ELSEVIER

Coordination Chemistry Reviews
164 (1997) 575–666

COORDINATION CHEMISTRY REVIEWS

Copper 1995

Diane R. Smith *

Universität Basel, Inst. für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland

Contents

---

* Corresponding author. E-mail: smithd@ubaclu.unibas.ch

PII S0010-8545(97)00038-6

1. Introduction

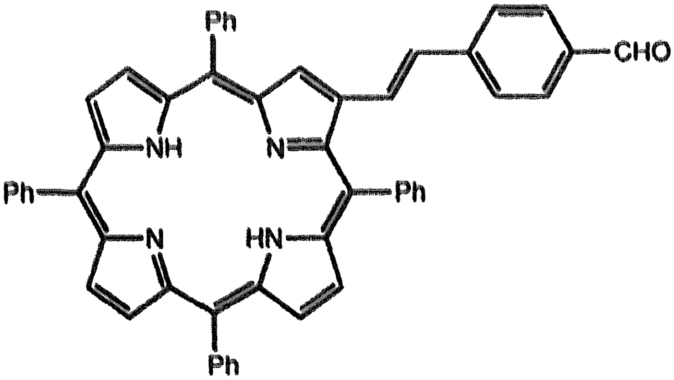
This review provides an overview of the coordination chemistry of copper published in 1995 and follows a similar form as the previous copper review [1]. The large volume of publications arising during 1995 has made it necessary to limit the literature reviewed. The method chosen has been to select only those complexes with full structural characterisation and located in the Cambridge Crystallographic Database and then further restricted to mainly those published in major journals. Organometallic complexes are generally not included in this article.

2. Copper(I)

2.1. *Mononuclear complexes with macrocyclic ligands*

The first X-ray crystallographic structure of a 2-vinyl-substituted tetraphenylporphyrin (**1**) has been determined [2]. This structure shows the olefin and aldehyde units are coplanar, while the torsion angle between the olefin and the porphyrin ring is small (≈ 17°). The overall planarity of this molecule and the fact that the solution UV/VIS spectra of the ligand and the copper complex showed red-shifted Soret bands (relative to tetraphenylporphyrin and its copper(I) complex) suggests that there is nothing to prevent conjugation between the porphyrin and aldehyde moieties. π–π-Interactions are observed in the crystal structure. The porphyrin ligand has since been used in the synthesis of porphyrin arrays.

(**1**)



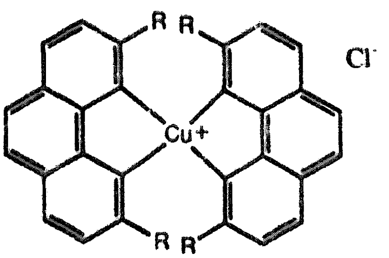
2.2. *Mononuclear complexes with acyclic ligands*

Copper(I) complexes of the potentially terdentate ligands 6-(2-dimethylaminophenyl)-2,2′-bipyridine and 2-(2-dimethylaminophenyl)-1,10-phenanthroline have been prepared [3]. Both complexes have highly distorted tetrahedral structures in which only the α,α′-diimine fragments are coordinated. The $C_6H_4NMe_2$ fragments are pendant and are twisted with respect to the coordinated bpy or phen fragments such that the pendant aromatic ring of one ligand lies stacked above the coordinated unit of the other ligand. This results in 'partial encapsulation' of the copper(I) centres which confers chemical stability (no autoxidation in the presence of O_2) and electrochemical stability (wide 'redox-existence ranges' for the Cu(I) oxidation states) on the complexes. The inter-ligand stacking also results in distortion away from pseudo-tetrahedral geometry at the metal centres towards square planar; this is maintained in solution (as shown by ^1H NMR and electronic spectra). Oxidation of the complexes to the copper(II) complexes with ferrocenium afforded stable solutions whose EPR spectra indicate that the metals have geometries that are much more flattened towards square-planar geometries.

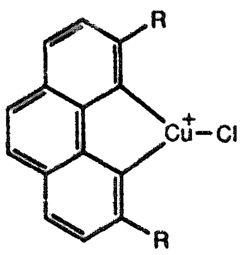
Several new complexes of the type $[Cu(NO_3)(PPh_3)_2(L)_m]$ (L = 3-methylpyrazole, 4-methylpyrazole, 3,5-dimethylpyrazole, 4-bromopyrazole or bis(4-methylpyrazol-1-yl)methane, m = 1; L = pyrazole, 1,2,4-triazole or 2-methylimidazole, m = 2), $[Cu(NO_3)(PPh_3)(L)]$ (L = 3,4,5-trimethylpyrazole or 4-phenylimidazole), $[Cu(NO_3)(PAr_3)_n(L)_3]$ (Ar = *p*- or *m*-tolyl, n = 0 or 1, L = pyrazole), $[CuX(PPh_3)_2(L)]$ (X = Cl, Br or I, L = pyrazole or 3,5-dimethylpyrazole) and $[CuX(PPh_3)(L)]$ (X = Cl or Br, L = bis(pyrazol-1-yl)methane, bis(3,5-dimethylpyrazol-1-yl)methane or bis(triazol-1-yl)methane) have been prepared and characterised by analytical and spectral data [4]. The compounds $[CuX(PPh_3)_2(L)]$ (X = Cl, Br or I, L = pyrazole or 3,5-dimethylpyrazole) are fluxional at temperatures above 240 K. The dinuclear compound $[Cu_2(PPh_3)_3(pzH)_2]$ was obtained from the reaction between $[Cu^I(PPh_3)_3]$ and pyrazole (pzH) in methanol containing alkali. The crystal structure of nitrato bis(tri-*p*-tolylphosphine)copper(I) shows the copper atom has a strongly distorted tetrahedral geometry (P–Cu–P = 128.0(1)°).

A study has been carried out on the complexation of copper(I) chloride with a series of 2,9-dialkyl-1,10-phenanthrolines [5]. Those complexes having a phen:Cu(I) ratio of 2:1 have the well known structure (**2**) containing a cation with a distorted tetrahedral geometry about the copper atom of the general form $[(2,9\text{-dialkylphen})_2Cu]^+Cl^-$. The resonances of the alkyl groups show a marked upfield shift in their ^1H NMR spectra with respect to the free ligands which is ascribed to an aromatic ring current effect. The complexes with a 1:1 stoichiometry can have either of two isomeric structures, (**3**) and (**4**), depending upon the bulk of the alkyl groups in the 2- and 9- positions of the phen system, how they are prepared and whether they are in solution or in the solid phase. Isomer (**3**) is favoured with bulky alkyl groups and has the copper centre in a distorted trigonal geometry with a coordinated chlorine atom and does not exhibit a ring current effect as seen in (**2**). The structures of two of these complexes where R = *tert*-butyl and neopentyl, were determined by X-ray crystallography. In the case of R = *tert*-butyl, the copper centre shows substantial distortion from trigonal planar geometry because of the steric bulk of the *tert*-butyl groups. Complexes (**4**) were found to ^1H NMR spectra identical to (**2**), but are isomeric with (**3**), having the formula $[(2,9\text{-dialkyl-phen})_2Cu]^+CuCl_2^-$. The structure of $[(2,9\text{-}n\text{-pentyl-1,10-phen})_2Cu]^+CuCl_2^-$ has been determined and shows the alkyl groups of each ligand to lie directly over the face of the aromatic system of the other with a distorted tetrahedral geometry about the copper centre.

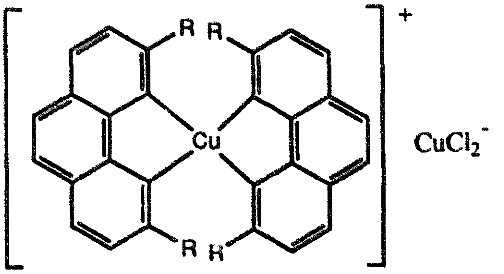
The mechanism by which Cu(I) and Zn(II) influence the decarboxylation of malonic acid derivatives has been investigated comprehensively by means of kinetic



(2)



(3)

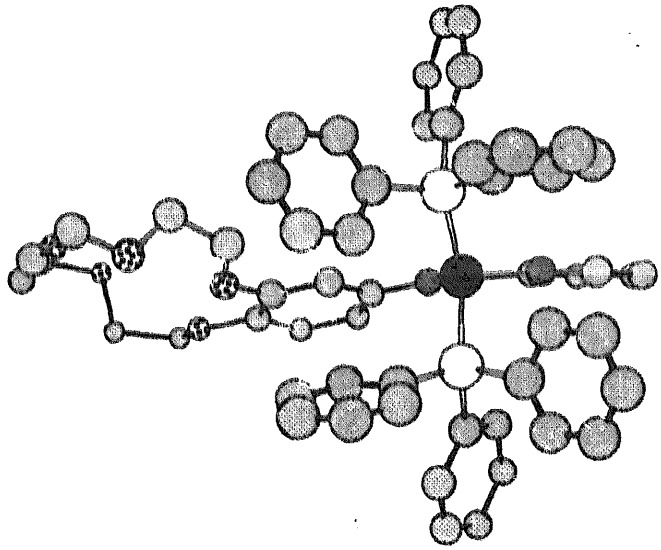


(4)

and structural studies [6]. The air-sensitive bis(phosphine)copper(I) complexes of phenylmalonic acid and its benzyl hemi-ester have been synthesised from one equivalent of the acid and cuprous butanoate in the presence of phosphine ligands. The X-ray structure of $[(Ph_3P)_3CuO_2CCEtPhCO_2H]$ shows that the copper centre is three-coordinate and contains two phosphine ligands and a carboxylate group bound in a monodentate manner. Kinetic evidence demonstrates that decarboxylation of malonic acid or hemi-ester derivatives in the presence of bis(phosphine)copper(I) or η^3-HB(3-Phpz)$_3$Zn^{II} carboxylate salts (HB(3-Phpz)$_3$ = tris(3-phenylpyrazolyl)-hydroborate) occurs *via* a predissociation step involving metal-carboxylate bond rupture. In accord with this mechanistic proposal, the rates of decarboxylation are greatly enhanced upon sequestering the metal cations with chelating nitrogen bases or upon replacing the Cu(I) or Zn(II) cations with a non-interacting counter-ion. In a related study, the mechanism by which Cu(I) influences the decarboxylation of cyanoacetic acid has also been studied comprehensively by means of structural and kinetic investigations [7]. The Cu(I) complexes $[(R_3P)_2CuO_2CCH_2CN]_{1,2}$ have been synthesised from the reaction of copper(I) butanoate with one equivalent of cyanoacetic acid and two equivalents of phosphine. When R = Ph, the complex has been shown to be a dimer both in the solid state and in solution and consists of two copper(I) centres bridged by two cyanoacetate groups that are bound to the copper centre through both the carboxylate functionality and the nitrogen atom. In contrast, with the bulky phosphine (R = Cy = cyclohexyl), the complex is found to be monomeric in the solid state and to contain a monodentate carboxylate group. The monodentate nature of the cyanoacetate binding was demonstrated to be a function of the electron-withdrawing ability of the cyanoacetate ligand as revealed from the solid state structure of the $(Cy_3P)_2$Cu(butanoate) analogue, where the more basic butanoate ligand binds in a didentate manner. Both phosphine derivatives of copper(I) cyanoacetate were observed to readily undergo reversible decarboxylation/carboxylation processes as evidenced by their exchange with $^{13}CO_2$. The phosphine derivatives of copper(I) cyanoacetate were found to be efficient catalysts for the decarboxylation of cyanoacetic acid to afford CH_3CN and CO_2 at rates similar to the CO_2 exchange process. These reactions were first-order in copper(I) complexes and zero-order in cyanoacetic acid at concentrations below 0.05 M. At higher acid concentrations, the reaction is inhibited by cyanoacetic acid due to its complexation with the copper(I) ion. A mechanism for decarboxylation is proposed which involves CO_2 elimination from a cyanoacetate ligand that is nitrile-bound to the metal centre, *i.e.* electrophilic catalysis.

The synthesis, crystal structure and cation-binding properties of the copper(I) complex $[Cu(PPh_3)_2(L)]BF_4$ (**5**) where L = *N*-(2-pyridinylmethylene)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodein-16-ylamine] which could serve as a model for the design and development of efficient alkali/alkaline earth metal ion probes is reported [8]. The complex consists of a copper(I) centre coordinated to a diimine ligand in conjugation with a benzo-15-crown-5 moiety. Its photophysical and electrochemical properties are compared with those of the uncrowned model complex $[Cu(PPh_3)_2(L1)]BF_4$ (**6**) (L1 = *N*-(2-pyridinylmethylene)-phenylamine). Both complexes show low-energy absorption bands at 374 and 350 nm for (**5**) and (**6**), respectively, in methanol. The addition of alkali or alkaline earth metal ions to a methanolic solution of (**5**) results in a significant blue shift of the spectrum. Both (**5**) and (**6**) show dual luminescence with a high energy intraligand emission and a lower energy MLCT orange–red luminescence upon irradiation of light with $\lambda > 350$ nm (**5**), 639 nm in MeOH; (**6**) 675 nm in MeOH). Unlike most Cu(I) diimine complexes which have been found to be non-emissive in donor solvents such as MeOH, owing to solvent-induced quenching *via* exciplex, both (**5**) and (**6**) are emissive in MeOH. Upon addition of alkali and alkaline earth metal ions to a methanolic solution of (**5**) enhanced emission intensity is observed.

(5)

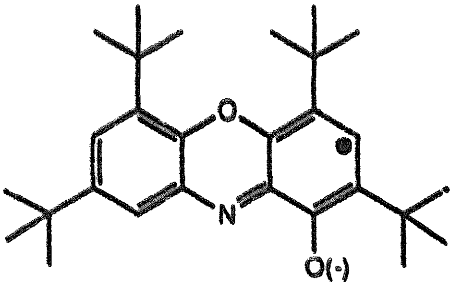


The use of isocyanides as ligand-directed probes of Cu(I) coordination in proteins has been investigated [9]. The reaction of 2,6-dimethylphenyl isocyanide (DIMPI) with reduced dopamine-*β*-monoxygenase (D*β*M) indicates the initial formation of monoisocyanide complexes at each of the two coppers (Cu_A and Cu_B) with different IR spectroscopic frequencies (2148 and 2129 cm^{-1}) indicating inequivalent Cu^I coordination at each copper centre. Further addition of DIMPI leads to the formation of a species containing multiple isocyanide ligands which is believed to be a trisisocyanide adduct having a single IR band at 2160 cm^{-1}. This titration behaviour can be interpreted by the active site model $Cu^I_A(His)_2X \cdots Cu^I_B(His)_2Y$ (X = His;

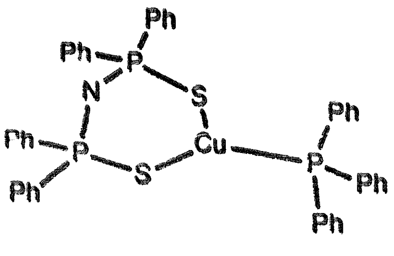
Y = Met) where the first stage of the reaction with isocyanide is the formation of a mono-DIMPI four coordinate complex at each Cu centre, giving rise to the two observed IR bands (2148 and 2129 cm^{-1}) provided the protein ligands are different. The second stage is the displacement of protein-bound ligands by the isocyanide group to form a protein-bound bis or tris complex (2160 cm^{-1}). Closely analogous chemistry involving the reaction of DIMPI with deoxyhemocyanin is also described, which illustrates the generality of isocyanides as probes of Cu(I) coordination in copper proteins. A model system [Cu(Mepy$_2$)(DIMPI)]ClO$_4$ is also described in which identical isocyanide-binding chemistry can be described thus validating the conclusions on the protein systems. The crystal structure is described and the clean conversion to a triscyanide complex is demonstrated by FTIR and FT Raman spectroscopies.

Iminosemiquinone complexes of copper have been prepared by treating copper metal with 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) (7) [10]. Reactions carried out with PPh$_3$ gave Cu^{I}(PPh$_3$)$_2$(PhenoxSQ). X-Ray crystallographic analysis has shown the copper centre to have a tetrahedral geometry. EPR Spectra indicate the unpaired electron is ligand-based and the electrochemical properties consist of one-electron oxidation and reduction reactions at the iminoquinone ligands. Reactions carried out in the absence of coligand or in the presence of a nitrogen-donor coligand gave Cu^{II}(PhenoxSQ)$_2$. This has been determined to have a distorted tetrahedral structure. Electrochemical characterisation has indicated that this complex undergoes two one-electron oxidations and two one-electron reductions, all occurring at the iminoquinone ligands. EPR spectra and variable-temperature magnetic measurements indicate that exchange between the PhenoxSQ is ferromagnetic, while Cu–PhenoxSQ exchange is antiferromagnetic. At low temperature, the complex has a ligand-based $S = 1/2$ magnetic ground state.

(7)



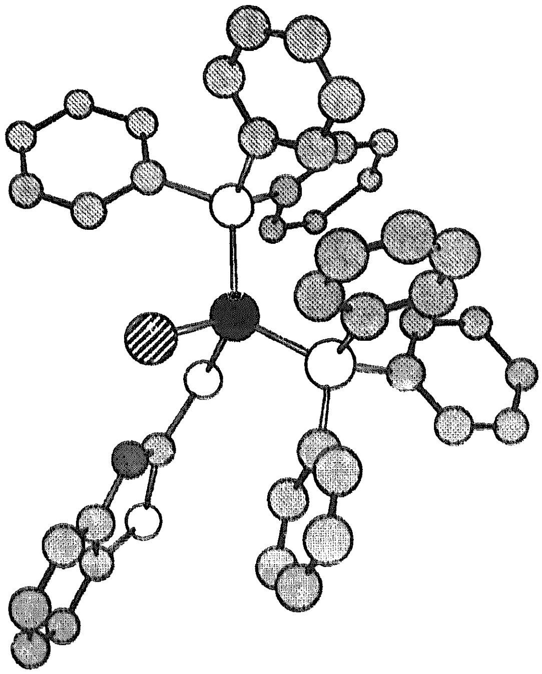
(8)



The mononuclear compound (Ph$_3$P)Cu(SPPh$_2$)$_2$N (8) was prepared from the reaction of (Ph$_3$P)$_2$CuNO$_3$ with K[(SPPh$_2$)$_2$N] in MeOH/CHCl$_3$ [11]. The ^{31}P NMR spectrum gave the first indication that the product had formed by the presence of two signals in an intensity ratio of 2:1 indicating that only one molecule of triphenylphosphine remained coordinated. The solid state structure showed the lattice to contain monomeric $(Ph_3P)Cu(SPPh_2)_2N$ units with three-coordinate copper(I) atoms in a distorted trigonal geometry. The dithioligand acts in a didentate mode resulting in the formation of non-planar six-membered inorganic CuS_2P_2N ring, the conformation of which is best described as a distorted boat.

