copper metal in pyridine enabled the dinuclear complex (**206**) to be isolated. The addition of triphenylphosphine has been shown to result in the formation of a mixed oxidation state species which EPR measurements indicate is a radical-based magnetic centre. This has been explained in terms of electron transfer from the catechol unit to the Cu(II) centre. The same structural core has been found in $[Cu_2(py)_4(OCH_2CO_2)_2].(CH_2OH)_2$, formed in the aerial oxidation of ethane-1,2-diol in the presence of copper metal and pyridine and room temperature and atmospheric pressure [160].

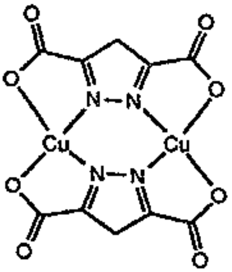
The coordination of 3,5-pyrazoledicarboxylic acid to metal ions capable of sustaining a square planar geometry has been studied [161]. The reaction with $Cu(NO_3)_2$ in the presence of tetrabutylammonium hydroxide afforded a dinuclear complex (**207**) with a Cu···Cu separation of 3.99 Å which allows for significant magnetic coupling between the two centres. Another example of the coordination

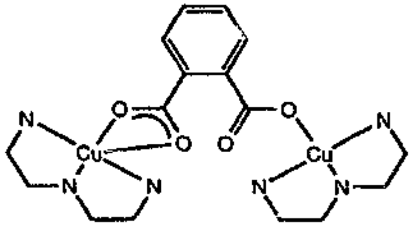


(206)

of copper(II) ions to a bis-deprotonated dicarboxylic acid has been reported [162]. In this case the Cu(II) ions are non-equivalent due to the dianion of phthalic acid coordinating in both a unidentate and didentate fashion (**208**). The coordination spheres of both metal centres is completed by the nitrogen atoms of diethylamine.

(207)

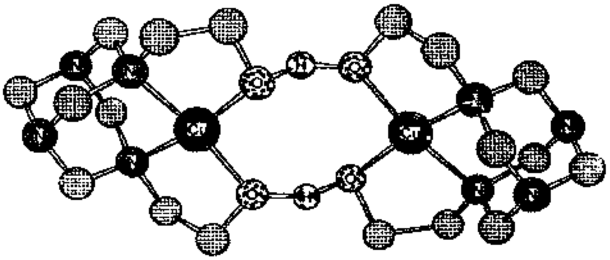




(208)

An investigation has been performed into the formation of dinuclear complexes through cooperative hydrogen bonding [163]. The condensation of the Cu(II) complex of 2-aminoethanol resulted in the formation of (**209**) in which two hydrogen bonds hold the two ligand units together. The Cu···Cu separation of 4.555 Å is claimed to be the shortest distance observed in hydrogen-bonded Cu(II) dimers. The bicyclononane ligand is shown to exert a very strong ligand field effect as evident by the *d-d* transition occurring at a very low wavelength (583 nm) and shows a very small magnetic coupling between the two metal centres.

A study has been carried out to determine the magnetic susceptibility measurements between two copper(II) centres separated by a linearly-coordinated organic unit [164,165]. The neutral complexes examined have been assembled using the anion of bis(2-pyridylcarbonyl)amide as the end-cap unit which coordinates to the Cu(II) ion through its three nitrogen atoms and the dianion of an organic ligand which coordinates in either a didentate (**210**) or bisdidentate mode (**211**). In both



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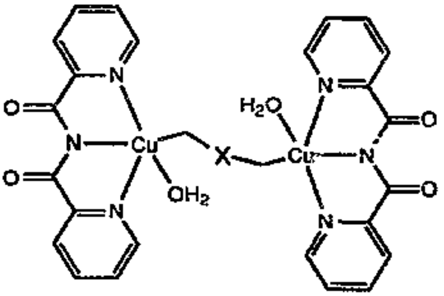
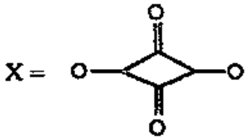
cases, only a very weak, but significant, exchange interaction is observed between the two copper centres.





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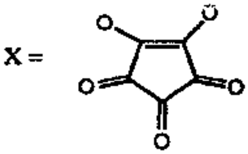
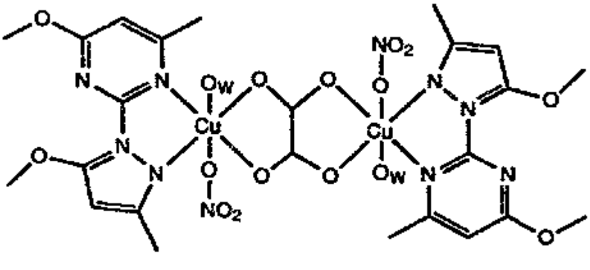


(211)

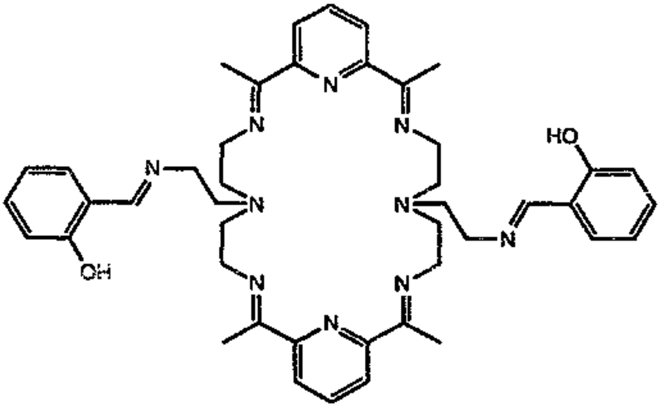
The structure of a new μ-oxalato dinuclear Cu(II) complex **(212)** has been reported [166]. The complex is not centrosymmetric and the difference in the ligand environments around the copper(II) centres induces an energy separation between the magnetic orbitals which is large enough to weaken the antiferromagnetic interaction by ~60 cm^{-1} ($J = -142\ \mathrm{cm}^{-1}$) compared to that of symmetrical μ-oxalato dinuclear complexes.



(212)

3.5. Trinuclear complexes

A prototype for the Type 3 copper oxidase site has been synthesised [167,168]. Transmetallation of the disilver complex of the macrocycle (**213**) using copper(II) ions resulted in the formation of the trinuclear complex $[Cu_3(OH)(\mathbf{213})(OH_2)][ClO_4]_3$. The solid state structure shows the complex to consist of a triangular cluster of copper(II) ions held within the ligand perimeter. Furthermore the cluster is comprised of one Type 2 and two Type 3 copper centres. The Type 3 copper centres are 3.6 Å apart and bridged by a hydroxyl group and are 4.9 and 5.9 Å away from the Type 2 centre. Magnetic susceptibility measurements show an antiferromagnetically coupled pair of Cu(II) ions ($2J = -202\ cm^{-1}$) and one magnetically independent Cu(II) centre.

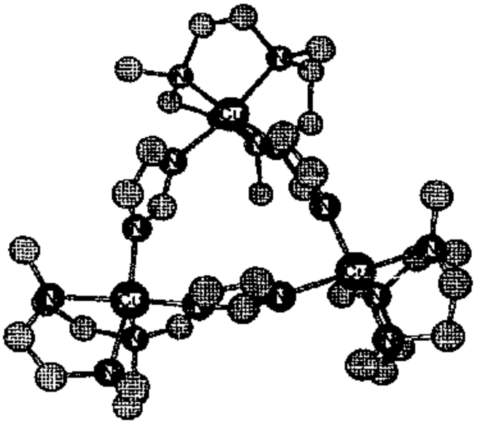


(213)

Another study has also sought to investigate the properties of a trinuclear copper cluster as a mimic for copper oxidases [169]. The reaction of $Cu(MeCO_2)_2.H_2O$, 1,4,7-triazacyclononane and imidazole enabled the isolation of the blue trinuclear complex (**214**). The copper centres are all equidistant at 5.92 Å, larger than the Cu···Cu separation in ascorbate oxidase (~3.9 Å). This complex is also reported to show spin frustration, *i.e.* when the exchange interaction between two of the copper centres is antiferromagnetic in nature, then the third copper centre simultaneously senses parallel and antiparallel spins.

A trinuclear copper(II) complex containing a 1,2,4-triazole bridging unit has been synthesised as a model for superoxide dismutase [170]. The crystal structure of the complex (**215**) shows the Cu(II) ions to be linearly aligned with the copper(II) centres bridged by two triazole units coordinating via two nitrogen atoms and by an asymmetric chloride ion giving a Cu···Cu distance of 3.568 Å. The antiferromagnetic coupling between adjacent copper centres was determined to be $J = -16.9\ cm^{-1}$.

A series of trinuclear complexes incorporating the [1,3-propanediylbis(oxamato)] cuprate(II) complex as a bridging unit between two terminal complexes (**216**) have been investigated [171]. The solid state structures of the complexes show the Cu···Cu



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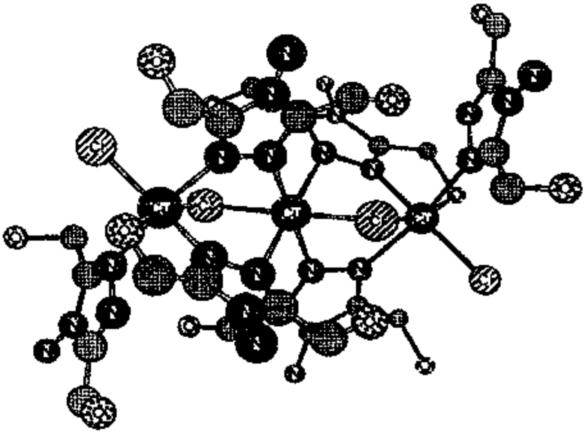
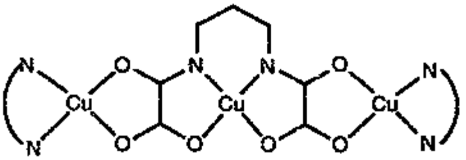


(215)

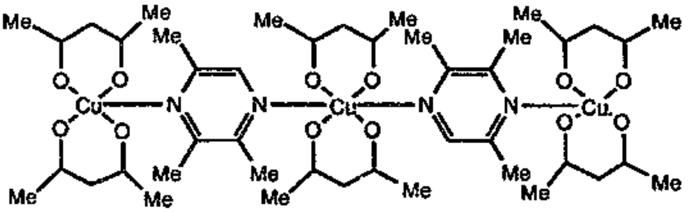
distances to be nearly the same (5.1–5.3 Å), but that the magnitudes of the magnetic interactions vary over a large range (J = -400 to -80 cm^{-1}). The results of this study demonstrate that by choosing the appropriate terminal ligands it is possible to tune the exchange interaction between the Cu(II) ions within the trinuclear complexes. This stresses the fact that the mechanism of the exchange interaction is governed by the magnitude of the overlap between the metal orbitals, with the Cu···Cu separation being only a secondary parameter.

The reactions of [Cu(hfac)$_2$] (hfac = 1,1,1,5,5,5,-hexafluoropentane-2,4,-dione) with diazines has been investigated and a range of complexes from monomeric to polymeric characterised [172]. The reaction of [Cu(hfac)$_2$] and 2,3,5-trimethylpyrazine gave a trinuclear complex **(217)** that was characterised by X-ray crystallography. Adjacent copper centres are bridged by a pyrazine ligand resulting in a separation of 7.280(3) Å. The environment around the N(4) centre is more



(216)

crowded than around the N(1) atom on account of the extra methyl group. This results in large N(4)-Cu-O angles of 135.0 and 135.6° and an unusually low O-Cu-O angle of 89.4°.