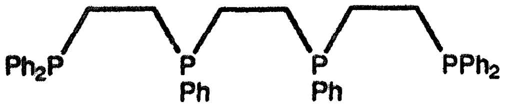
Copper(I) complexes of the general formula $[Cu(PAr_3)_2(bztzdtH)X]$ (where X = Cl, Br, I; PAr_3 = tri-*m*-tolylphosphine, diphenyl-*p*-tolylphosphine; bztzdtH = benz-1,3-thiazolidine-2-thione) and $[Cu(PAr_3)(bztzdtH)X]$ (where X = Cl, Br; PAr_3 = tri-*o*-tolylphosphine) were characterised [12]. The X-ray structure of $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$ (**9**) has been resolved and shows the complex to contain a distorted $CuSP_2Cl$ core.

(**9**)

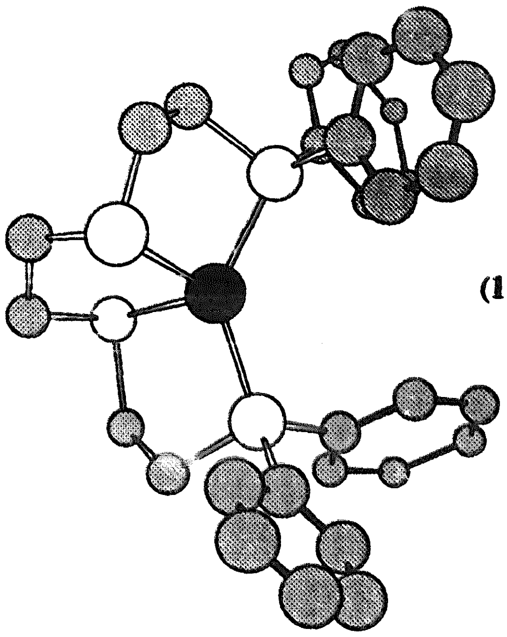


Reaction of $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ with 1 equivalent of tetraphos-1, P_2S_2 (**10**) in degassed acetone afforded the complexes $[M(\mathbf{10})]^+X^-$, M = Cu, X = PF_6; M = Ag, X = BF_4, in high yield [13]. The complex $Cu(L)PF_6$ (**11**) contains discrete $[Cu(P_2S_2)]^+$ cations and PF_6^- anions. The Cu(I) ion is tetra-ligated to the P_2S_2 ligand *via* both *P*- and *S*-donor atoms. The geometry at the copper centre is a severely distorted and flattened tetrahedron.

Bis(triarylphosphine)copper(I) derivatives with the anionic tetrakis(1H-pyrazol-1-yl)borato (pzTp) or dihydridobis(1H-pyrazol-1-yl)borato (Bp) have been prepared from $(Ar_3P)_2CuNO_3$ and KpzTp or KBp and characterised by IR and ^1H, ^{13}C and ^{31}P NMR spectroscopies [14]. Each complex contains a tetrahedral Cu^I centre and a didentate ligand. The pzTp complexes are fluxional in solution with all the pyrazolyl groups equivalent down to a temperature of ≈ −60°. The X-ray structure of $(Ph_3P)_2CupzTp$ (**12**) has been determined and shows the copper(I)



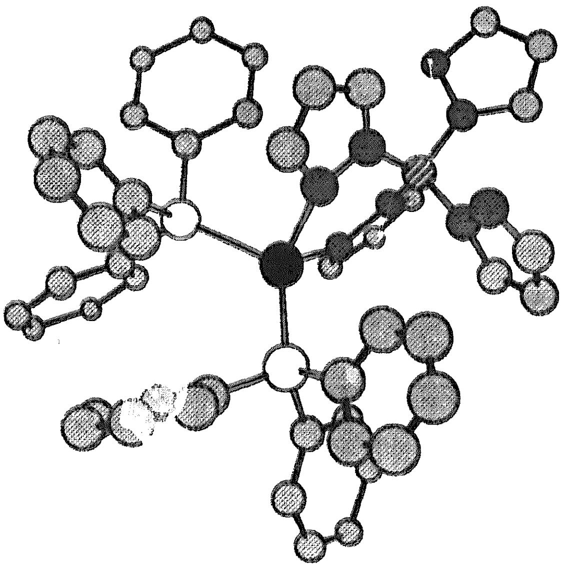
(10)



(11)

centre to have a distorted tetrahedral geometry, with the six-membered B(NN)$_2$Cu ring adopting a boat conformation.

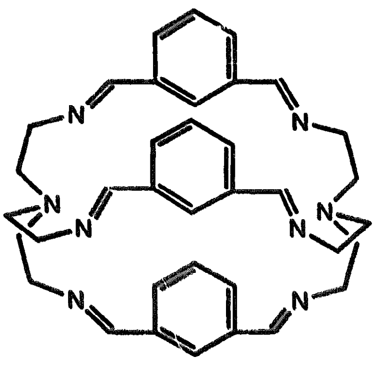
(12)



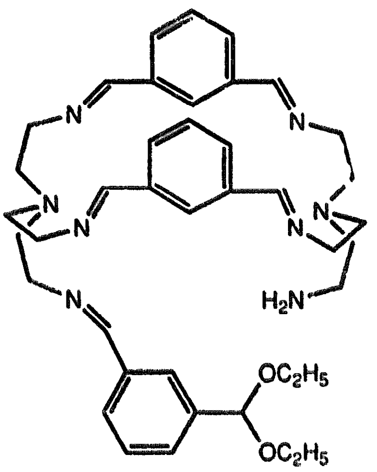
2.3. Dinuclear complexes with macrocyclic ligands

The hexa-Schiff-base cryptand (**13**) has been shown to encapsulate a pair of Cu^{I} cations without hydrolytic attack on the imine bonds: a problem which is evident when the [Cu$_2^{II}$(OH)]$^{3+}$ assembly is incorporated [15]. A similar observation is seen for the encapsulation of Ag^{I} ions. The structure of the dicopper complex of a singly ring-opened ligand (**14**), derived from (**13**), has been determined. The octaamine cryptand (**15**) more easily accommodates a [Cu$_2$(μ-X)]$^{3+}$ assembly where X=

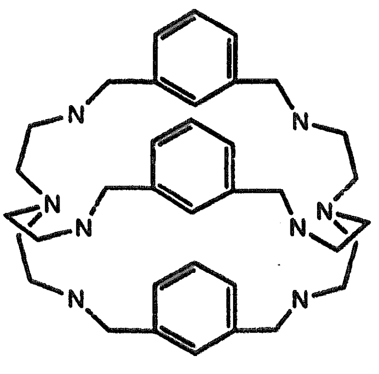
imidazolate, N_3^- or OH^-. The dicopper(I) complex is air-sensitive, while many stable dicopper(II) cryptates can be formed. The dicopper(I)-imidazole complex, the imidazolate ring is sandwiched between two aromatic rings of the cryptand strands. These rings are almost parallel, but are offset by ≈1.4 Å with respect to each other with an unusually short stacking distance of 3.05 Å. The aromatic ring of the third strand is almost perpendicular to the other three rings resulting in an edge-to-face relationship with one of the stacked rings, such that there is a H···ring plane distance of 3.15 Å. Each copper ion has a distorted trigonal-bipyramidal coordination geometry.



(13)



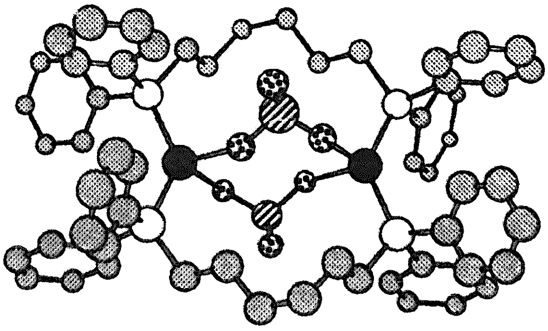
(14)



(15)

New dinuclear macrocyclic systems of 1,6-bis(diphenylphosphino)hexane (dpph) and 1,4-bis(diphenylphosphino)butane (dppb), $[Cu_2(dppb)_2(ClO_4)_2]$, $[Cu_2(dpph)_2(\mu\text{-}X)_2]$ (X = ClO_4 (**16**), NO_3 (**17**), PF_2O_2 (**18**), CH_3CO_2, $C_2H_5CO_2$) and $[Ag_2(dpph)_2(\mu\text{-}ClO_4)_2]$ have been synthesised and characterised [16]. The mononuclear Cu(I) complex $[Cu(dppp)_2](ClO_4)$ has also been prepared, (dppp = 1,3-bis(diphenylphosphino)propane). For complexes (**16**)–(**18**), each copper atom shares a tetrahedral geometry with the P_2O_2 donor set giving a molecular structure having two rings: the common outer, larger, ring of $-CuP(CH_2)_6PCu(CH_2)_6P-$ is composed of copper atoms and the bridging diphosphine ligands while the inner ring is $-CuOXOCuOXO-$ (X = Cl, N, P) for (**16**)–(**18**) respectively. The Cu···O distances fall within the shortest range for Cu(I) complexes of each anion, indicating that the Cu-anon binding is strong even for anions having weak coordination ability. The size of the cavity for the anion trap is estimated as the distance between the two metal centres in a molecule and ranges from 4.99 to 5.22 Å. The complex $[Cu(dppp)_2](ClO_4)$ shows a typical mononuclear structure with the chelating dppp ligand, while $[Cu_2(dppb)_2(ClO_4)_2]$ gives a dinuclear complex with terminally coordinated ClO_4^- anions and a single macrocycle (L = 4.63 Å) of $-CuP(CH_2)_4PCuP(CH_2)_4P-$. The ClO_4^- ion is prevented from adopting a bridging mode by the ring size and the spatial blocking of the phenyl groups of dppb. On this basis, the ligand having six methylene groups provides a cavity able to include anions such as tetrahedral ClO_4^- and Y-shaped NO_3^-.

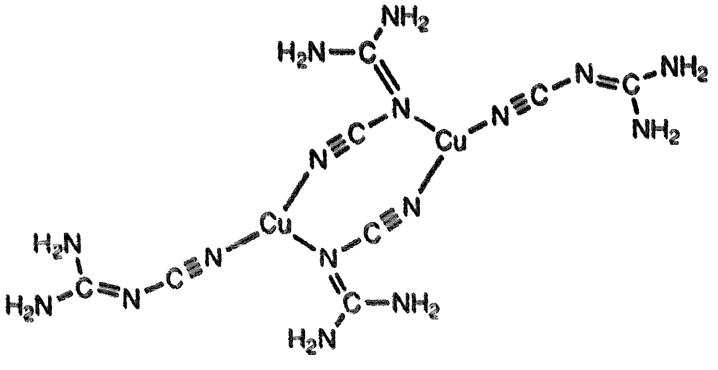
(17)



2.4. Dinuclear complexes with acyclic ligands

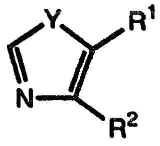
The air and moisture-sensitive Cu(I) salts of $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X.H_2O$ (cnge = 2-cyanoguanidine, $X = S_2O_6^{2-}$ or SO_4^{2-}) have been prepared by the reduction of aqueous solutions of Cu(II) chloride containing cnge by sodium sulfite [17]. The solid state structures of the two salts have been determined and show the two $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations to be very similar (**19**), but with the dithionate structure being more symmetrical than that of the sulfate. Both cations contain two trigonal-planar Cu(I) atoms bridged by two cnge molecules forming an eight-membered $(Cu–N–C–N)_2$ ring with the cnge molecules coordinating through its nitrile and imino nitrogen atoms, giving a Cu···Cu separation of 5.052 and 5.048 Å in the dithionate and sulfate salts, respectively. The coordination geometry of the copper(I) centres is completed by a terminally coordinated monodentate cnge molecule, coordinating through its nitrile nitrogen atom. In both structures the interaction between the in-plane π-systems of the bridging cnge molecules is minimised by them being separated by ≈3.1 Å and angled such that they really lie on two parallel planes separated by ≈0.75 Å. The cation structures are stacked in a parallel fashion separated by ≈3.8 Å. The anions and water molecules lie between the cations and are hydrogen bonded to the cnge molecules by oxygen-amino hydrogen contacts.

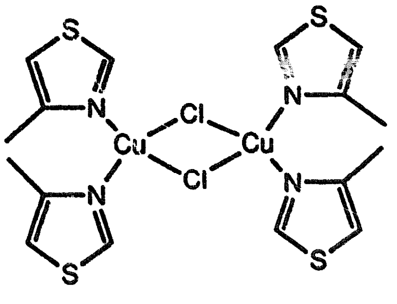
(19)



The complexes $[Cu_2(\mu\text{-}X)_2(\mathbf{20})_4]$ (X = Cl or I; Y = S or NMe; R^1 = H, R2 = Me; $R^1 = R^2$ = Me or $R^1 = R^2 = C_4H_4$) were prepared during a study to prepare copper(I) carbene complexes by quenching a mixture of CuCl or CuI and thiazolyllithium or imidazolyllithium with CF_3SO_3H [18]. The X-ray structure of the complex (**21**) where X = Cl, Y = S, R^1 = H, R^2 = Me has been determined. The Cu···Cu separation is 2.926(1) Å. The pseudo-tetrahedral arrangement around the copper centres forces the two 4-methylthiazole ligands into a non-coplanar arrangement.

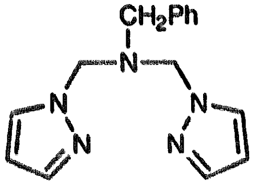
(20)



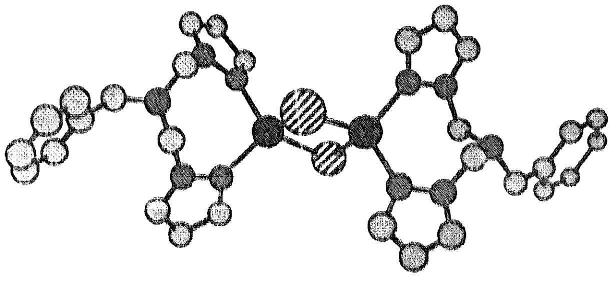


(21)

A new ligand *N,N*-bis(pyrazol-1-ylmethyl)benzylamine (**22**) has been reacted with metal ions to form [Fe(**22**)Cl_3], [Ni(**22**)$(NCS)_2$(MeOH)], [M(**22**)X_2], (M = Co^{II}, Cu^{II}, Zn^{II}, X^- = Cl^-, Br^-, NCS^-) and [{Cu(**22**)I}$_2$] [19]. The solid state structure of [Cu(**22**)Cl_2] shows the copper(II) centre to have a distorted square pyramidal geometry, while the complex [{Cu(**22**)I}$_2$] (**23**) displays a distorted tetrahedral geometry around copper(I). Two copper(I) ions and two bridging iodide ions form a planar Cu_2I_2 four membered ring. The Cu···Cu distance of 3.028(2) Å is larger than that in other known examples of Cu_2X_2 rhombohedra.

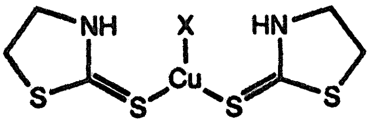


(22)

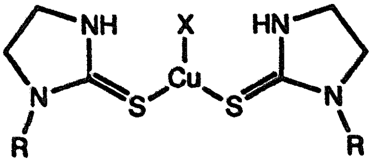


(23)

The X-ray structures of seven 3-coordinated complexes of copper(I) halides with thione ligands, [$CuXL_2$], where L = 1,3-thiazolidine-2-thione and X = Cl or Br (**24**), L = *N*-ethylimidazolidine-2-thione and X = Br, L = *N*-isopropylimidazolidine-2-thione and X = Cl or Br, and L = *N*-propylimidazolidine-2-thione and X = Cl or I (**25**) have been determined [20]. In all of the complexes, the copper centre lies in a trigonal-planar environment and the thiazolidine or imidazolidine rings show no major distortion from planarity. The presence of hydrogen bonding between the halogen atom and the NH group results in the complexes adopting a W-shaped conformation. The c3Cu NQR frequencies of these complexes depend, for a given halide on the S–Cu–S bond angle, with a decrease in angle producing an increase in resonance frequency: $\nu_{Cl} = 28.7 - 0.544\Delta\theta$ and $\nu_{Br} = 26.9 - 0.229\Delta\theta$ MHz, where $\Delta\theta$ is the difference between the S–Cu–S bond angle and 120°. This behaviour has been rationalised in terms of a partial field-gradient model of the resonance frequencies.