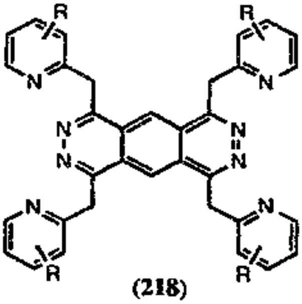
(217)

An investigation of the magnetic interactions between Cu(II) centres and imino nitroxide free radicals has been carried out [173]. The X-ray structure of one of the complexes has been determined and shows a trinuclear complex in which the metal centres are linked by two μ-1,3-bridging nitroxide ligands. The high temperature magnetic behaviour of the complexes is governed by a large ferromagnetic interaction ($J > 300$ cm^{-1}) which develops within the imino coordinated metal ion and the free radical. By contrast, the low temperature magnetic properties are strongly dependent on weak additional interactions.

3.6. Tetranuclear complexes

The coordination of Cu(II) ions with the potentially octadentate, tetranucleating ligands 1,4,6,9-tetrakis((R-2-pyridyl)amino)benzodipyridazine (**218**) has been studied [174,175]. The ligands are found to complex to four copper(II) centres in a rectangular structure involving two distant copper pairs bridged by hydroxyl groups in one molecular entity. Variable temperature magnetic studies indicate there is strong local intrapair coupling ($J = -167$ cm^{-1}) in the hydroxide-bridged complexes and also the presence of significant, distant, interpair antiferromagnetic coupling across the benzodipyridazine ring system ($J = -60$ cm^{-1}). A similar coordination geometry and magnetic properties have been observed in the tetranuclear complex of (**219**) with copper(II) ions [176].

A study of the complexation of the tridentate ligand 2,6-bis(morpholinomethyl)-4-methylphenol (**220**) with Cu(II) ions has been carried out [177]. This has allowed the characterisation of the two tetranuclear complexes $[Cu_4OBr_4(\mathbf{220})_2].2MeOH$ (**221**) and $Cu_4O(OBz)_4(\mathbf{220})_2].H_2O$ (**222**). The first complex (**221**) has a central μ_4-bridging oxygen surrounded tetrahedrally by four copper ions (Cu-O = 1.917 Å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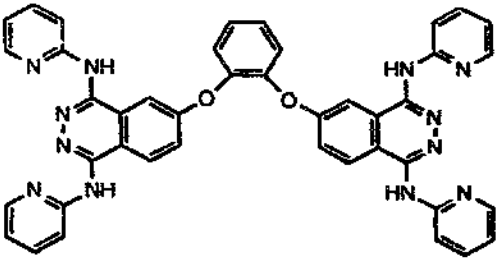
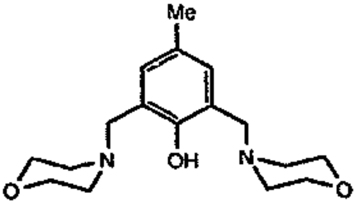

(219)

(avge)). The four bromine ligands and the two phenoxo groups of the deprotonated ligand are in a μ_2-bridging mode and bridge each pair of copper centres. The structure is completed by four terminal *N*-bonded morpholine groups, one of them coordinated to each of the copper ions. The second complex (**222**) consists of a central Cu_4O tetrahedron. The bromine ligands in (**221**) are replaced by μ_3-bridging benzoate groups. The more rigid benzoate framework leads to three different coordination polyhedra around the copper centres: one octahedral, one square planar and two square pyramidal.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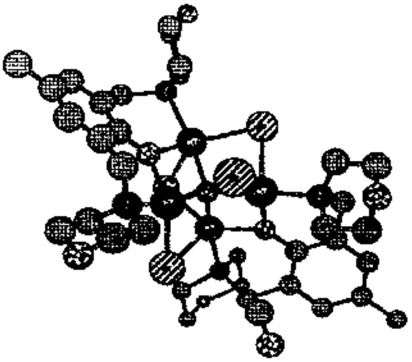
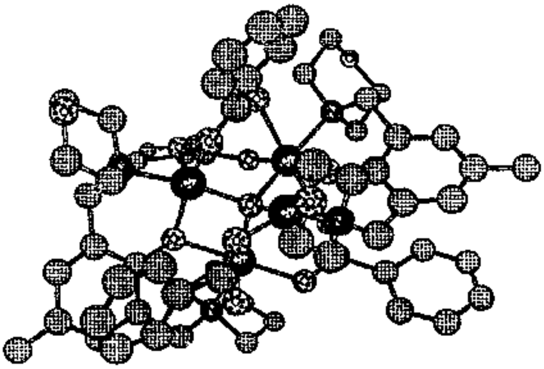

(221)

An investigation of the formation of copper(II) complexes with the tetranucleating macrocycles (**223**) has been performed [178]. A total of seven tetracopper(II) and three octacopper(II) complexes have been synthesised. The tetranuclear complexes have been shown by X-ray crystallographic analysis to contain planar $Cu_4(\mu\text{-}OH)$ cores (**224**).

A tetranuclear complex containing a vitamin B_6 ligand, pyridoxine (5-hydroxy-6-methylpyridine-3,4-dimethanol) and bpy has been synthesised [179]. The solid state structure (**225**) shows a copper(II) complex with a "stepped-cubane" structure with each copper in a trigonally distorted square pyramidal environment. The unusual structure is stabilised by π-stacking between the various bpy units and by the plasticity effect of the copper(II) ions.



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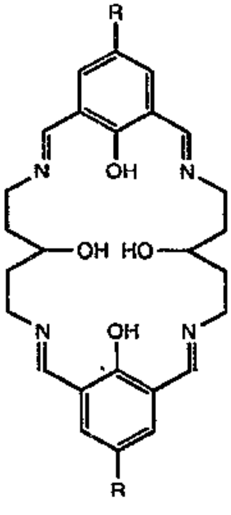
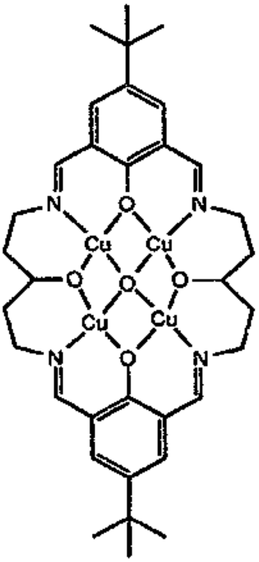
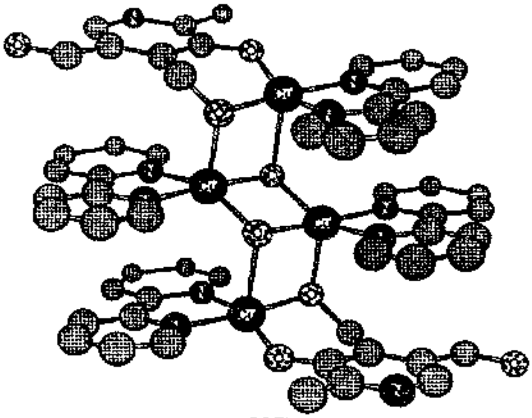




(224)

The synthesis and solid state structure of a peroxo Cu(II) complex with unusual μ_4-coordination have been reported [180]. The reaction of $Cu(ClO_4)_2$ and 4-methyl-2,6-bis(pyrrolidinomethyl)phenol afforded dark green crystals corresponding to the tetranuclear complex (**226**). The four copper centres lie in an almost planar rectangle and above the rectangle a peroxo group is bound end on in a 4-fold bridging μ_4,$(\eta^1)_4$-coordination. A perchlorate ligand is situated below the Cu_4 rectangle and is similarly bound to all four copper centres. The copper centres are coordinated with typical Jahn-Teller distortion in a square pyramidal fashion.



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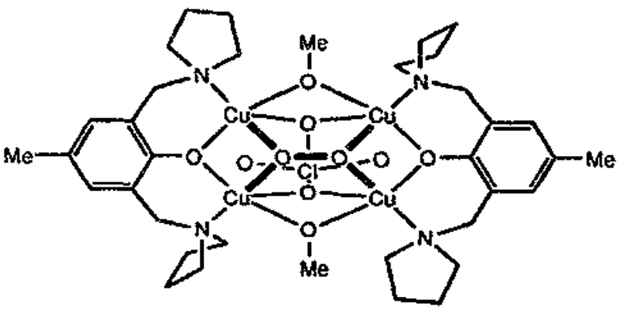


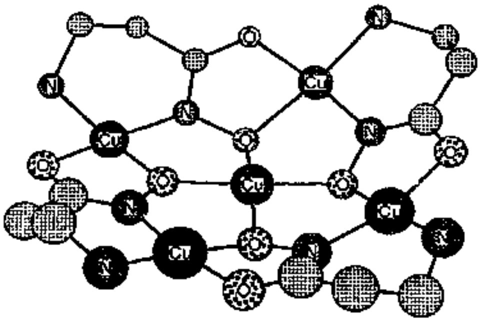
(226)

3.7. Higher nuclearity complexes

The potentiometric and X-ray crystallographic studies on the copper(II) complex of L-β-alaninehydroxamic acid have shown the formation of a very stable pentanuclear complex **(227)** at pH ~4 [181]. In this species, all of the donor atoms of the alaninehydroxamic acid are involved in metal coordination. Four peripheral metal ions form an almost planar structure and the central metal ion is 0.4 Å above the plane. The stability of the complex is attributed to there being twelve 5- and 6-membered rings having different conformations.

A chiral hexanuclear copper(II) complex having a propeller structure has been synthesised [182]. Although there are two possible diastereoisomers, only one of them has been identified. The core structure of **(228)** consists of six copper(II) ions and five oxygen atoms and resembles a cryptand and has a proton trapped inside. Magnetic susceptibility measurements show the complex has an antiferromagnetically coupled ground state.

A study has been performed on the coordination of copper(II) ions with substituted pyridones [183]. Whereas 3- and 4-substituted pyridones, as well as 6-chloro-



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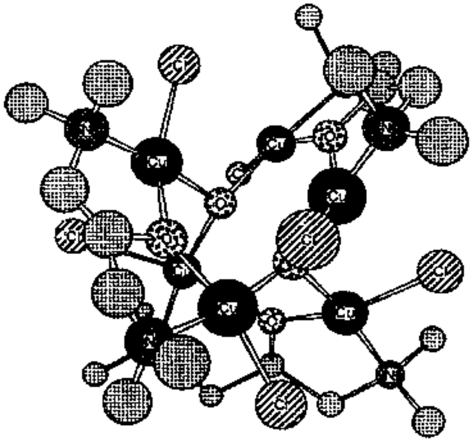


(228)

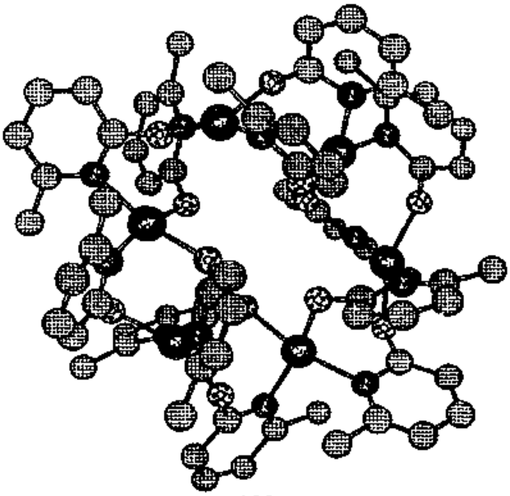
2-hydroxypyridine, form dimeric complexes on coordination with Cu(II) ions, 6-methyl-2-hydroxypyridine has been shown to form a hexanuclear structure (**229**). This difference in structure is attributed to unfavourable steric interactions between the methyl substituents of the ligand if a dimeric structure were to form.

A dodecanuclear complex has been formed in a template reaction [184]. The complex consists of a dimeric cation of two almost flat hexagonal macrocyclic rings each involving an array of nominally square planar Cu(II) centres (**230**) which are coupled together by three axially bridging hydroxy groups. The CV shows three quasi-reversible redox waves at $E_{1/2}$ 0.075, -0.44 and -0.92 V associated with the Cu^{II}/Cu^{I} couple.