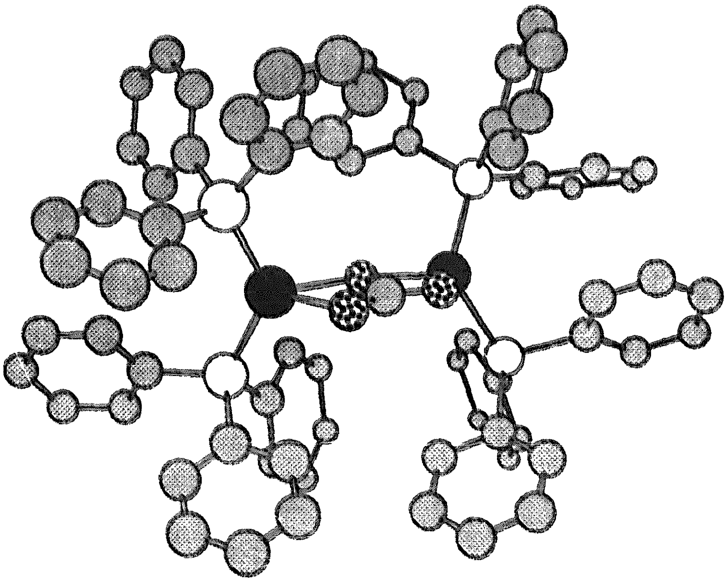
(24)



(25)

The X-ray structures of the copper(I) carbonate and bicarbonate complexes of triphenylphosphine are reported providing valuable insight into the coordination modes of these ligands bound to Cu^I in carbonic anhydrase and to transition metal catalysed organic reactions with carbon dioxide [21]. These are the first examples of (triphenylphosphine)copper(I) carbonates and bicarbonates to be structurally characterised, although a vast number of copper(II) complexes have been characterised. The dimeric structure of complex **(26)** contains two non-equivalent copper(I) ions possessing distorted tetrahedral geometries, where each metal centre is coordinated to two PPh_3 ligands and two oxygen atoms of an apportioned carbonate anion. The two copper(I) ions are bonded to the bridging oxygen of the carbonate ligand in an asymmetrical fashion with Cu···O distances differing by 0.09(1) Å. The Cu···P bond distances which average 2.24(1) Å are typical of bis(triphenylphosphine)copper(I) complexes. The bis(triphenylphosphine)cuprous bicarbonate complex exhibits a distorted tetrahedral geometry at each metal centre. Two symmetrically coordinated bicarbonates bridge the two copper ions to form a four membered planar $(Cu–O)_2$ ring. The coordination sphere of each copper(I) is completed by two triphenylphosphine ligands. The dimeric units are intermolecularly hydrogen-bonded at an O···O distance of 2.50 Å to provide polymeric chains.

(26)



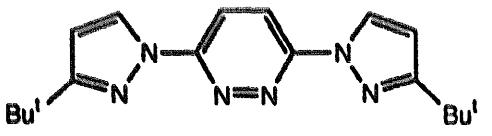
1,3-Bis(triphenylphosphonio)isophosphindolium bromide reacts with CuBr to give a dinuclear complex which is shown by X-ray crystallography to contain a

μ_2(P)-bridging cationic bis(triphenylphosphonio)isophosphindolium ligand [22]. The structure is composed of discrete dinuclear complexes LCu_2Br_3 which contain a planar, four-membered ring consisting of the P atom of the μ_2-coordinated ligand, a μ-bromine and the two trigonal planar copper atoms. The cationic ligand contains a delocalised 10π-electron system extending over both anellated rings and the bonding in the complex is best described in terms of electron-deficient three-centre bonds as in organometallic aryl copper compounds.

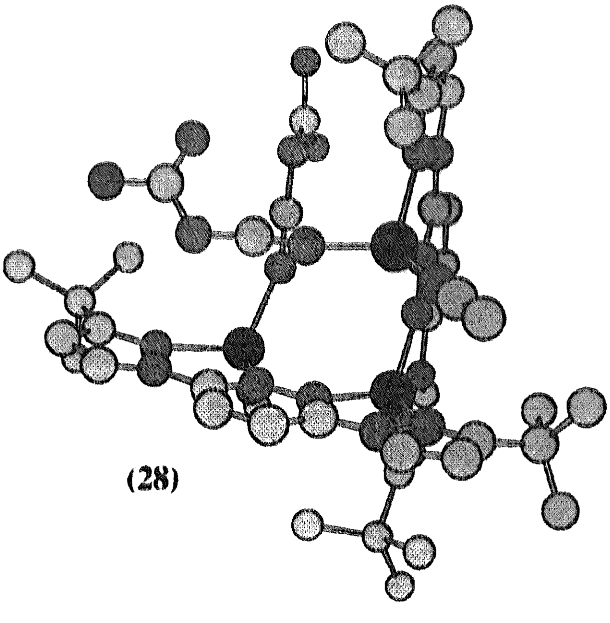
The synthesis and crystal structures of three dinuclear complexes with bridging trithiooxalate (trto) or 1,1-dithiooxalate (1-dto) are reported with Ag and Cu(I) ions [23]. The structure $[(Ph_3P)_2Cu]_2$(1-dto) shows a bridging 1-dto ligand linking the copper centres in a side-on/side-on symmetrical mode, but is far from being planar, exhibiting a torsion angle along the C–C bond of 19.3(5)°. This is in contrast to other dinuclear symmetrically-bridged thiooxalate complexes which are planar.

2.5. Trinuclear complexes

The salt $[Cu(\mu\text{-}\mathbf{27})_2\{Cu(cnge)(MeCN)\}_2](BF_4)_3 \cdot MeCN$ (**28**) (**27** = 3,6-bis[*N*-{3-*tert*-butyl)pyrazolyl}]pyridazine, cnge = 2-cyanoguanidine) containing a trinuclear copper(I) cation, has been synthesised by the addition of a dichloromethane solution of (**27**) to an acetonitrile solution of $[Cu(MeCN)_4](BF_4)$ containing cnge [24]. This structure is structurally reminiscent of the active site of ascorbate oxidase and comprises three copper atoms held together in an isosceles triangle (Cu···Cu = 3.62, 3.63 and 5.01 Å) by two approximately perpendicular (dihedral angle 86.9°) planar (**27**)bridging ligands.



(**27**)



(**28**)

2.6. Tetranuclear complexes

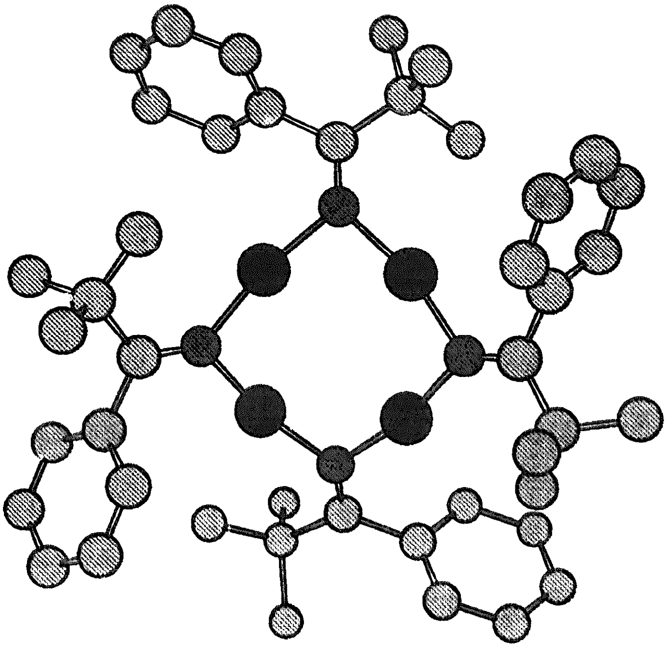
The complex formed by grinding together the solid sodium salt of 6-fluoro-2-hydroxypyridine (L) and hydrated copper nitrate has the formula $[\{Cu_2L_4\}_2]$ as determined by X-ray crystallographic analysis [25]. The complex consists of a dimer of dinuclear units linked by two μ-O atoms from the ligands. The four bridging ligands within each dinuclear unit are arranged head-to-head, with all of the nitrogen donor atoms attached to one copper and all of the oxygen donor atoms attached to the second, giving a dinuclear unit with approximate C_{4v} symmetry. The two distinct copper atoms have quite different geometries, one bound to five oxygen atoms and the other to four nitrogen atoms. The intra-dimer Cu···Cu distance is 2.54 Å, while the inter-dimer Cu···Cu distance is 3.12 Å. Recrystallisation of this complex from methanol-dichloromethane gave a polymeric complex $[\{Cu_4(OMe)_4L_4\}_n]$ which contains a tetranuclear array as a repeating unit with a rectangular array of copper atoms bridged alternately by two μ-O atoms from methoxide or by two 1,3-bridging ligands. The ligands within the tetramer are arranged in a head-to-head fashion which allows further inter-tetramer ligation to one of the copper atoms, leading to a polymeric species.

The group 11 metal imino complexes $[\{Cu[\mu\text{-}N{=}C(Bu^t)Ph]\}_4]\cdot$thf (**29**) and $[\{Cu[\mu\text{-}N{=}C(Bu^t)Ph]\}_4(PPh_3)_2]\cdot$6thf have been prepared by ligand-transfer reactions of the tris(imino)stannate complex $Sn[\mu\text{-}N{=}C(Bu^t)Ph]_3Li\cdot$thf with CuCl [26]. X-Ray crystallographic analyses show both complexes to have planar Cu_4 cores. In (**29**), the square-planar Cu_4 core ($Cu\cdots Cu_{av} = 2.76$ Å, $Cu\cdots Cu\cdots Cu_{av} = 89.9°$) is held together by imino ligands in a saddle-shaped arrangement ($Cu\text{-}N_{av} = 1.857$ Å). This *cis,trans,cis,trans*-arrangement around the copper centres presumably minimises steric crowding of the Bu^t and Ph groups on the periphery of the molecule. In $[\{Cu[\mu\text{-}N{=}C(Bu^t)Ph]\}_4(PPh_3)_2]\cdot$6thf, two phosphine ligands are coordinated to only the two opposite centres of the Cu_4 core and this forces the surrounding imino-ligand framework into a chair shaped (*cis,cis,trans,trans*) conformation. The Cu_4 core is distorted into a diamond shape in which the uncomplexed copper centres are forced into closer contact (3.540(2) Å) compared to the Ph_3-substituted copper centres (3.89 Å). These complexes are claimed to be the first structurally characterised imino group 11 metal complexes.

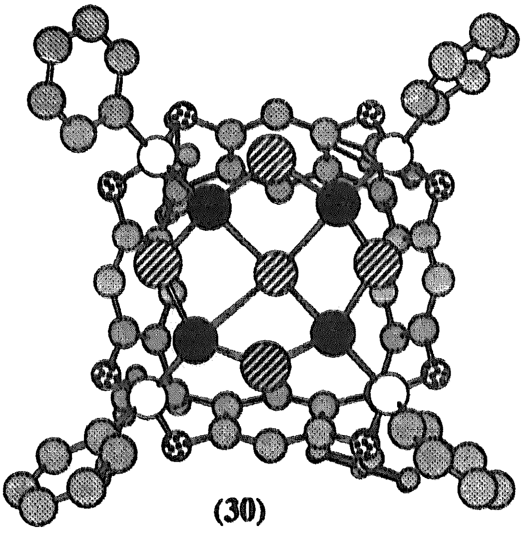
A bowl-shaped calixresorcinarene has been derivatised to incorporate four phosphate units to give a phosphonitocavitand (L) which can act as a tetradentate ligand [27]. This ligand has been used in the syntheses of several tetracopper(I) and tetrasilver(I) complexes, such as $[pyH]^+[(L)Cu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$ (**30**) and $[pyH]^+[(L)Ag_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$. The tetracopper(I) complex, (**30**), and the tetrasilver(I) complex have been shown to act as size-selective hosts for halide inclusion. Iodide is preferred over chloride as guest in (**30**) since it is large enough to coordinate to all four copper atoms in an unusual μ_4-face-bridging bonding mode.

2.7. *Cluster complexes*

The reaction system $(NH_4)_3[VS_4]/CuCl/R_2dtcNa/PhSNa$ in dmf (Scheme 1) affords two types of V/Cu/S complexes [28]. One is the VS_4Cu complex $[VS_4Cu_4(R_2dtc)n(PhS_4\text{-}n]^{3-}$ ($R_2 = Et$ or OC_4H_8; n = 0, 1, or 2; R_2dtc^- = dialkyldithiocarbamate), the other one is the cubane-like cluster $[V_2Cu_2S_4(R_2dtc)_2(PhS)_2]^{2-}$ ($R_2 = Me_2$ or OC_4H_8). All of the VS_4Cu_4 complexes



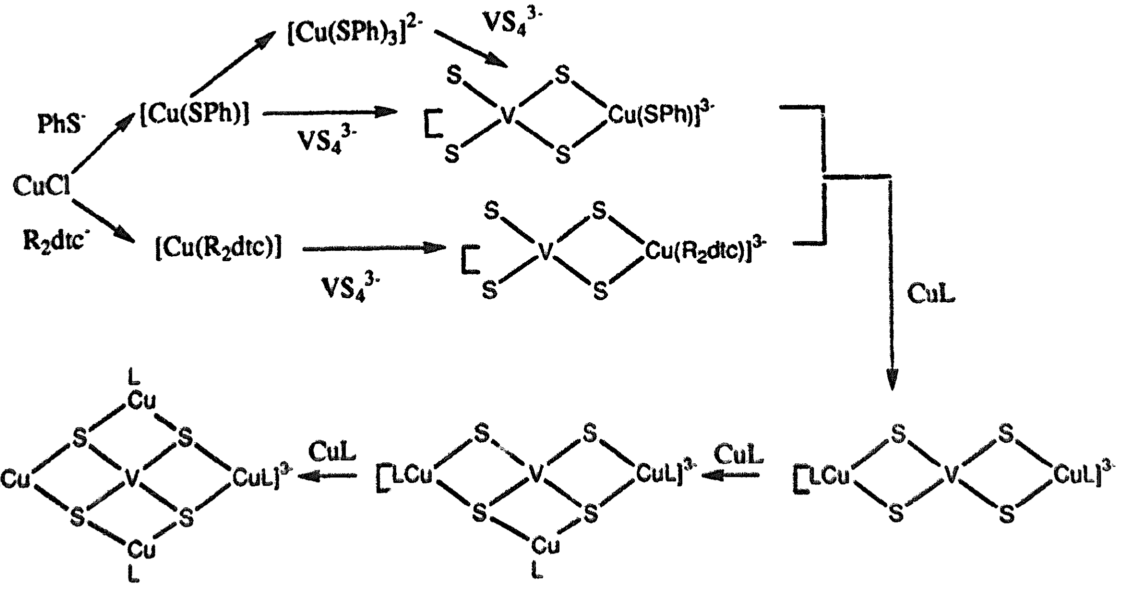
(29)



(30)

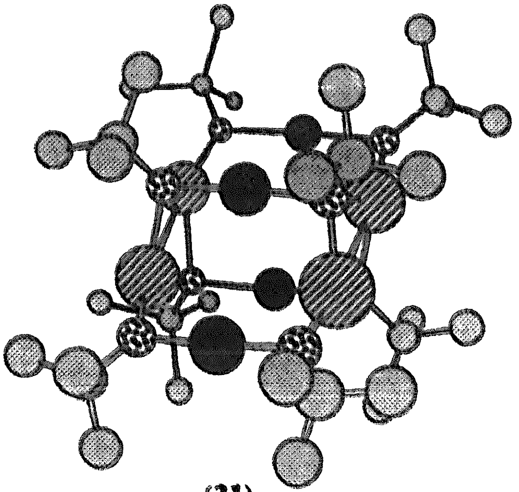
contain a VS_4 tetrahedral core and have a near planar VCu_4 array. The overall symmetry of the VS_4Cu_4 unit closely approaches D_{2d}, but the presence of the ligands lowers the symmetry of the anions. Structural, spectroscopic and magnetic data indicate that the VS_4Cu_4 complexes contain metal ions with formal oxidation levels of V(V)+4Cu(I). Vanadium-51 NMR spectra of dmso solutions of the complexes show that disproportionation of the complexes occurs.

The heterometallic Cu(I) alkoxides $Li_4Cu_4(OCMe_3)_8$ (**31**) and $Ba_2Cu_4(OCEt_3)_8$ (**32**) have been synthesised from the component single metal alkoxides in anhydrous thf solution [29]. Compound (**31**) sublimes without decomposition under vacuum at 150°C, while (**32**) is non-volatile. The crystal structures of both structures were



Scheme 1.

determined. Compound (**31**) has a nearly identical structure to $Na_4Cu_4(OCEt_3)_8$ consisting of two puckered M_2O_2 rings related by a centre of symmetry and joined at the oxygen atoms by two bridging copper atoms and at the M edges by two nearly linear O–Cu–O units. Compound (**32**) has a $Ba_2(OR)_2$ ring containing the centre of symmetry and is bridged by two $Cu_2(OR)_3$ units that are nearly perpendicular to the Ba_2O_2 ring. The two $BaCu_2O$ planes in (**32**) are parallel, but separated by 0.48 Å. Hydrolysis of (**31**) and (**32**) in thf afforded an orange or orange-brown solid that was converted to the mixed metal oxide by thermolysis, but copper and Cu_2O were also produced from the $Li_4Cu_4(OCMe_3)_8$ hydrolysis product.