3.8. Polymeric complexes

3.8.1. Nitrogen coordination

The reaction of copper(II) ions with the macrocycle (**231**) has been shown to result in an infinite chain polymeric structure in which the 4-coordinate



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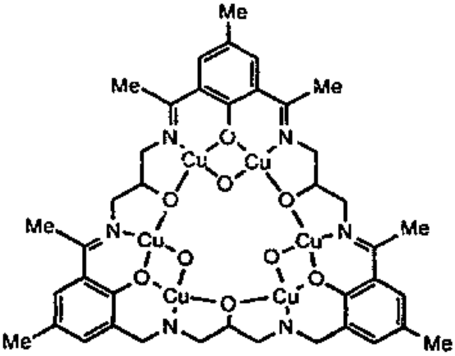
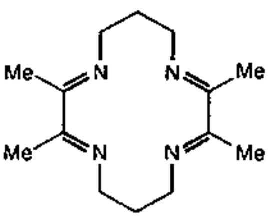


(230)

$[Cu(\mathbf{231})]^{2+}$ cations are bridged by distorted tetrahedral $CuCl_4^{2-}$ [185]. The bridging of the $[CuCl_4]^{2-}$ anions is asymmetric and leads to alternating magnetic exchange pathways along the chain. Magnetic susceptibility measurements confirm the existence of two different exchange parameters, one ferromagnetic and the other antiferromagnetic. It has been demonstrated that the related macrocyclic system, 6,6′-spirocyclam (**232**), also reacts with copper(II) ions to form a polymeric structure [186]. In this case chlorine atoms bridge the copper centres to form a μ-bridged 1-dimensional zigzag polymer in which the Cu···Cu distance is 5.25 Å.

The condensation reaction between ethylenediaminetetraacetic dianhydride with ethylenediamine has resulted in the characterisation of a 12-membered macrocycle with two pendant acetato groups (**233**) and a 14-membered macrocycle with four pendant acetato groups [187]. The reaction of (**233**) with copper(II) ions forms a



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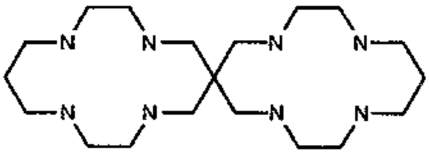
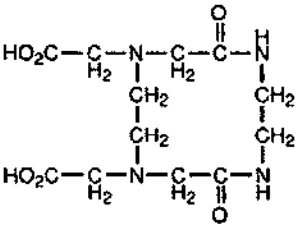


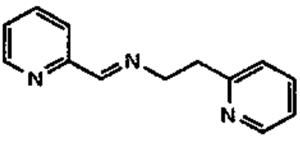
(232)

1-dimensional chain structure in which the copper centres are joined by carboxylate groups.



(233)

The polymeric structure formed from the reaction of *N*-[(2-pyridylethyl)pyridine-2-carbaldimine] (**234**) and copper bromide is comprised of cationic mono-μ-bromocopper(II) chains [188]. Two crystallographically independent cations form -Cu(**234**)-Br-Cu(**234**)-Br- units which repeat by translation to form the chain structure (**235**).



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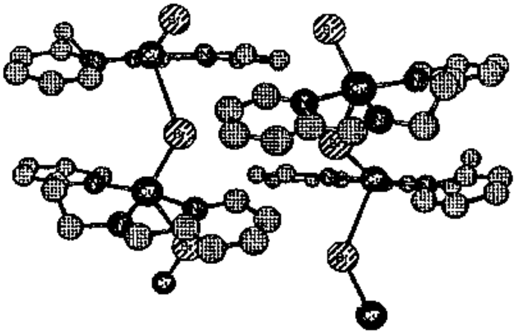
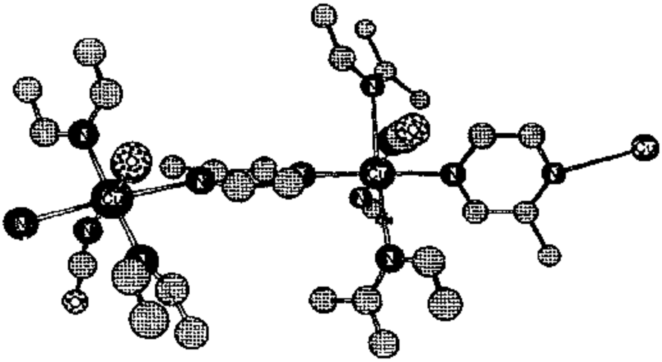


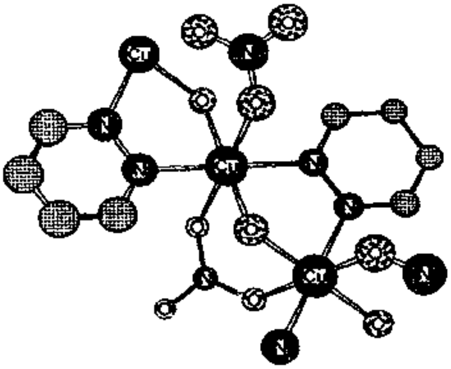
(235)

A study of the complexation of copper(II) cyanate with pyrazine, methylpyrazine and pyridazine has been carried out [189]. X-ray crystallographic analysis of the complex formed with methylpyrazine shows a polymeric structure (**236**) containing unsymmetrical bridging methylpyrazine ligands and terminal cyanate groups. Whereas the complex formed with methylpyrazine was found to be magnetically dilute, those formed with both pyrazine and pyridazine exhibit antiferromagnetic exchange. The complex formed between tetramethylamine, pyrazine and $CuCl_2$ has been characterised and can be considered as a polymeric structure in which the copper centres are 6-coordinate with two weak apical Cu-Cl bonds, or the copper centre can be considered as having a 4-coordinate square planar geometry [190].



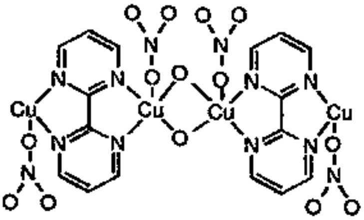
(236)

An investigation into the reaction of $Cu(NO_3)_2$ with pyridazine has shown that the nature of the product depends upon the solvent and stoichiometry used [191]. In water using a 1:1 (salt: ligand) ratio a linear polymeric species **(237)** is obtained with a Cu···Cu separation of 3.3215(5) Å and with each metal ion pair symmetrically bridged by a η^2-pyridazine molecule, a hydroxyl group and a nitrate ion. In contrast, when a 1:2 and a 1:3 (salt:ligand) ratio were used a trinuclear and a mononuclear complex were obtained.



(237)

The coordination of copper(II) ions with bipyrimidine (bpm) has been studied [192–194]. The reaction of bpm with $Cu(NO_3)_2$ has been shown to result in the formation of a polymeric chain structure in which the copper centres are alternately bridged by ligand and hydroxyl groups **(238)**. The polymer grows as a linear chain with the two nitro groups in a *cis* arrangement with respect to the $(bpm)Cu(OH)_2(bpm)$ plane and with adjacent pairs of nitro groups alternately up and down along the chain. Magnetic susceptibility measurements have demonstrated an alternating ferromagnetic coupling ($J = 105\ \mathrm{cm^{-1}}$) and an antiferromagnetic coupling ($J = -140\ \mathrm{cm^{-1}}$) to exist in the chain associated with the μ-bpm and di-μ-hydroxo fragments of the polymer respectively. The reaction of bipyrimidine with $Cu(SCN)_2$ has enabled two polymeric structures to be characterised, a 1-dimensional chain of $[Cu(bpm)(NCS)_2]_n$ (**239**) and a 3-dimensional network $[Cu(bpm)(NCS)_4]_n$. The 3-dimensional polymer shows a strong antiferromagnetic exchange of $J = -230\ \mathrm{cm^{-1}}$) while (**239**) shows only a very weak magnetic exchange ($J = -0.6\ \mathrm{cm^{-1}}$). A polymeric chain structure has also been characterised from the reaction of bpm with $Cu(ClO_4)_2$.



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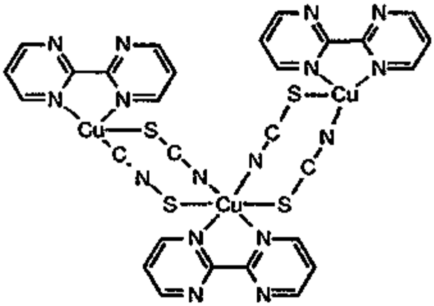
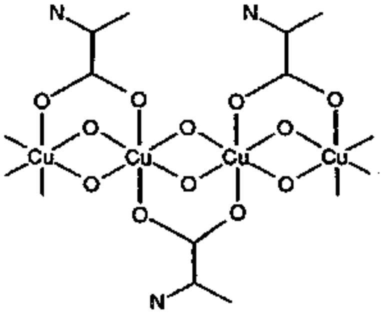


(239)

3.8.2. Oxygen coordination

The solid state structure of the polymeric Cu(II) complex of L-alanine has been determined [195]. The natural amino acid is shown to have an unusual mode of coordination, behaving as a carboxylic acid rather than as an amino acid (**240**).



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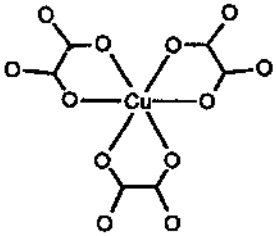
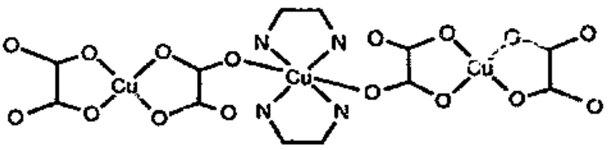


(241)

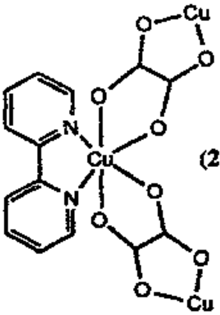
A study has been performed to synthesise a stable coordination complex derived from ascorbic acid, and test its biological effect against melanoma cells [196]. The oxidation of a mixture of Cu(II) ions, vitamin C and 2-diethylaminoethanol in the presence of hydrogen peroxide resulted in the formation of a polymeric *catena*-μtris(oxalato)-Cu(II) complex (**241**). The central Cu(II) ion is surrounded by six oxygen atoms of three oxalate ions each one starting a helical chain.

3.8.3. Nitrogen and oxygen coordination

A study has been carried out to synthesise oxalato-bridged Cu(II) polymers and the two polymeric complexes (**242**) and (**243**) have been characterised [197]. In (**242**) the oxalato anions act as tridentate ligands while in (**243**) they act as tetradentate bridging ligands. Magnetic susceptibility measurements have shown that (**242**) is weakly antiferromagnetic while (**243**) is weakly ferromagnetic. EHMO calculations have demonstrated that the molecular orbitals of the anion and cation in (**242**) do not mix and so lead to only a very weak magnetic exchange interaction.



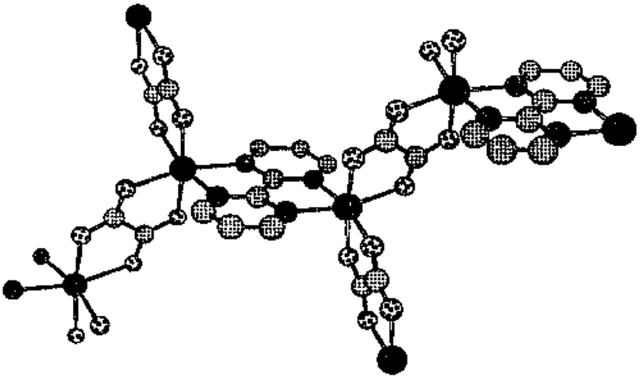
(**242**)



(**243**)

An investigation into synthesising polymetallic compounds with exchange interactions has resulted in the characterisation of a polymeric species (**244**) composed of parallel sheets of hexagonal arrays of copper centres bridged by bisdidentate oxalato and bipyrimidine ligands [198]. The layers are stacked by graphite-like interactions between the bipyrimidine rings of different layers. Five disordered water molecules are accommodated in each hole of the polymer and are linked together by hydrogen bonds to form a planar ring. The polymer shows only a weak antiferromagnetic interaction between the copper centres.