(**31**)

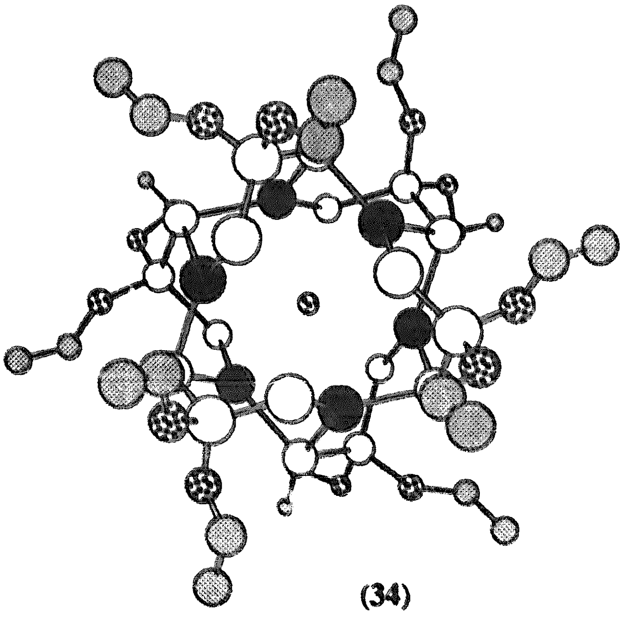
Methylisothiocyanate, MeN=C=S, in ethanol reacted with copper(I) giving a tetranuclear complex $[Cu\{\mu_3\text{-}SC(=NMe)(OEt)\}]_4$ [30]. The similar reaction of allylisothiocyanate, $CH_2=CHCH_2N=C=S$, and copper(I) in methanol gave a hexanuclear complex, $[Cu\{\mu_3\text{-}SC(=NC_3H_5)(OMe)\}]_6$ (**33**). They show tetrahedral Cu_4 and octahedral Cu_6 cores, respectively. The two structures have two structural similarities; a thiolato moiety $[-N=C(S^-)-]$ which bridges three copper atoms with a monodentate nitrogen atom and a bridging sulfur atom and a trigonal planar geometry for copper(I) coordinated by one nitrogen atom and two sulfur atoms. The structure of (**33**) has a paddle wheel-like structure with six planes made by the ligands. Six copper atoms form a distorted octahedron and six surfaces of the eight are capped by six $C_3H_5N=C(OMe)S^-$ ligands (formed *in situ*). Each copper atom shows a trigonal, almost planar geometry coordinated by one nitrogen and two sulfur atoms.

(**33**)

The preparation of the heptanuclear heterometallic clusters $[VS_4(Cu(PPh_3))_5Br_2CuX]$ and $[VS_4(CuPPh_3)_5Br_2CuX]\cdot CH_2Cl_2$ ($X=0.5Br+0.5Cl$) by heating a mixture of $(NH_4)_3VS_4$, CuCl, PPh_3 and Et_4NBr in a solid state reaction at low temperature has been investigated and structures characterised by X-ray crystallographic analysis [31]. The clusters consist of a tetrahedral VS_4 core bound to an octahedral array of six copper atoms which have two different coordination environments, *viz* trigonal planar and tetrahedral. Each copper atom is bound to a terminal ligand, five of these are PPh_3 molecules and one a halogen atom. The geometries of the two additional bridging bromine atoms are different in the two clusters, in $[VS_4(Cu(PPh_3))_5Br_2CuX]$, both bromine atoms are μ_2 atoms, while for

$[VS_4(CuPPh_3)_5Br_2CuX]\cdot CH_2Cl_2$ ($X=0.5Br+0.5Cl$) one is μ_2-Br and the other μ_3-Br.

The syntheses and structures of the first sulfur-centred Cu_8 cubic cluster, a cluster in which each edge of the cube is bridged by a sulfur atom of the dithiophosphate ligands, and the first example of an octahedral Cu_6 cluster formed with a dialkyl dithiophosphate ligand are reported [32]. Treatment of $[Cu(CH_3CN)_4]PF_6$ with an equimolar amount of $(NH_4)[S_2P(O^iPr)_2]$ in the mixed solvent system CH_2Cl_2/H_2O for 1 day afforded a light brown solution from which two products were isolated. The major product (>60%) was the tetranuclear complex $Cu_4[S_2P(O^iPr)_2]_4$ while the Cu_8 cluster $[Cu_8[S_2P(O^iPr)_2]_6(S)]$ (**34**) was isolated as an air stable colourless crystalline material in <5% yield. A third dialkyl dithiophosphate cluster $[Cu_6\{S_2P(OEt)_2\}_6]\cdot 2H_2O$ was obtained in high yield when $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2/H_2O was treated dropwise with NH_4OH to adjust the pH to 9.5. After the addition of $NH_4[S_2P(OEt)_2]$ and stirring overnight, evaporation of the solvent afforded the hexanuclear complex. The structure of (**34**) reveals a sulfur-centred Cu_8 cubic cage with six diisopropyl dithiophosphate ligands bridging across each cube face. The interstitial atom was established to be S^{2-} from crystallography. The copper atoms are located at the corners of a nearly perfect cube with the average Cu···Cu distance along the edge of the cube being 3.105(6) Å and with an average Cu···Cu···Cu angle of 90.6(3)°. The 12 μ_2-S atoms are arranged in a nearly regular icosahedron. In addition to the trigonal coordination by three sulfur atoms, each copper atom is weakly bound to the central sulfur atom at a mean distance of 2.694(2) Å. This structure is claimed to be the first with a μ_8-S bridging ligand. The cluster in $[Cu_6\{S_2P(OEt)_2\}_6]\cdot 2H_2O$ is composed of a trigonal antiprism of the six Cu(I) atoms with Cu···Cu distances of 3.13 and 4.31 Å. The water molecules appear to be hydrogen-bonded to the non-bridging S atoms and TGA indicates that these water molecules are strongly held to the cage.

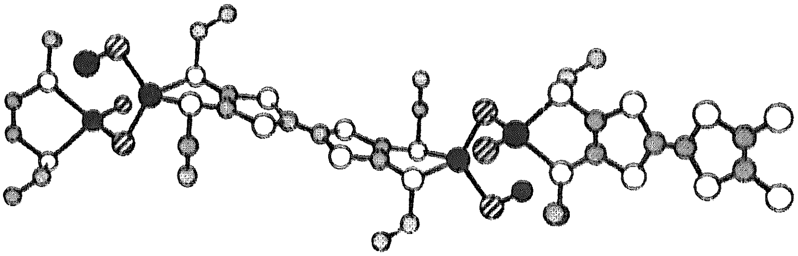


(**34**)

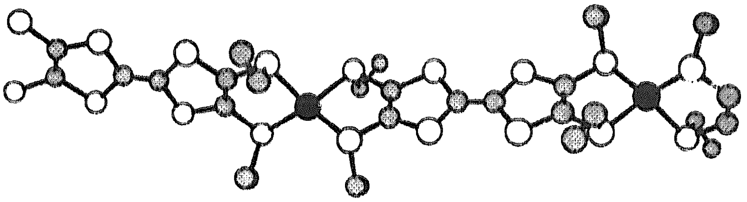
2.8. Polymeric complexes

A series of complexes incorporating tetrathiafulvalene units have been synthesised with the aim of developing potential organic superconductors. In one study, two copper(I) complexes with tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF), $[(CuCl)_2TTC_2\text{-}TTF]$ (**35**) and $[(CuBr)_2TTC_2\text{-}TTF]$ (**36**), have been synthesised and characterised by spectroscopic and X-ray crystallographic methods [33]. Both (**35**) and (**36**) are neutral 2:1 (metal/ligand) complexes in which each metal ion is coordinated in a distorted tetrahedral geometry to two bridging halide ions and two sulfur atoms from TTC_2-TTF. The complex (**35**) has a 2-dimensional structure in which TTC_2-TTF molecules are connected between novel helical CuCl frames, while (**36**) has a one-dimensional polymeric chain structure. The average Cu–Cl and Cu–S bond lengths are 2.282(2) and 2.405(2) Å in (**35**) and Cu–Br and Cu–S bond lengths are 2.445(2) and 2.349(1) Å in (**36**). Compounds (**35**) and (**36**) were doped with iodine to afford $[(CuCl)_2TTC_2\text{-}TTF]I$ and $[(CuBr)_2TTC_2\text{-}TTF]I$ which exhibit electrical conductivities of 6×10^{-7} and 3×10^{-7} S cm^{-1}, respectively at 25°C for compacted pellets. The reaction of copper(I) perchlorate and tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF) in acetone under argon has resulted in the formation of a linear coordination polymer $[Cu(TTC_2\text{-}TTF)]ClO_4$ (**37**) [34]. Study of the polymer by X-ray crystallography shows it to be a 1:1 metal:ligand complex in which each copper(I) ion is tetrahedrally coordinated to four sulfur atoms from the bridging TTC_2-TTF molecules to form coordination polymeric chains separated from each other by the perchlorate anions in the crystal. Doping of the crystal with iodine afforded $\{[Cu(TTC_2\text{-}TTF)]ClO_4\}I$ which behaves as a semiconductor exhibiting a conductivity of 6×10^{-4} S cm^{-1} at 25°C for a compacted pellet.

(35)

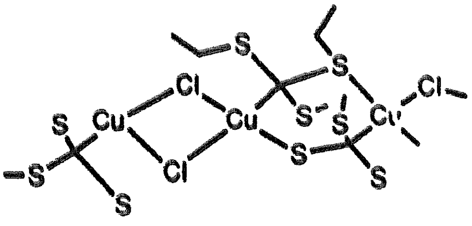


(37)

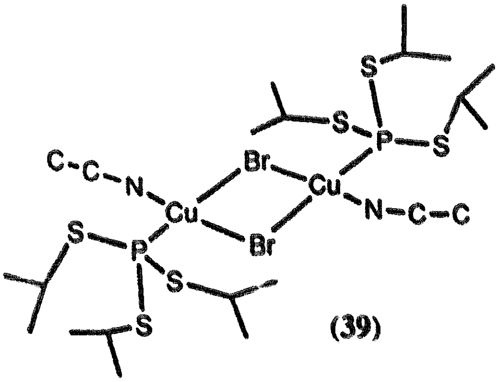


Three Cu(I) complexes with tetrakis(methylthio)tetrathiofulvalene (TMT-TTF) $[(Cu_2(\mu\text{-}X)_2(\mu\text{-}TMT\text{-}TTF)]_\infty$ (X = Cl, X = Br, and X = I,) have been synthesised and their molecular structures and packing determined by X-ray crystallographic techniques [35]. The chloro-bridged species displays a 2D-sheet composed of TMT-TTF molecules arranged between zigzag frames of CuCl. S···S contacts of 3.53 and 3.63 Å between the 2D-sheets results in an overall 3D-structure. The bromo complex has a 2D-structure in which TMT-TTF molecules are connected between helical chains of CuBr with S···S contacts of 3.68 Å between neighbouring molecules. In the iodo complex, methyl thioethyl groups of TMT-TTF are coordinated to the copper atoms of rhomboid Cu_2I_2 to give linear chains. Iodine-doping of the complexes afforded compounds which showed a new broad band at ≈880 nm in the absorption spectra which is indicative of the oxidation of the TMT-TTF molecules and gave electric conductivities of $10^{-3.6}$, $10^{-2.1}$ and $10^{-1.7}$ S cm^{-1}, for the chloro, bromo and iodo species, respectively.

A series of copper(I) complexes with trialkyl trithiophosphite ligands $[(EtS)_3PCuHal$ with Hal = Cl, Br and I, (Hal = Cl, **(38)**) and $({}^{i}PrS)_3PCuBrCH_3CN]$ **(39)** have been prepared and characterised by X-ray crystallographic analysis in order to investigate the possible binding modes of potentially terdentate ligands [36]. The complexes of the copper(I) monohalides with triethyl trithiophosphite appear to be isostructural, exhibiting a didentate coordination mode *via* the phosphorus atom of one thiophosphite molecule and the sulfur atom of another resulting in the formation of polymeric chains. This is claimed to be the first example of didentate coordination for compounds containing a P–S bond. In the complex of copper monobromide with triisopropyl trithiophosphite in acetone, monodentate coordination *via* the phosphorus atom and *via* the nitrogen atom of the acetonitrile water is observed, with the sulfur atoms remaining uncoordinated. This is the more usual coordination mode for ligands containing a P–S bond. This results in a dimeric copper(I) complex. Thus the type of coordination depends on the reaction conditions and the bulkiness of the alkyl groups bonded to the sulfur atoms.



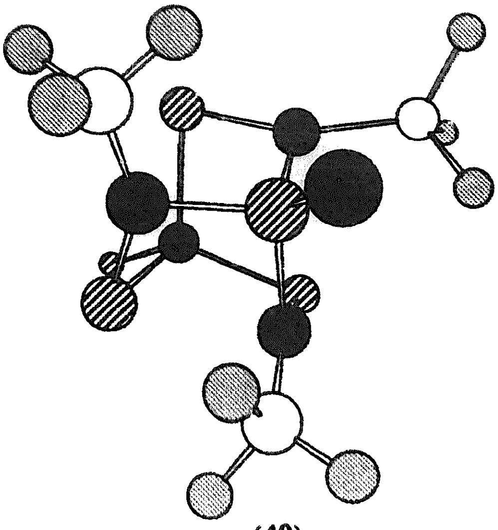
(38)



(39)

Copper(I) halide-trimethylphosphine adducts were prepared by the reaction of CuHal with PMe_3 in a benzene suspension [37]. The X-ray structures of $[(Me_3P)_2Cu(\mu\text{-}I)_2Cu(PMe_3)_2]$ and $[\{Cu_4Cl_4(PMe_3)_3\}_\infty]$ **(40)** have been determined. The latter is a one-dimensional polymer of quasi-cubanoid Cu_4Cl_4 units linked by Cu–Cl bonds between the four co-ordinate apical atoms of successive Cu_4Cl_4 units. A comparison of the Raman spectra for the complexes has allowed the first rational assignment of $\nu_{(MP)}$ modes for multinuclear complexes of this type.

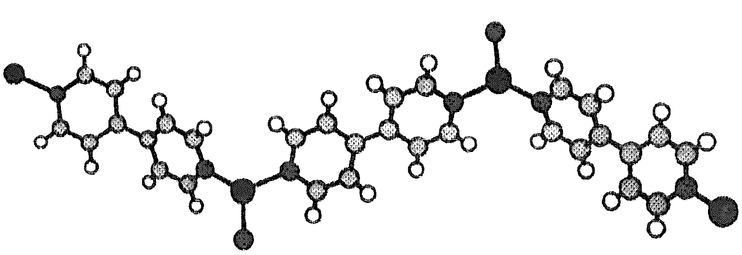
Hydrothermal synthesis is presented as a route to accessing crystalline, metal–



(40)

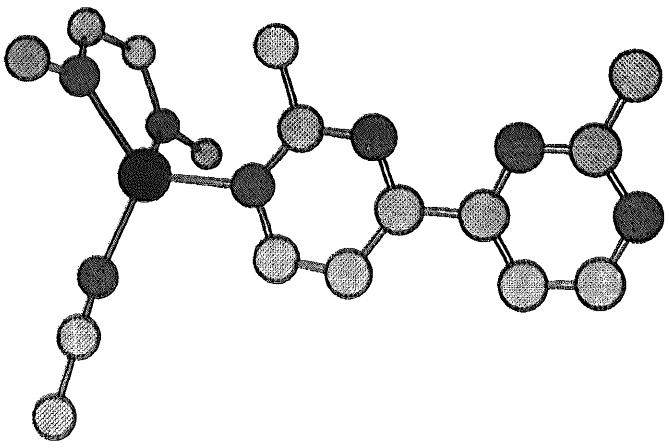
organic, open frameworks having extended channel systems and composed of uncommon metal coordination [38]. This is demonstrated for the extended framework in crystalline $Cu(4,4'\text{-bpy})_{1.5} \cdot NO_3(H_2O)_{1.25}$ **(41)**. A mixture of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.74 mmol), 4,4'-bpy (1.11 mmol) and 1,3,5-triazine (0.49 mmol) in deionised water (15 ml) was transferred to a stainless steel bomb which was sealed and placed in a programmable furnace. The temperature was raised to 140°C at 5 deg min^{-1} and held there for 24 h then cooled to 90°C at 0.1 deg min^{-1}. After holding at 90°C for 12 h the temperature was cooled to 70°C at 0.1 deg min^{-1} and held for another 12 h and finally cooled to room temperature at 0.1 deg min^{-1}. This resulted in the formation of rectangular parallelpiped orange crystals of $Cu(4,4'\text{bpy})_{1.5} \cdot NO_3(H_2O)_{1.25}$. X-Ray structural determination of a single crystal showed an extended cationic framework composed of slightly distorted trigonal planar copper(I) centres linked by rod-like 4,4'-bpy ligands to form six porous and identical interpenetrating 3D-networks. Unlike many other solids with interpenetrating networks, the extent of interpenetration in this structure does not fill all the available voids but leaves a significant portion of it in the form of two rectangular channels (8 × 6 and 4 × 5 Å) which are occupied by nitrate anions that are hydrogen bonded to solvent water molecules. Attempts to prepare the complex outside the bomb failed.

(41)



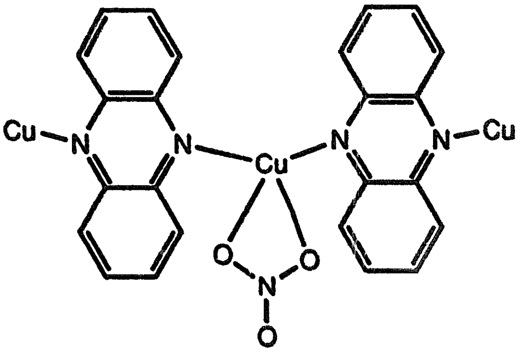
The synthesis of $[Cu(6,6'\text{-dimethyl-}2,2'\text{-bipyrazine})_2](BF_4)$, $[Cu(2,2'\text{-dimethyl-}6,6'\text{diphenyl-}4,4'\text{-bipyrimidine})_2](PF_6)$ **(42)** and *catena*-poly-[(2,2'-dimethyl-4,4'-

bipyrimidine-*N*,*N*′,*N*″)bis(acetonitrile)-dicopper(I) (**43**) have been prepared [39]. Crystallographic analysis of the last two compounds have shown that both the inner and outer nitrogen atoms of bipyrimidine molecules may be potentially involved in the complexation process with transition metal ions. In (**42**), a steric effect from the phenyl rings prevent the outer nitrogen atoms of bipyrimidine from complexing with the Cu(I) ion. The torsion angle between the two pyrimidine rings is 3° and with the phenyl groups nearly in the same plane as the pyrimidine rings. The bipyrimidine molecules are stacked in a parallel manner at a distance of 3.5 Å. In the absence of these groups, as in (**43**), the two types of nitrogen atoms are linked to the central copper atom. This results in the formation of a helicoidal polymeric structure. The chains interact by face-to-face bipyrimidine molecules with overlapping distances of 3.6 Å. The PF_6 anions are located in the free spaces between two parallel chains. The torsion angle between the two pyrimidine rings is slightly larger than (**42**) at 9°. Both structures show the copper centres to have distorted tetrahedral geometries.