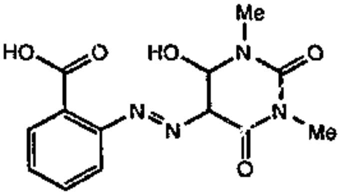
A polymer containing neutral chains of Cu(II) ions with alternating azide and oximidato bridges has been characterised [199]. The solid state structure shows the *N,N'*-bis[(2-dimethylamino)ethyl]oxamide group acts as a bis(terdentate) ligand and the azide group bridges the metal centres in an asymmetric end-on fashion with the Cu···Cu separation being 5.286(1) Å through the oxamidate bridge and 3.395(1) Å through the azide bridge. An investigation of the magnetic properties show a strong antiferromagnetic interaction through the oxamidate group and a weaker ferromagnetic coupling through the end-on azide bridge. An oxamidato bridged Cu(II) polymer has been formed from the reaction of *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamide with $CuCl_2$ [200]. In this case the polymeric product consists of zigzag chains of copper atoms bridged by *trans* oxamidato ligands and chloride groups. Magnetic susceptibility measurements have shown a strong ferromagnetic exchange interaction of $J = 409\ \mathrm{cm^{-1}}$. A 2-dimensional sheet-



(244)

like polymer composed of copper centres bridged by *N*,*N'*-bis(2-aminoethyl)oxamide and azide groups has been shown to have an antiferromagnetic exchange interaction of -519 cm^{-1} [201]. Further evidence of the efficiency of the oxamidato bridges in facilitating antiferromagnetic coupling between copper centres which are separated by more than 5.2 Å has been supplied by the polymeric structures containing 4,4'-bipyridine and pyrimidine bridges in place of the azide group which show strong magnetic exchange interactions of $J = -335$ and -560 cm^{-1}, respectively [202]. A copper(II) polymeric structure bridged simultaneously by three different types of polyatomic ligands (betaine, nitrate and azide) has been characterised [203]. The polymer has a zigzag arrangement with a Cu···Cu separation of 3.436 Å.

The reaction of $Cu(NO_3)_2$ with 5-[(carboxyphenyl)azo]-1,3-dimethylbarbituric acid (**245**) has been shown to result in the formation of [Cu(**245**)$(H_2O)]_4$ [204,205]. The reaction of this complex with pyridine/ethanol (1:1) results in a zigzag polymeric product {[Cu(**245**)Py].3$H_2O\}_n$ in which the ligand acts in a tetradentate mode. The Cu···Cu separation is 6.322 Å and the polymer is weakly ferromagnetic. Adjacent chains are linked through hydrogen bonding interactions. The reaction of the polymeric structure with py causes the polymer to break up to form discrete [Cu(**245**)$(Py)_2$] molecules in which the ligands act in a tridentate manner. The same mononuclear product is also formed from the reaction of [Cu(**245**)$(H_2O)]_4$ in neat pyridine.

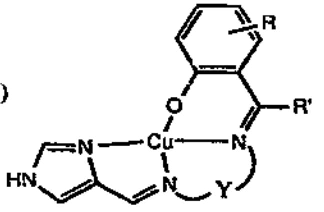


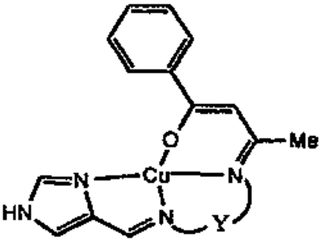
(245)

A study of ligand-field control in the assembly of polymeric metal complexes has been carried out [206]. A series of "ligand complexes" containing an imidazole moiety have been prepared from the reaction of copper(II) ions with tetradentate

Schiff base ligands. Under alkaline conditions the complexes composed of salicylaldehyde derivatives (**246**) readily undergo deprotonation of the imidazole ring giving insoluble imidazole-bridged polymeric species. Potentiometric pH titrations have shown the deprotonation to be irreversible. Under alkaline conditions, the complexes composed of benzoylacetone derivatives (**247**) give monomeric species that are soluble in common organic solvents. The potentiometric pH titration curves for the forward and back reaction are almost the same indicating that the protonation/deprotonation step is reversible. Hence the presence of the higher ligand field strength in (**247**) prevents the formation of polymeric structures in alkaline conditions.

(246)



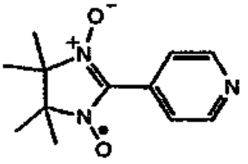


(247)

The structure and magnetic properties of diaqua(L-asparto)copper(II) have been investigated [207]. The solid state structure reveals the existence of a chain structure of copper centres bridged by aspartic acid molecules. These chains are linked by a network of interchain hydrogen bonds involving the water molecules and the amino acid groups. Magnetic susceptibility measurements indicate an antiferromagnetic exchange interaction between neighbouring copper ions in a chain. Another naturally occurring amino acid L-proline has also been shown to form 1-dimensional polymeric chains on reaction with copper(II) ions [208]. The reaction of $Cu(NO_3)_2$ with glycine has been shown to result in the formation of a helical polymer [209].

The reaction of Cu(II) ions with a nitronyl nitroxide radical $[Cu(hfac)_2]_3$(**248**)$_2$, where hfac = hexafluoroacetylacetonato, has been shown to produce a polymeric material which acts as a one dimensional antiferromagnet [210]. The polymer consists of chains in which dimeric units of $[Cu(hfac)_2]_3$(**248**)$_2$ are bridged by $Cu(hfac)_2$ units to give a compound in which each nitronyl nitroxide radical binds to three metal ions. Magnetic susceptibility data show a predominance of ferromagnetic interactions between Cu(II) centres and the radical rather than the antiferromagnetic interactions through the pyridyl group.