(**43**)

Four novel copper(I) phenazine (phz) compounds, $[\{Cu(phz)(NO_3)\}_\infty]$ (**44**), $[\{Cu(acr)_2(NO_3)\}_2(phz)(H_2O)]$, (acr = acridine) $[\{Cu_2(phz)(PFO_3)\}_\infty]$ (**45**) and $[\{[Cu(phz)(MeCN)]_2(C_{16}H_{10})(PF_6)_2\}_\infty]$ (**46**) ($C_{16}H_{10}$ = pyrene) have been synthesised and their molecular structures and packing have been determined [40]. The copper atoms in (**44**) are bridged by phz forming an infinite one-dimensional zigzag chain. These bridging phz molecules have a π–π interaction between neighbouring chains forming an infinite columnar stack of phz molecules. The monomer complex, $[\{Cu(acr)_2(NO_3)\}_2(phz)(H_2O)]$, has an infinite columnar stack of metal-free phz and metal-coordinated acridine molecules. The copper(I) ions in $[\{Cu_2(phz)(PFO_3)\}_\infty]$ are bridged by phz and PFO_3^{2-} alternately. The resulting one-dimensional chains are connected through a tetradentate, asymmetric PFO_3^{2-} bridge, with π–π interaction between the phz molecules forming an infinite two-dimensional sheet structure. The backbone of (**46**) is almost the same as in (**44**), except that a pyrene molecule is intercalated into every other phz stack in a one-dimensional chain. The electrical conductivity of (**45**) was determined as $1\times10^{-7.6}$ S cm^{-1} and that of $[\{[Cu(phz)(MeCN)]_2(C_{16}H_{10})(PF_6)_2I_{1.3}\}_\infty]$, obtained by iodine doping of (**46**), determined as $1\times10^{-4.7}$ S cm^{-1}. The electronic absorption bands of compounds (**44**), (**45**) and (**46**) which appeared at around 700 nm are characteristic of copper(I) coordination polymers with bridging phz ligands



(**44**)

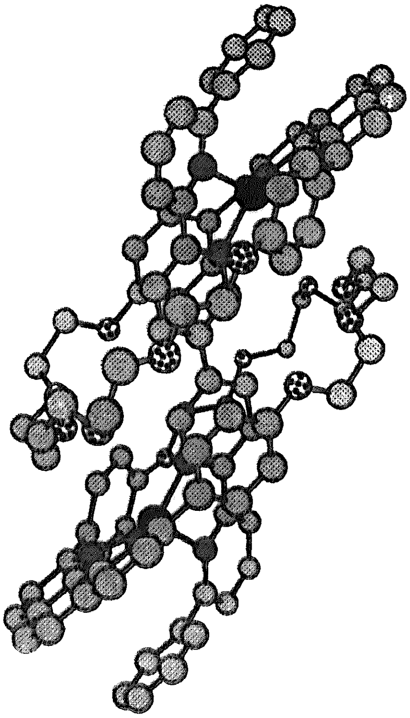
Copper(I) salts have been shown to react with pyrazinic acid (pyz-H) to give complexes of the types Cu(pyz-H)$_2$X·2H$_2$O for X=Cl or Br, Cu(pyz-H)X·H$_2$O for X=Br, NO$_3$ or ClO$_4$ and Cu$_2$(pyz-H)$_n$X$_2$·3H$_2$O where n=3 for X=Cl and n=2 for X=I [41]. Spectroscopic analysis suggest that pyz-H acts as a monodentate ligand in the Cu(pyz-H)$_2$X·2H$_2$O complexes and as a N,O-didentate neutral ligand in the hydrated 1:1 complexes, whereas Cu$_2$(pyz-H)$_3$Cl$_2$·3H$_2$O contains both types of acid molecules. The structure of the trihydrated copper(I) iodide complex of pyrazinic acid was determined by X-ray crystallographic analysis and shows it to contain asymmetric Cu$_2$(pyz-H)$_2$I$_2$·3H$_2$O units which are linked together forming a stair or ribbon polymeric structure with tetrahedral copper(I) environments. The two pyrazinic acid molecules in the asymmetric unit behave differently: one as a neutral ligand and the other as a zwitterion. Both molecules, however act as monodentate ligands. The neutral pyrazinic acid molecule forms hydrogen bonds with two water molecules and the zwitterion forms the third water molecule through a hydrogen bond. The Cu···Cu distance within the cyclic Cu$_2$I$_2$ unit is 2.771(1) Å.

2.9. *Supramolecular complexes*

The self-assembly of a rigid-rack multinuclear complex of rotaxane type is reported [42]. The system is built up from a linear ligand built on bpy subunits and a macrocyclic phenanthroline component. Assembly of the rack system was achieved using metal ions having a preference for a tetrahedral geometry, *i.e.* Cu(I). The phen unit was used in order to prevent two such ligands from coordinating to the same copper centre and thus competing with the multicomponent self-assembly process. The construction of the rack-like structure was confirmed by X-ray crystallographic analysis of (**47**) which showed that two macrocycles are threaded onto the linear quaterpyridine ligand to form a dimetallic rotaxane in which the ligand presents a planar arrangement between the central rings. The structure is centrosymmetric and is in the transoid conformation; the pentaoxyethylene fragment of one fragment of one macrocyclic ligand faces the phen fragment of the other ligand on the qtpy ligand. The copper(I) centres are encapsulated by the phenyl groups on the 6-position of the qtpy ligand and on the 2- and 9- positions of the phen units.

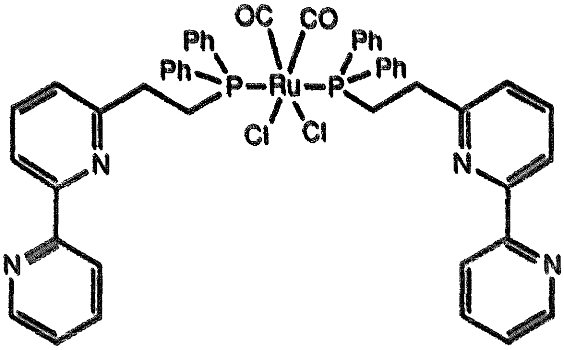
The phen units and the Ph groups on the 6-position of the qtpy are oriented in a face-to-face arrangement separated by ≈3.4 Å, suggestive of a π-stacking interaction. The complexes are all formed in high yield (>85%) by simply mixing the components together at room temperature or heating in the case of the larger system.

(47)

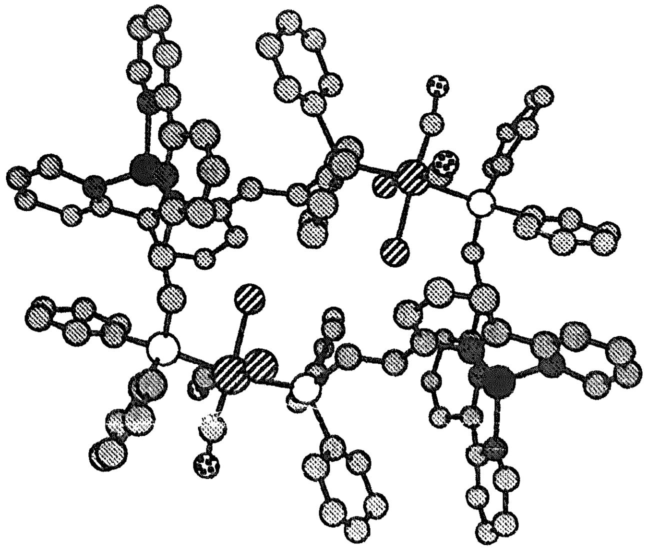


The reaction of the metallo-synthon comprising two bipyridine-phosphine ligands (**48**) in a *trans*-arrangement, with $[Cu(MeCN)_4]ClO_4$ results in the self-assembly of a 36-membered metallocycle (**49**) containing two ruthenium and two copper atoms in a yield of 92% [43]. The X-ray structure shows the coplanar metal ions form a parallelogram with sides of 8.078(5) and 6.767(5) Å with interior angles of ≈113° and ≈67°. Each Cu(I) cation shows a tetrahedral coordination with a dihedral angle of 102.5(1)° between the mean planes of the bipyridine subunits. The wrapping of the two bis-bpy metallosynthons around the two copper centres leads to the formation of an achiral complex and not the alternative double-stranded helix.

(48)



A [2+2] condensation reaction was used to prepare 32-membered, (**50**), and 34-membered, (**51**), macrocyclic Schiff base type ligands with $(N_2S_2)_2$ donor sets [44].



(49)

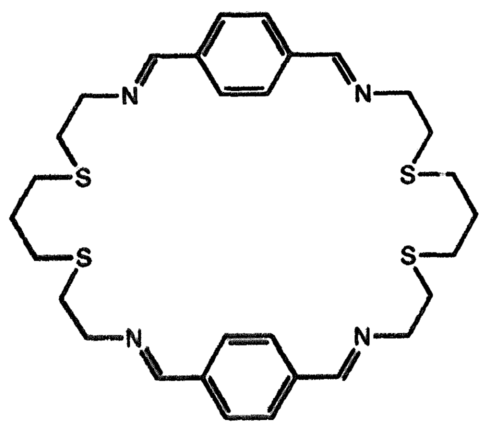
The fact that both imines and thiaethers favour soft metal centres has been used in the synthesis of their dicopper(I) complexes. The X-ray structures of the complexes (**52**), which crystallise as racemates, are rather similar, both having the following features: i) the two N_2S_2 donor sets are each tetrahedrally coordinated to the Cu^I centres, ii) the two bridging *para*-substituted phenyl rings are parallel, about 3.5 Å, which indicates stabilisation by π-stacking, iii) the dihedral angles between the bridging phenyl rings are about 80°, resulting in a double helical arrangement (figure-of-eight) of the ligand backbone. The distance between the two copper centres is about 7.8 Å in both compounds. ^1H NMR spectroscopic studies show the methylene protons of the free ligand (**51**) are chemically equivalent (singlet at δ 2.68), while for the dicopper copper(I) complex of (**51**), the methylene protons are diastereotopic and appear as a single AX system with a geminal coupling of 10.5 Hz and a chemical shift difference of $\Delta\delta$ 1.5. This indicates that the free ligand has an open macrocyclic structure on the NMR spectroscopic timescale while the dicopper complex is chiral in solution and kinetically inert on the NMR spectroscopic timescale. The cyclic voltammogram of the dicopper(I) complex of (**51**) shows a single oxidation wave at $E_{1/2} = 1.34$ (vs NHE) showing that the two copper centres behave independently.

3. Copper(II)

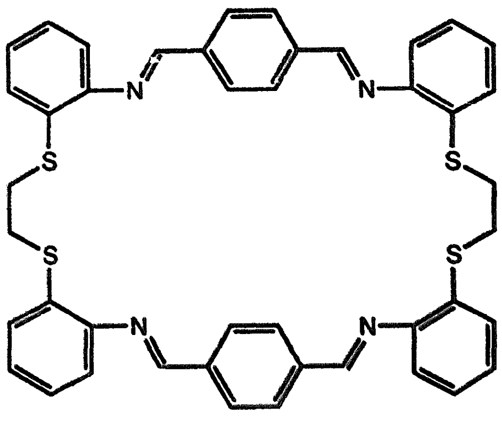
3.1. Mononuclear complexes with macrocyclic ligands

3.1.1. Nitrogen coordination

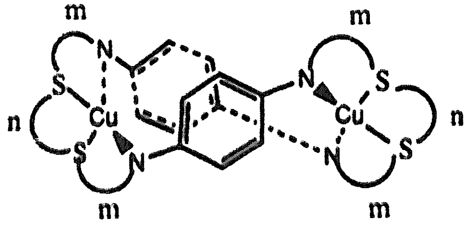
The effect of an increasing electronic preference for octahedral *vs* trigonal prismatic coordination on the stereochemistry of the dicationic species $[M^{II}L]^{2+}$ has been studied in the reaction of the hexadentate ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-



(50)



(51)



(52)

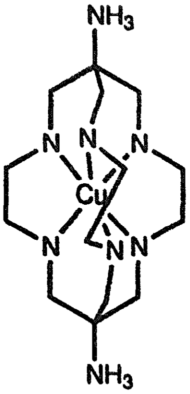
1, n = trimethylene, m = ethylene
2, n = ethylene, m = phenylene

triazacyclononane (L) in ethanol with perchlorate salts of divalent transition metal ions $M^{II}(ClO_4)_2.6H_2O$ to give the crystalline salts $[ML](ClO_4)_2$ (M = Mn, Fe, Co, Cu) [45]. The copper ion (d^9) is five-coordinate with a square-based pyramidal CuN_5 polyhedron with one uncoordinated *o*-aminobenzyl arm. In the cases of Mn, Fe and Co, the salts are isostructural with the complex $[ZnL](ClO_4)_2$, for which it was shown that the zinc ion is in a distorted trigonal prismatic environment of six nitrogen donor atoms. Two of the six-membered aniline chelate rings adopt a boat whereas the third has a twist-boat conformation.

The hexaamine complexes $[M\{NH_3)_2sar\}]^{4+}$ and $[M\{NMe_3)_2sar\}]^{4+}$ (M = Cu(II), Zn(II); sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) have been synthesised and characterised as $[M\{NH_3)_2sar\}](NO_3)_4 \cdot H_2O$ (**53**) and $[M\{NMe_3)_2sar\}](ClO_4)_4$ [46]. Visible-near-infrared absorption, circular dichroism, magnetic circular dichroism and electron paramagnetic resonance spectroscopic studies reveal distorted CuN_6 chromophores. The trigonal distortions arise from the steric requirements of the ligands, whereas the tetragonal distortions arise from Jahn–Teller coupling in the Cu(II) complexes. Partial resolution of $[M\{NMe_3)_2sar\}]^{4+}$ into its enantiomeric forms was achieved to give the first stable chiral molecule where Cu(II) is the stereogenic atom.

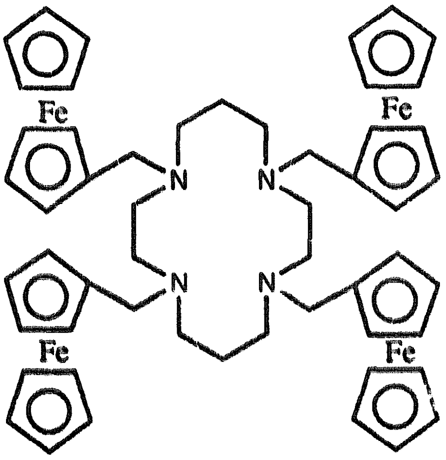
As part of a study in developing potential electrocatalysts, small crystals of $[Cu(\mathbf{54})](ClO_4)_2$ were isolated from the reaction of Fc_4cyclam (**54**) with $Cu(O_2CMe)_2 \cdot H_2O$ in methanol [47]. The crystal structure shows the copper centre to be coordinated to four coplanar nitrogen atoms from the ligand and with the Fc_4cyclam ligand showing the more thermodynamically favourable isomer with

(53)



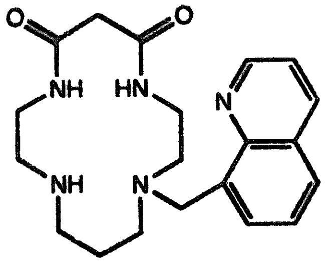
the two ferrocenylmethyl groups above the N_4 plane and the remaining two below the N_4 plane. The ligand and the copper complex were investigated by electrochemical studies. The free ligand shows a single oxidation wave at $E_{1/2}=0.385$ V *vs* SCE in its cyclic voltammogram. The addition of copper to the solution resulted in the solution turning blue in colour and a shift in the half-wave potential to a more anodic value (0.479 V). A similar value was observed for the complex $[Cu(Fc_4cyclam)](ClO_4)_2$ as well as an additional reduction wave at $E_{1/2}=-0.142$ V which is attributed to the reduction of the copper(II) central atom.

(54)

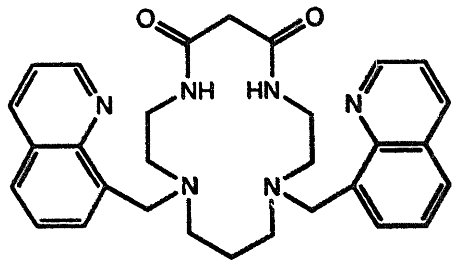


Two macrocyclic dioxotetraamine ligands 4-(quinolin-8-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (**55**) and 4,7-bis(quinolin-8-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (**56**) have been synthesised [48]. The resulting dioxomacrocycles readily coordinate to Cu^{2+} with a concomitant double deprotonation of the ligands. The absorption spectra show remarkable red shifts for the band maxima (598 nm for $[Cu^{II}(\mathbf{55}\text{-}2H)]$ (**57**) and 600 nm for $[Cu^{II}(\mathbf{56}\text{-}2H)]$ (**58**)) in comparison to that of the copper(II) complex of the unsubstituted ligand (516 nm). In (**57**) the Cu atom is five coordinate and forms a distorted square-based pyramid in which the nitrogen atom of the quinoline pendant is at the apical site. This apical bond is longer than the equatorial bonds (2.266(3) *vs* 1.985(3) Å, respectively). In complex (**58**) the copper centre is again five-coordinate with one of the quinoline pendants coordinated while the other remains uncoordinated.

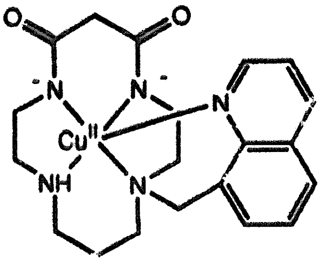
(55)



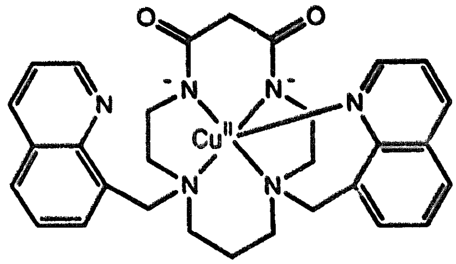
(56)



(57)

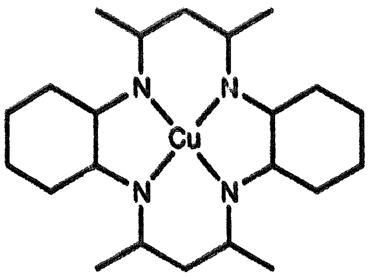


(58)



The reaction of equimolar amounts of Li_2(tmtaa) (H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetrazacyclotetradecine) with $Cu(O_2CMe)_2$ afforded the complex [Cu(tmtaa)] (**59**) in quantitative yield [49]. The solid state structure of this complex shows it to have a saddle conformation, similar to that of the ligand itself. The Cu centre is displaced from the N_4 plane by only 0.070 Å and the average Cu–N distance is 1.929 Å. The electronic structure of the complex strongly resembles that of the unmethylated congener [Cu(taa)], in spite of the quite different conformation of the two macrocyclic ligands. This is explained in terms of negligible electronic effects of the deformation from planarity on going from taa to tmtaa on the nature and energy of the macrocycle orbitals involved in the interactions with the metal.

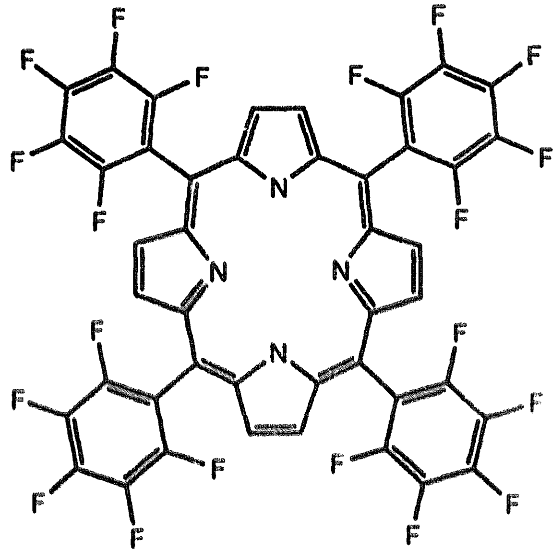
(59)



Using a combination of the angular overlap model (AOM) and molecular mechanics (MM) on a series of copper(II) tetraamines ($[Cu((R)\text{-ahaz})((S)\text{-ahaz})]^{2+}$, [(*R*)-ahaz = (*R*) -3-aminohexahydroazepine, (*S*)-ahaz = (*S*)-3-aminohexahydroazepine], $[Cu((S)\text{-ahaz})_2(OH_2)]^{2+}$, $[Cu(mn[13]aneN_4)(OH_2)_2]^{2+}$, [mn[13]ane$N_4$ = 12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane], $[Cu(mn[13]aneN_4)(OH_2)]^{2+}$, $[Cu(mn[14]aneN_4)(OH_2)]^{2+}$, [mn[14]ane$N_4$ = 6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane], $[Cu(mn[15]aneN_4)(OH_2)]^{2+}$, [mn[15]ane$N_4$ = 10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane], $[Cu(mn[15]aneN_4)(OH_2)_2]^{2+}$, $[Cu(mn[16]aneN_4)(OH_2)]^{+}$, [mn[16]ane$N_4$ = 3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane] and $[Cu(en)_2(OH_2)_2]^{2+}$) with square planar, square pyramidal and distorted octahedral chromophores exhibiting various degrees of tetragonal distortion of the central coordination plane, has produced a series of structures in good agreement with published X-ray structures and the two crystal structures determined in this study [50]. The spin Hamiltonian parameters and electronic transitions, estimated with the angular overlap model based on the strain energy minimised structures of the chromophores, where water is generally used as the axial ligand are in reasonable agreement with the calculated spectroscopic parameters based on experimental structures and with the experimental spectroscopic data.

Fluorine-19 NMR spectra of a series of halogenated porphyrins have been used to create a spectral library of different types of fluorine splitting patterns for tetrakis-(pentafluorophenyl) porphyrins (**60**) complexed with diamagnetic and paramagnetic metal ions [151]. The paramagnetic shift, line broadening and fine structure of the resonances from the peripheral pentafluorophenyl rings are found to be dependent on the symmetry and core environment of the porphyrin macrocycles. This study shows that in combination with crystal structure data, ^{19}F NMR spectroscopy helps to define the behaviour of the halogenated porphyrins in solution.

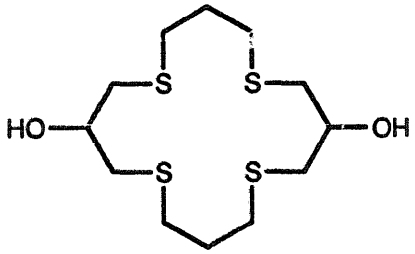
(60)



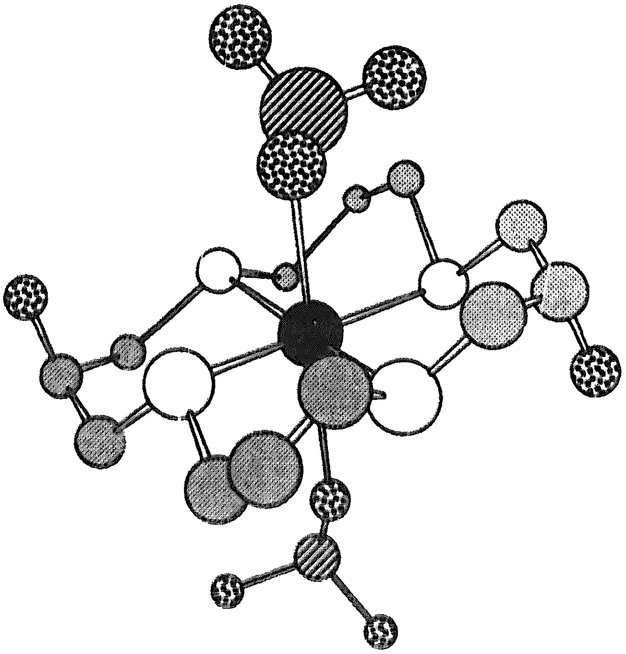
3.1.2. Sulfur coordination

The crown thioether copper(II) complex [Cu(**61**)](ClO_4)$_2$ (**62**), where (**61**)= 1,5,9,13-tetrathiacyclohexadecane-3,11-diol, has been prepared by reaction of the ligand with a copper(II) salt [52]. The solid state structure consists of discrete monomers in which the tetradentate macrocycle is in the endodentate conformation with four thioether donors in a precisely square planar arrangement around the copper centre. The copper(II) ion forms a monomeric complex with the ligand of *endo* conformation because the metal ion prefers a square-planar geometry and fits well the cavity size of the ligand. This is in contrast to silver(I) which forms a polymeric complex with the ligand in an exodentate conformation because of the large metal-ion size and the preferred tetrahedral coordination mode.

A multifaceted study has been conducted on the electron transfer reactions of the



(61)

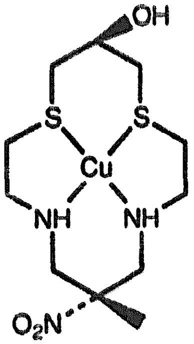


(62)

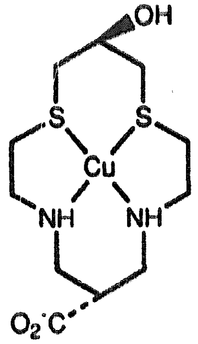
copper(II/I) complexes formed with 2,3-*cis*- (63) and 2,3-*trans*-cyclohexanediyl-1,4,8,11-tetrathiacyclotetradecane (64) [53]. Each system has been studied by (i) ^1H NMR spectroscopic line broadening in D_2O to determine the electron self-exchange rate constants at zero driving force, (ii) rapid-scan cyclic voltammetry in 80% methanol–20% water to determine the rate constants for conformational changes and heterogeneous electron transfer, and (iii) stopped-flow spectrophotometry using a total of eight oxidising and reducing counter-reagents to determine the cross-reaction electron-transfer rate constants from which self-exchange rate constants can be calculated for various driving forces. The crystal structures of both Cu^{II} complexes and of $[Cu^I(\mathbf{64})]$ have been determined. The crystal structures of the Cu^{II} cations reveal the copper centres to have a square pyramidal geometry with the four sulfur atoms occupying the basal plane and a coordinated water molecule (or anion) occupying the apical site. In the structure of the copper(I) complex, the copper centre has a flattened tetrahedral geometry in which all four sulfur donor atoms remain coordinated. These structures imply that for each $Cu^{II/I}L$ system, two sulfur donor atoms must invert during the overall electron transfer process. The self-exchange rate constant representative of the electron-transfer step itself, corrected for the separate conformational change step, is estimated to be of the order of $10^6\,M^{-1}\,s^{-1}$ for both systems, equivalent to the largest self-exchange rate constants known for rigid $Cu^{II/I}L$ systems.

3.1.3. Nitrogen, oxygen and sulfur coordination

The copper(II)-directed condensation of 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine with nitroethane or diethylmalonate and formamaldehyde resulted in the formation of (*anti*-6-methyl-6-nitro-1,11-dithia-4,8-diazacyclotetradecan-13-ol)copper(II) (**65**) and (diethyl 13-hydroxy-1,11-dithia-4,8-diazacyclotetradecane-6,6-dicarboxylate)copper(II) (**66**) respectively in good yields [54]. Complex (**66**) was readily converted to the copper(II) complex of *anti*-13-hydroxy-1,11-dithia-4,8-diazacyclotetradecane-6-carboxylic acid (**67**) by decarboxylation and hydrolysis in aqueous base. Zinc-acid reduction of the copper ion afforded the free ligand. Zinc-acid reduction of (**65**) resulted in the direct isolation of the hydrochloride salt of the free *anti*-6-amino-6-methyl-1,11-dithia-4,8-diazacyclotetradecane-13-ol ligand. The condensations were expected to result in the formation of 13-membered macrocycles with a pendant hydroxymethyl group fused to a macrocyclic ring carbon atom, but the molecules are found to undergo a Wagner–Meerwein or other carbon skeleton rearrangement to yield the 14-membered macrocycles with a pendant alcohol group. The pendant alcohol can act as an axial donor group as illustrated in the crystal structure analyses of (**65**)$(ClO_4)_2$ and (**67**)$(ClO_4)_2$. In both complexes, the alcohol is arranged *anti* to the nitro or carboxylate group. In (**65**)$(ClO_4)_2$, the copper ion lies in a distorted octahedral environment of two sulfur donor atoms (Cu–S_{av} 2.333 Å), two nitrogen donor atoms (Cu–N_{av} 2.016 Å), the pendant alcohol oxygen atom (Cu–O 2.365 Å) and a perchlorate anion (Cu–O 2.544 Å), whereas in (**66**)$(ClO_4)_2$ a dimer with each copper in a very distorted octahedral environment exists where each carboxylate bridges to the alternate copper ion (Cu–O 2.293 Å) and the alcohol is weakly bound (Cu–O 2.520 Å) in addition to the macrocycle heteroatoms (Cu–N_{av} 2.035, Cu–S_{av} 2.353 Å).



(**65**)

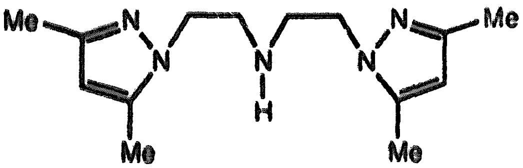


(**67**)

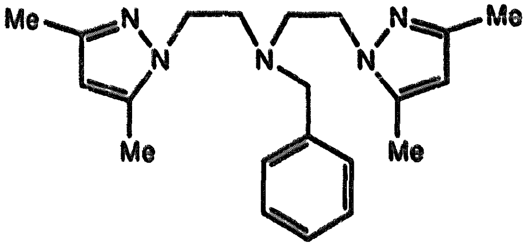
3.2. Mononuclear complexes with acyclic ligands

3.2.1. Nitrogen coordination

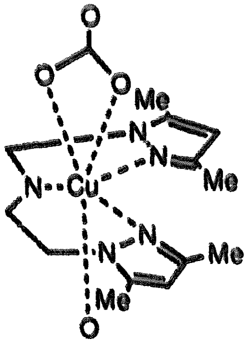
With the aim of elucidating the factors that control geometry, electrochemical behaviour and reactivity of Cu(II) bis(pyrazole) complexes the copper complexes of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**68**) and its benzylated derivative (**69**) have been studied as single crystals by X-ray crystallography and as solutions and powders by a variety of techniques [55]. The structures analysed by X-ray crystallography are [Cu(**68**)$\cdot$2NO_3] (**70**) [Cu(**68**)$ClO_4\cdot C_2H_5OH$]ClO_4 (**71**), [Cu(**69**)$\cdot$2NO_3] (**72**) and [Cu(**69**)C_2H_5OHY]$(ClO_4)_n$ (**73**) ($Y=H_2O$, $n=2$ or ClO_4, $n=1$). In complexes (**70**), (**71**) and (**73**), the ligand coordinates Cu(II) with a T-shaped arrangement of the nitrogen donor atoms. In complexes (**70**) and (**73**), an ethanol molecule is coordinated in the apical sites. The largest difference between (**70**) and (**73**) is a lengthening of 0.1 Å in the bond between the Cu(II) and the amine nitrogen atom. Conductivity measurements have shown the nitrate complexes behave as 1:1 electrolytes in acetonitrile whereas the perchlorate complexes behave as 2:1 electrolytes. The half-wave potentials, measured in acetonitrile by cyclic voltammetry, were found to be −0.01, +0.15, +0.10 and +0.28 V for (**70**)-(**73**), respectively. The high redox potentials of the copper(II) bis(pyrazole) complexes, in particular for complex (**73**), are explained by the fact that the Cu(II) complexes have the correct ligand geometry for the stabilisation of Cu(I).



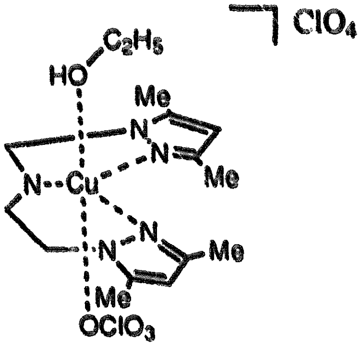
(**68**)



(**69**)

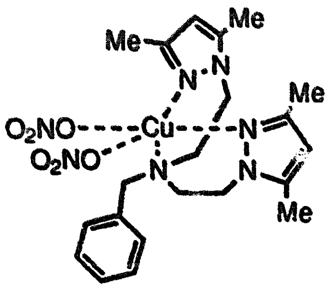


(**70**)

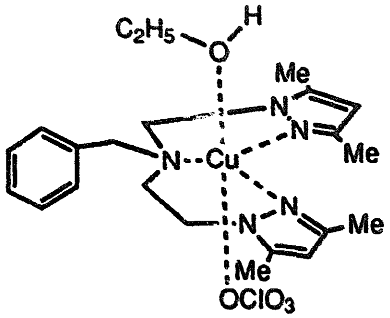


(**71**)

The crystal and molecular structures of [Cu(NMIm)$_4$$(ClO_4)_2$] (**74**) and [Cu(NMIm)$_4$$(H_2O)_2$]$Cl_2\cdot(H_2O)$ (**75**) (NMI = *N*-methylimidazole) have been determined [56]. The structure of (**74**) consists of discrete centrosymmetric [Cu(NMI)$_4$$(ClO_4)_2$] units having a CuN_4 plane with a set of *trans* *N*-methylimidazole ligands nearly perpendicular to the CuN_4 plane (dihedral angle 87.8°) and another

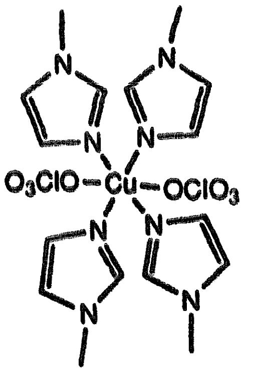


(72)

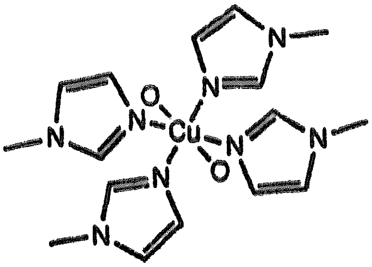


(73)

set approximately parallel (dihedral angle 4.4°) and with two perchlorate anions completing the coordination sphere of the metal centre. The structure of (**75**) consists of two discrete structurally-similar centrosymmetric $[Cu(NMIm)_4(H_2O)_2$ cations interconnected with Cl^- ions and hydrate molecules by hydrogen bonds. The dihedral angles between the imidazole and the CuN_4 planes are 98.8° and 57.6° for one unit and 97.0° and 50.6° for another. The electronic spectra of (**74**) and (**75**) reveal that the former has D_{2h} symmetry with non-degenerate d_{xz} and d_{yz} orbitals and the latter has D_{4h} symmetry with degenerate d_{xz} and d_{yz} orbitals. This difference is ascribed to the difference in donor abilities of the axial ClO_4^- and H_2O ligands.