An investigation has been carried out to develop a precursor system for the

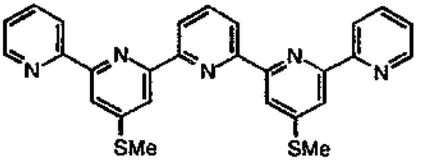


(248)

$YBa_2Cu_3O_{7-x}$ superconductor [211]. Using $[Cu_2(O_2CCH_3)_4(H_2O)_2]$, $Ba(O_2CCH_3)_2$ and $[Y(O_2CCH_3)_3(OH_2)_4]$ as starting materials and acetic acid and 1,3-bis-(dimethylamino)propan-2-ol (Hbdmap) as the cross-linking agents, a powder sample of $YBa_2Cu_3O_{7-x}$ was obtained which exhibited an onset superconducting temperature of 92 K. The related polynuclear complexes $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$, $[LaCu_2(bdmap)_3(O_2CCF_3)_4]$ and $[Cu_3(bdmap)_3(O_2CCF_3)_2]_2[Y_2(bdmap)_2(O_2CCF_3)_6]$ have been characterised and have been shown to readily decompose to their corresponding oxides when heated under a dioxygen atmosphere. This observation may explain the ready formation of the superconductor in this system.

3.9. *Supramolecular complexes*

A study has been carried out on the complexation of copper salts with *S*-alkyl-substituted quaterpyridines and quinquepyridines [212]. The reaction of the disubstituted quinquepyridine (**249**) with copper(II) ions at room temperature afforded either a homo- or mixed-valence dimetallic system, or a trimetallic complex depending on the copper salt used. The solid state structure has been determined of the homonuclear complex and shows it to have a double stranded helical structure with the copper centres both having distorted octahedral geometries, but in different chemical environments. One of the Cu(II) centres is coordinated to three pyridine rings of two ligand strands while the other is bound to the two remaining pyridine rings on each ligand and an acetate group.



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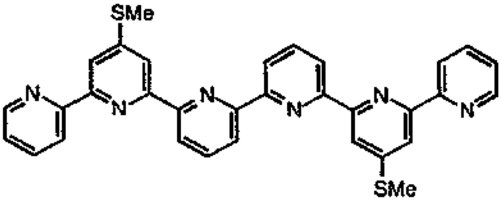
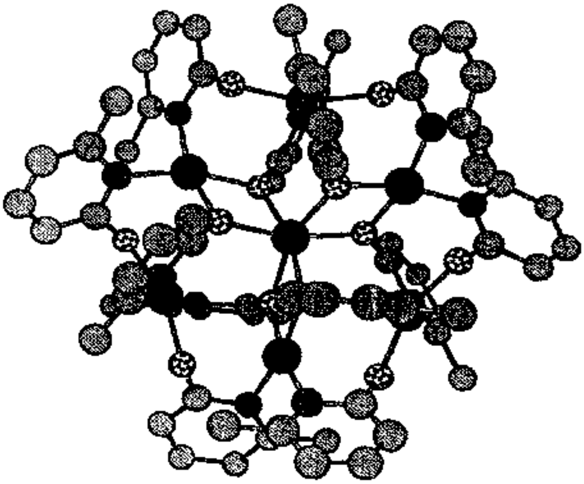


(250)

The reaction of $4',4''''$-bis(alkylthio)sexipyridines with a range of octahedral metal ions has been studied [213]. The solid state structure of the complex formed between Cu(II) ions and (**250**) shows the two metal centres to be in identical distorted octahedral environments each being bound to three pyridine rings from two ligand strands which twist around the metal centres in a helical fashion. A redox-induced transformation between the dinuclear Cu(II) complex and the trinuclear Cu(I) complex has been demonstrated both chemically and electrochemically.

The reaction of the potassium salt of 2-hydroxy-6-methylpyridine with copper nitrate has resulted in the formation of a hexanuclear copper(II) complex in which a sodium cation is found at the centre of the metallocrown [214]. The sodium ion has been replaced by both a Mg^{2+} and a Cu(II) cation and the solid state structure of the heptanuclear copper(II) complex (**251**) has been determined. The complex consists of six copper centres having 4-coordinate geometries which form the cavity in which the seventh copper centre is bound. This central copper centre has a coordination geometry which is distorted from a regular octahedron towards a trigonal prism.

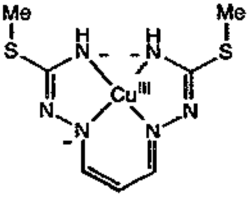


(251)

4. Copper(III) complexes

Only a very few complexes containing Cu(III) centres are characterised unambiguously. An investigation into the synthesis of $[Cu(CF_3)_4]^-$ salts has been carried out [215]. The oxidation of a mixture of Cu^ICF_3 compounds in dmf with a stoichiometric amount of XeF_2, I_2, Br_2, Cl_2 or ICl_2 followed by the addition of Bu_4NBr resulted in the formation of $[Bu_4N]^+[Cu(CF_3)_4]^-$ as colourless solids which were not sensitive to light, air or moisture. The solid state structure of the complex cation shows the copper(III) ion in an approximate square planar geometry surrounded by four CF_3 groups in which neighbouring CF_3 groups have a staggered arrangement and the *trans* groups are eclipsed. The carbon atoms are displaced from the ideal plane and two sets of six fluorine atoms form a planar hexagon above and below the CuC_4 plane thereby protecting the copper centre from nucleophilic attack.

The synthesis of a copper(III) complex in which the high oxidation state is stabilised by *S*-alkylated isothiocarbazide derived ligands which exert a strong ligand field has been investigated [216]. The X-ray structure of the complex **(252)** shows the geometry of the copper centre to be intermediate between square planar and tetrahedral with short Cu-N bonds of average length 1.898 Å. The solid state structure also shows the presence of a hydrogen bond between a pair of the neutral complexes. This is also evident from IR spectroscopy which reveals a sharp band at 3363 cm^{-1} for the N-H not involved in hydrogen bonding and a broad band at 3215 cm^{-1} for the N-H···N group. The ^{1}H NMR spectrum of the complex is diamagnetic, which is consistent with the copper centre having a +3 oxidation state.



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