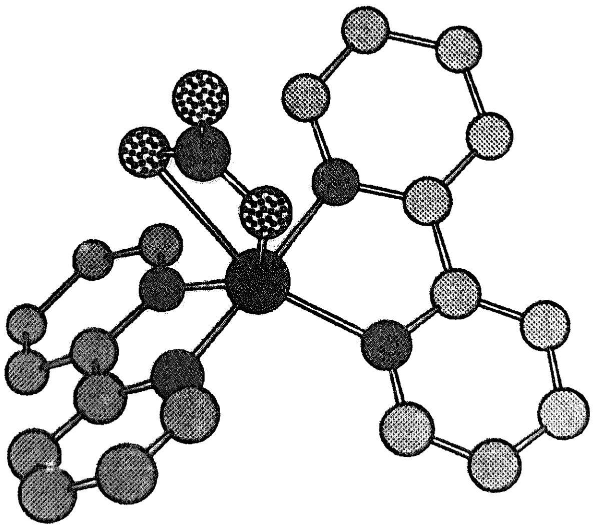
(74)



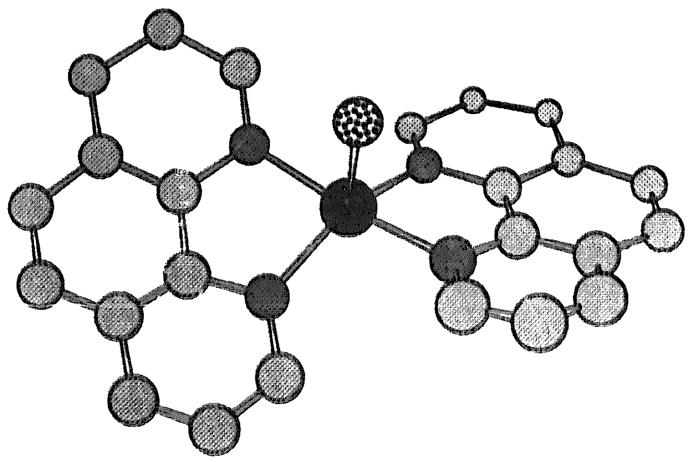
(75)

The crystal and molecular structures of $[Cu(NO_3)(2,2'\text{-bipyridine})_2](NO_3).H_2O$ (**76**) and $[Cu(H_2O)(1,10\text{-phenanthroline})_2](NO_3)_2$ (**77**) have been determined [57]. The copper cation in **76** displays pseudo-octahedral geometry with ligand nitrogen donor atoms occupying four positions, a coordinated nitrato oxygen atom a fifth and a non-bonded oxygen a sixth. The copper cation in **77** shows a trigonal bipyramidal geometry with ligand nitrogen donors occupying the axial and two of the equatorial positions, and a coordinated aqua oxygen atom the other.

The preparation and characterisation of mixed ligand complexes, $[Cu(acac)(NN)(ClO_4)]$ (acac = acetylacetonate; NN = *N,N,N′,N′*-tetramethylethylenediamine, bpy, phen or neocuproine), are reported [58]. The crystal structure of $[Cu(acac)(phen)(ClO_4)(0.5CH_3CN)]$ has been determined and shows



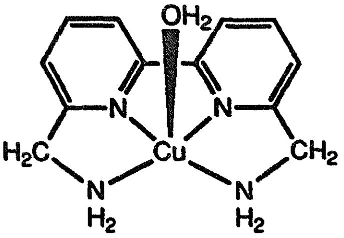
(76)



(77)

the complex to consist of discrete [Cu(acac)(phen)(ClO_4)] and [Cu(acac)(phen)(CH_3CN)](ClO_4) units with the perchlorate or the CH_3CN occupying the apex of each square pyramidal unit. The acetonitrile molecule is found to be coordinated in an unusual bent mode with a Cu–N–C angle of 129.2(9)°. By analysis of the electronic spectra of the complexes the sequence of d orbitals is suggested as $d_{xy} \gg d_{z^2} > d_{x^2-y^2} \approx d_{xy} > d_{yz}$. In these square pyramidal complexes the acetylacetonate ligands act as π-donors whilst the heterocyclic diimines do not participate in π interactions.

An improved four-step synthesis of the tetradentate compound 6,6′-bis(aminomethyl)-2,2′-bipyridyl is reported as well as the X-ray structures of the Cu^{II} and Ni^{II} complexes [59]. The copper ion in [Cu(L)(H_2O)]Br_2 (**78**) is five coordinate while the Ni complex, [Ni(L)(H_2O)Br]Br, contains a 6-coordinate metal centre. The order of stability for the chelates of the divalent metal ions was determined as $Cu^{II} > > Ni^{II} > Co^{II} > Zn^{II} > Fe^{II}$, although the stability constants were unusually low, *e.g.* 15.05 in the case of the copper complex. The unusually low stabilities of the complexes are attributed to the low basicity of the ligand and to the unfavourable spacing of its donor groups as evident in the solid state structures.

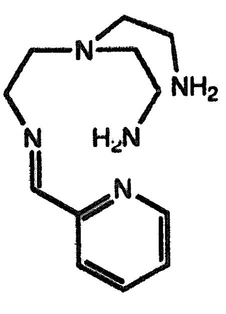


(78)

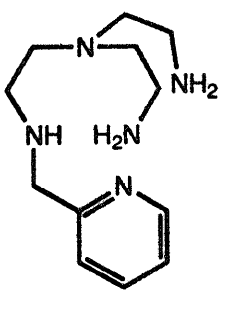
A study has been carried out on the complex formed between the tripodal ligand tris(2-pyridyl)methane and $Cu(NO_3)_2$ and it illustrates the differences between the information provided by various techniques [60]. The crystal structure of bis[tris(2-pyridyl)methane]copper(II) dinitrate has been determined at 295 K and 173 K. At 295 K the Cu atom lies in a special position so that all six Cu–N bonds are crystallographically equivalent with Cu···N distance of 2.103(4) Å. The structure at 173 K is very similar with Cu···N distance of 2.095(3) Å. However, the electronic spectrum suggests that the Cu^{2+} ion experiences a ligand field of tetragonal symmetry. This has been confirmed by the EXAFS of the compound, which showed four nitrogen atoms at 2.04 Å and two at 2.25 Å from the copper. The apparent trigonal symmetry revealed by the X-ray analysis therefore arises from the disorder of the long and short Cu–N bonds about the 3-fold axis. The EPR spectrum shows an isotropic signal at 295 K, but a signal characteristic of a tetragonally elongated octahedral complex at 150 K. This suggests that the directions of the long and short bonds interchange rapidly on the EPR spectroscopic time-scale at room temperature, but that the complexes become frozen into particular orientations on cooling.

The syntheses and characterisation of five-coordinate Cu(II) complexes of the pentadentate ligands 4-[4-(2-pyridyl)-3-aza-3-butenyl]-1,4,7-triazaheptane (**79**), 4-[4-(2-pyridyl)-3-azabutyl]-1,4,7-triazaheptane (**80**) and 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (**81**) are described [61]. The solid state structures of $[Cu(\mathbf{79})](ClO_4)_2$ and $[Cu(\mathbf{80})](ClO_4)_2$ have been determined. The geometry of the Cu(II) in the $[Cu(\mathbf{79})]^{2+}$ cation is close to square pyramidal while that of the Cu(II) in $[Cu(\mathbf{80})]^{2+}$ is intermediate between square pyramidal and trigonal bipyramidal. Cyclic voltammetry of the complexes revealed a quasi-reversible redox wave corresponding to the Cu(II)–Cu(I) couple at −0.80, −0.94 and −0.81 V for $[Cu(\mathbf{79})]^{2+}$, $[Cu(\mathbf{80})]^{2+}$ and $[Cu(\mathbf{81})]^{2+}$, respectively. Thus some stabilisation of the Cu(I) state results from the greater ability of trenimpy and dmptacn (cf. (**80**)) to accept electron density from Cu(I).

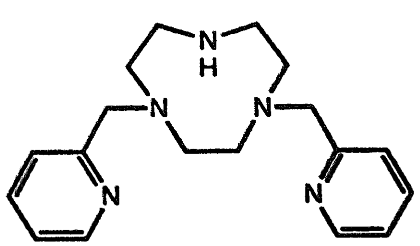
The synthesis and characterisation of a new ligand, tris((6-phenyl-2-pyridyl)methyl)amine (**82**) and some of its copper complexes are described. The complexes $[Cu(\mathbf{82})]BPh_4$ (**83**) and $[Cu(\mathbf{82})(CH_3CN)]ClO_4$ (**84**) have been prepared and their solid state structures and redox potentials determined [62]. In (**83**), the copper(I) atom has a distorted trigonal bipyramidal coordination sphere, while in (**84**) the copper(II) atom has the expected trigonal bipyramidal geometry. In (**84**), a cavity suitable to accommodate the coordinating acetonitrile molecule is accomplished by



(79)

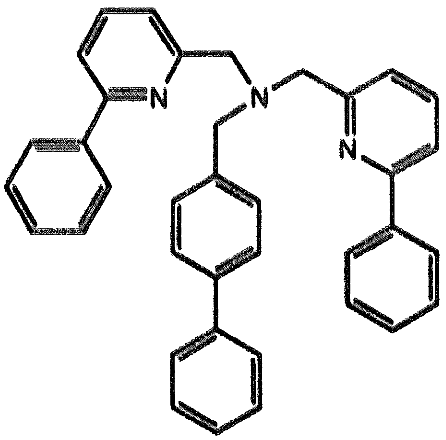


(80)



(81)

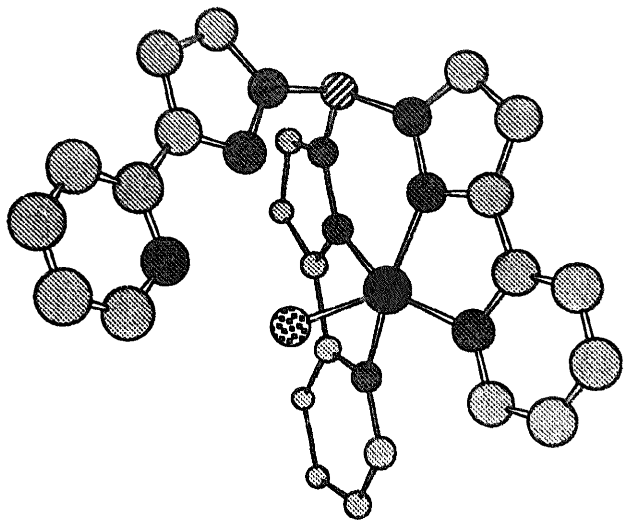
rotation of the three N–CH_2 bonds, resulting in a large propeller-like twist of the ligand. The X-ray structure of (**83**) shows a smaller twist as a result of the absence of the coordinated solvent molecule. In (**83**), the copper ion lies significantly below the basal plane in a distorted tetrahedral geometry. The redox potentials of (**83**) are more positive than the corresponding Cu(II) complex of TPA $[Cu(TPA)(AN)](ClO_4)_2$ (where TPA = tris(pyridylmethyl)amine) which demonstrates the greater stabilisation of the reduced state of the copper ion in the TPPA complex. The redox potentials between (**83**) and the TPA analogue are largest in solvents of larger molecular sizes which is consistent with steric interactions between the phenyl substituents destabilising the Cu(II) form.



(82)

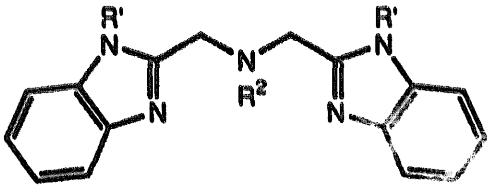
In a study of the synthesis of model systems for metalloenzymes the crystal structure of $[Cu\{HB(pypz)_3\}(H_2O)](PF_6)$ (**85**)$\{HB(pypz)_3$ = hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate$\}$ has been determined and shows a square-pyramidal Cu^{II} centre coordinated by two of the three didentate arms of the ligand and an axial water molecule whilst the third, pendant, didentate ligand arm is involved in a 'chelating' hydrogen-bonding interaction with one of the protons of the axial water molecule [63]. This interaction is not maintained in solution.

The 1:1 and 1:2 copper(II) complexes with the tridentate ligand bis(benzimidazol-2-ylmethyl)amine (**86**) and its benzimidazole (**87**) and amine (**88**) *N*-methyl-substituted derivatives have been prepared [64]. The 1:1 complexes have the formula $CuLX_2 \cdot nH_2O$ ($X = ClO_4^-$, NO_3^-, Cl^- or Br^-) while the 1:2 complexes are of the



(85)

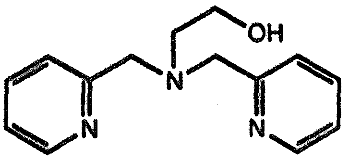
type $CuL_2(ClO_4)_2.nH_2O$. In all of the complexes, the ligands acts in a tridentate mode with the amine nitrogen atom and both of the benzimidazole nitrogens coordinating to the Cu^{II} ion. The X-ray structure of $[Cu(\mathbf{86})_2](ClO_4)_2.2H_2O$ is reported and shows the copper(II) ion to have an elongated octahedral geometry with four equatorial benzimidazole and two long-distance axial amine N donors. The $Cu\cdots N_{bzim}$ and $Cu\cdots N_{amine}$ distances are 2.011(4) and 2.597(6) Å, respectively. This facial coordination is favoured when the terminal donor sites in the tridentate N3 ligand possesses partial rigidity and hence reduced σ-donor ability as well as enhanced π-back bonding ability. In contrast, meridional coordination is favoured when primary amine nitrogen atoms with strong σ-donor ability form the termini of a non-rigid ligand or when a ligand like terpyridine is available for planar coordination.

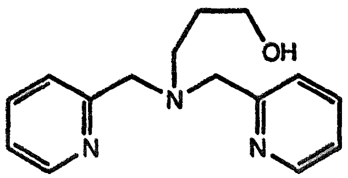


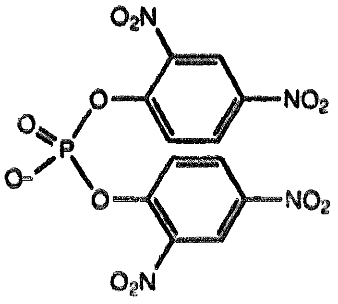
(86) $R'=R^2=H$
(87) $R'=Me\ R^2=H$
(88) $R'=H\ R^2=Me$

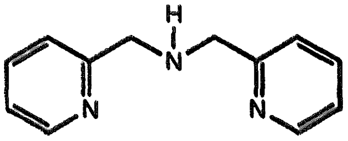
Two new copper(II) chloride complexes of *N*-(2-hydroxyethyl)bis(pyridylmethyl)amine [Cu(**89**)] and *N*-(3-hydroxypropyl)bis(pyridylmethyl)amine [Cu(**90**)] have been synthesised and characterised and the reactivities of [Cu(**89**)] and [Cu(**90**)] for cleaving bis(2,4-dinitrophenyl) phosphate (**91**) have been compared to that of the copper(II) chloride complex of bis(pyridylmethyl)amine [Cu(**92**)] [65]. The copper complex with the hydroxypropyl group [Cu(**90**)] has been shown to cleave the phosphate diester by transesterification, while the complex with the hydroxyethyl group [Cu(**89**)] or the complex without any pendant groups cleaves it by hydrolysis. Furthermore the rate of cleavage of the diester by [Cu(**90**)] ($k=7.2\times10^{-1}\,M^{-1}\,s^{-1}$ at 25°C and pH 8.8) is about two orders of magnitude higher than those by [Cu(**89**)] and [Cu(**92**)] ($k=9.5\times10^{-3}$ and $2.0\times$

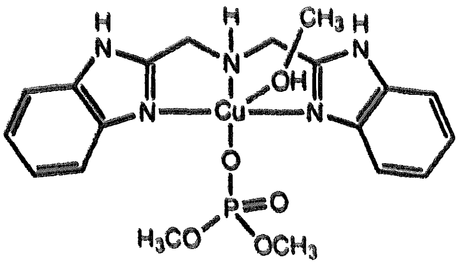
10^{-2} M^{-1} s^{-1}). On the basis of crystallographic analysis of two analogues, (**93**) and (**94**), the difference in reactivity and mechanism are explained in terms of differences in their structures. This study shows that a simple metal complex with a pendant alcohol group can cleave a phosphate diester effectively by transesterification. This process has been proposed for alkaline phosphatase catalysed cleavage of phosphate monoesters and the *Tetrahymena* ribozyme catalysed transesterification reaction.

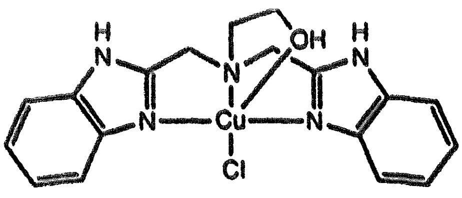

(89)


(90)


(91)


(92)


(93)


(94)

The five coordinate complexes $[Cu^{II}(tren)(H_2O)]Cl_2$, $[Cu^{II}(tren)(HAde)]Cl_2$, $[Cu^{II}(tren)(HAde)](NO_3)_2$ and $[Cu^{II}(tren)(Ade)]Cl \cdot 2H_2O$ [tren = tris(2-aminoethyl)amine and HAde = neutral adenine] have been synthesised and characterised [66]. In $[Cu^{II}(tren)(Ade)]Cl \cdot 2H_2O$, the adenine molecule is bound in its monoanionic form, while in $[Cu^{II}(tren)(HAde)]Cl_2$ and $[Cu^{II}(tren)(HAde)](NO_3)_2$, physicochemical data support the presence of neutral adenine coordinated to the Cu^{II} centres. In $[Cu^{II}(tren)(Ade)]Cl \cdot 2H_2O$, the copper(II) centre has an approximate trigonal bipyramidal geometry, with the equatorial sites occupied by the three primary amino nitrogen atoms and the axial positions filled by the tertiary amino nitrogen and the imidazole nitrogen from the adenine monoanion. The Cu···$N_{(imid)}$ distance is rather short at 1.965(9) Å.

A study has been carried out to synthesise metal-containing nucleoside analogues in which the metal-base interactions are modified [67]. The adenine N(3) site was the target for metallation since it is located in the minor groove of the DNA duplex and would not be expected to be involved in protein-DNA binding interactions. The crystal and molecular structure of a copper complex prepared by the reaction of copper(II) nitrate hemipentahydrate with the nucleobase-ligand conjugate, ethylenediamine-*N*,9-propyladenine, reveals the unprecedented coordination of adenine-N^3. The copper centre is five coordinate in a distorted square-pyramidal geometry. The metal is bound by three nitrogen atoms, one of which is adenine N(3). Such binding is unprecedented for an N^9-substituted adenine derivative and the complex is the first mononuclear complex involving N^3_{ade} – metal binding. The remaining nitrogen donor atoms arise from the ethylenediamine group. The tridentate binding mode of the adenine-ethylenediamine conjugate generates an eight membered chelate ring which adopts a boat-type conformation. The coordination of N(3) in the complex is a result of the ethylenediamine group directing the site of metallation and shows that the preferred nucleobase coordination sites can be modified through multidentate ligand conjugation. Hoogsteen-type interactions are exhibited in the complex with the formation of hydrogen-bonded chains. These chains are cross-linked forming sheets with chloride/nitrate anions alternating above and below the plane.

An investigation to help provide an understanding of the metabolic pathways of creatinine has been performed [68]. The creatinine ternary complex $[Cu(gg)(H_2O)(creat)]\cdot 1.5H_2O$ (gg = dianion of glycylglycine, creat = creatinine) has been crystallised from aqueous solution. The coordination geometry about the copper centre is approximately square pyramidal with the tridentate glycylglycine and the N(1) of creatinine occupying the corners of a square. The coordination sphere of the copper centre is completed by an axial water molecule.

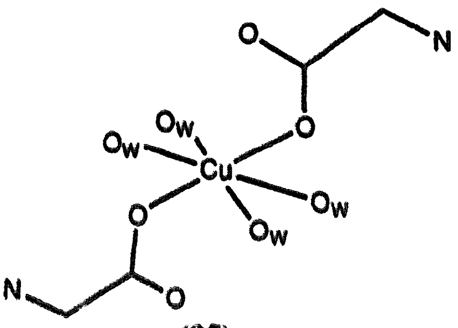
3.2.2. *Sulfur coordination*

Interest in molecular magnets, especially those based on charge transfer complexes, has resulted in several decamethylferrocenium (Fe(Cp*)/transition metal maleonitriledithiolate (mnt) compounds being synthesised and structurally characterised [69]. The compounds investigated have the general formula $[Fe(Cp^*)_2]_x[M(mnt)_2]_y(CH_3CN)_z$ where M = Cu^{II}, Co^{III} and Fe^{III}. In the case of $[Fe(Cp^*)_2]_2[Cu(mnt)_2]$, the dianion $[Cu(mnt)_2]^{2-}$ exhibits a planar monomeric and the mixed anion-cation stacks adopt a $\cdots A^{2-}D^+D^+A^{2-}D^+D^+A^{2-}\cdots$ arrangement with short anion-cation distances (Fe–S = 5.54 Å and Fe–Cu = 6.37 Å). In this copper complex magnetic measurements have shown each $[Cu(mnt)_2]^{2-}$ to interact antiferromagnetically with two adjacent $[Fe(Cp^*)_2]^+$ cations.

As an attempt to synthesise electrically-conducting materials, a series of $[NR_4][M(dpdt)_2]$ (R = Bu, M = Ni, Au or Cu, R = Me, M = Ni; H_2dpdt = 6,7-dihydro-6-methylene-5*H*-1,4-dithiepine-2,3-diol) complexes have been synthesised [70]. Magnetic susceptibility measurements indicate that the gold and copper complexes are diamagnetic whilst the Ni complex is paramagnetic over the temperature range studied (290-22 K). The X-ray structure of the complexes revealed crystal packing structures consisting of two crystallographically independent $[M(dpdt)_2]^-$ units possessing square-planar geometry in which there are no intermolecular S···S contacts shorter than the sum of the van der Waals radii.

3.2.3. Oxygen coordination

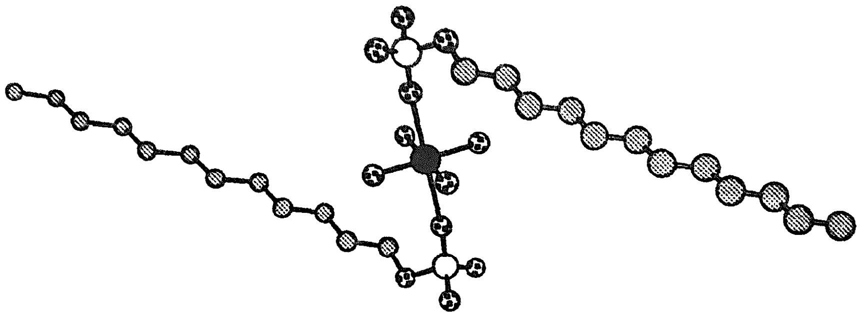
The compound of composition copper(II)–glycinate–picric acid–water (1/2/2/6) (**95**) has been synthesised and its crystal structure determined [71]. The structure contains a centrosymmetric copper(II) ion coordinated in a distorted octahedral geometry by two water molecules in *trans* positions, two monodentate glycine molecules linked to the metal in a *trans* arrangement *via* single carboxylate oxygen atoms, and two more distant water molecules. The monodentate glycine species, probably existing as zwitter-ions, represent an unexpected non-chelated form of the ligand. Similar compounds of (*S*)-alanine and (*S*)-lysine have also been prepared.



(95)

As part of a study in the interaction between surfactants and inorganic compounds the structure of copper(II) dodecylsulfate tetrahydrate $[Cu(OSO_3C_{12}H_{25})_2]\cdot 4H_2O$ (**96**) has been determined with crystals having been obtained from an aqueous mixture of copper nitrate and sodium dodecylsulfate [72]. The Cu^{II} centre is six coordinate in a tetragonally elongated octahedral geometry with the four oxygen atoms of water equatorial and the two oxygen atoms of the dodecylsulfate groups axial. The Cu–O(dodecylsulfate) bonds are much longer at 2.456(4) Å than the Cu–O(water) bonds at 1.860(4) and 1.870(4) Å. The extended alkyl chains are tilted between the planes of copper atoms but there is no interdigitating between the alkyl chains from two adjacent layers.

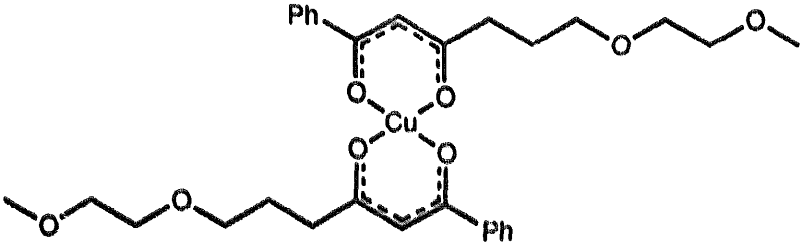
A range of new *β*-diketones of formula $RC(O)CH_2C(O)(CH_2)_3(OCH_2CH_2)_nOMe$ ($n = 1$, R = Me, Ph, 2,4,6-$Me_3C_6H_2$ or Bu^t; $n = 2$, R = Me) have been prepared [73]. Complexes of these *β*-diketones with copper(II) ($n = 1$, R = Me; $n = 1$, Ph giving complex (**97**)) have been prepared and are shown to be involatile because the polyether chain binds to a different metal atom from that to which the *β*-diketonate function is bound, thus forming polymers. The X-ray structure of complex (**97**) has been established and shows the copper atoms to exhibit Jahn–Teller distorted six-coordinate geometry with the oxygen atoms of two didentate *β*-diketonates occupying the equatorial positions (Cu···O = 1.92 Å) and the two terminal



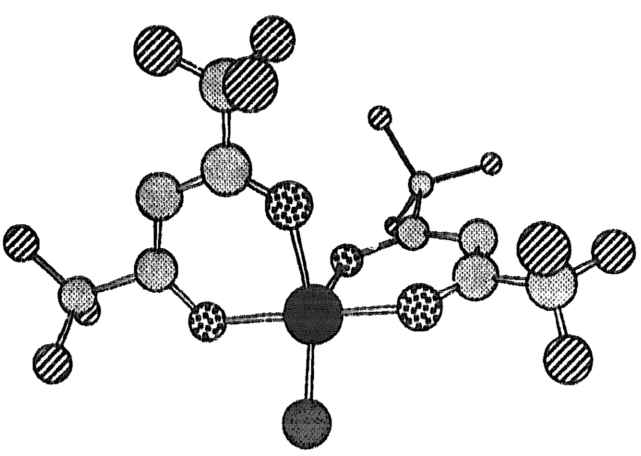
(96)

oxygen atoms from the polyether chains of different neighbouring molecules occupying the axial sites (Cu···0 = 3.065 Å). A study as to the origin of different coordination polyhedra for Cu(hhacac)$_2$L (hfacac = $CF_3C(O)CHC(O)CF_3^-$, L = H_2O, NH_3) has been performed. Cu(hfacac)$_2$(NH_3) (**98**) is shown to have a trigonal bipyramidal structure with Cu–O(axial) = 1.945(3) Å, Cu–O(equatorial) = 2.075(3) Å and Cu–N = 1.933(6) Å [74]. This contrasts with the square pyramidal structure of Cu(hfacac)$_2$(H_2O) which has a long Cu–OH_2 bond (2.204(3) Å). The ammine complex retains its NH_3 ligand upon vacuum sublimation, while the H_2O complex loses water. The difference in coordination and Cu–L distance (L = H_2O, NH_3) is ascribed to minimising σ-antibonding interactions with the stronger ligand, which by the criterion of $10Dq$, is NH_3.

Host molecules which satisfy both facile synthesis and strong as well as selective



(97)



(98)

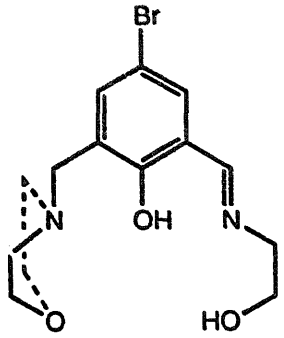
binding of metal ions have been developed by introducing an idea of metal-assisted organisation of linear molecules into crown ethers [75]. For this purpose, an oligo(oxyethylene) prehost having two β-diketone units in both terminal positions was synthesised. Intramolecular coordination of the two β-diketones to divalent transition metals, Cu, Zn or Ni, organised the linear prehost into a macrocyclic pseudo crown structure. The crystal structure of the Cu-organised host and K^+ picrate complex was determined and indicates that the intramolecular coordination of β-ketoenolate oxygens to the transition metal produced an organised cavity into which the potassium cation was entrapped. The metal-organised crowns show a good size-fit selectivity, characteristic of macrocycles, and a superior extraction efficiency for the picrate extraction of alkali and alkaline earth metal cations compared with dibenzo-18-crown-6.

The ferrocenylbis(phosphine) dioxide complexes $[Cu(odppf)_2(EtOH)](BF_4)_2$ and $[Cu(odppf)_2](BF_4)_2$ (odppf = 1,1′-bis(oxodiphenylphosphoranyl)ferrocene) have been prepared and characterised in the solid state by X-ray analysis and in solution by a combination of ESR, visible, and IR spectroscopies and electrochemical techniques [76]. In the cations the four oxygen atoms of two odppf ligands are directly bonded to the metal centre with Cu···O distances ranging from 1.92–2.078 Å. In $[Cu(odppf)_2(EtOH)](BF_4)_2$, the metal is pentacoordinate with a distorted trigonal bipyramidal geometry formed from the two chelated odppf moieties and the fifth site occupied by an ethanol molecule. In the complex $[Cu(odppf)_2](BF_4)_2$, the copper centre has a distorted square planar structure, with the two odppf moieties acting as chelating ligands with a bite angle of ≈153°. The lability of the EtOH ligand allows complex $[Cu(odppf)_2(EtOH)](BF_4)_2$ to be easily and reversibly coordinated to $[Cu(odppf)_2](BF_4)_2$ upon dissolution in non-coordinating solvents. ESR spectroscopic parameters indicate that *ca.* 95% of the unpaired electron resides in the metal centre, thus revealing a scarcely covalent character of the Cu^{II}–O bonds. Electrochemical studies have shown the ligand appears to stabilise the homoleptic species $[Cu(odppf)_2]^+$, which is claimed to be the first copper(I) complex to be stabilised by a purely hard coordination sphere. Although this species was found to be extremely reactive towards dioxygen, it was quite stable toward valence disproportionation in aprotic solvents.

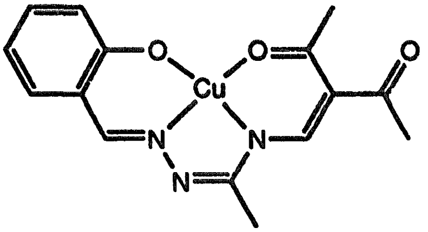
3.2.4. *Nitrogen and oxygen coordination*

The unsymmetrical and potentially dinucleating ligand 4-bromo-2-(2-hydroxyethyliminomethyl)-6-(morpholin-4-ylmethyl)phenol (**99**) has been synthesised *via* a Mannich reaction under non-aqueous aprotic conditions [77]. Reaction of the ligand with copper(II) yielded mono- and dinuclear complexes. The crystal structure of the mononuclear complex $[Cu(\mathbf{99})](ClO_4)_2 \cdot H_2O.MeOH$ has been determined and shows the coordination of the copper is square-based pyramidal with the ether oxygen atom of the morpholino group not involved in the coordination. The saturated six membered ring has a chair conformation.

The copper(II) and nickel(II) complexes ML (where H_2L = [9-(2′-hydroxyphenyl)-6-methyl-3-acetyl-5,7,8-triazanona-3,6,8-trien-2-one]) have been synthesised by the template reaction of salicylaldehyde acetamidrazone with the corresponding



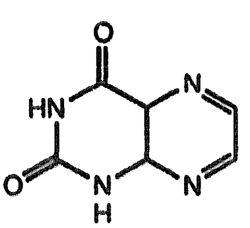
(99)



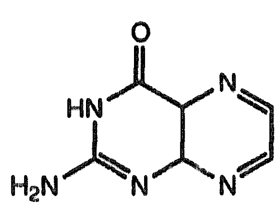
(100)

M(acac)$_2$ and Hacac in the presence of the orthoformic ester at 110°C [78]. The crystal structure of [CuL] (**100**) has been determined and shows the copper centre in a square planar mode. This complex has been shown to be an efficient catalyst for the epoxidation of norbornene with molecular oxygen (1 atm) in thf (or thf-EtOAc) at 70°C.

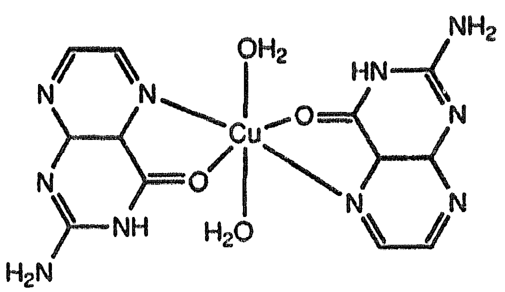
The crystal structures of some metal complexes having 3-dimensional hydrogen-bonded networks and stacking interactions based on pteridine ligands, [Cu(**101**-H)$_2$(H$_2$O)$_2$, [Cu(**102**-H)(H$_2$O)$_3$] (**103**) and [Zn(PR)$_2$(H$_2$O)$_2$]·2H$_2$O are reported [79]. All three structures contain the following features: (i) the two pteridine ligands chelate to the metal ion through the O(4) and N(5) donor atoms of the pteridine, (ii) the molecular units are connected to two-dimensional H-bonded molecular sheets by the coordinated water molecules (iii) in the molecular sheet, there are stacking structures of the pteridine skeleton (iv) the sheets are further connected to 3-dimensional H-bonded networks *via* the H-bonded sites of the pteridine ligands (v) almost all of the H-binding sites existing in the molecule participate in intermolecular H-bonding interactions.



(101)

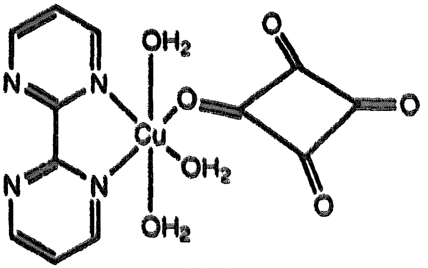


(102)



(103)

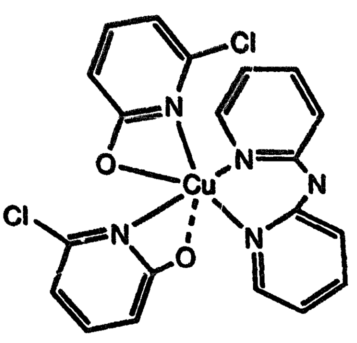
Two new mixed ligand complexes $[Cu(bpym)(C_4O_4)(H_2O)_3]\cdot 2H_2O$ (**104**) and $[Cu_2(bpym)(C_4O_4)_2(H_2O)_6]$ (bpym = 2,2'-bipyrimidine; $C_4O_4^{2-}$ = dianion of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione)) have been obtained from aqueous solutions containing $Cu(NO_3)_2\cdot 3H_2O$, bpym and $Li_2([C_4O_4]$ in 1:1:0.25 and 2:1:0.5 (Cu^{2+}:bpym:$C_4O_4^{2-}$) molar ratios respectively [80]. The solid state structures of both complexes have been determined. Compound (**104**) consists of mononuclear $[Cu(bpym)(C_4O_4)(H_2O)_3]$ units in which the copper centre has a slightly distorted elongated octahedral geometry, coordinating to two bpym nitrogen atoms, one squarate oxygen atom and one water oxygen atom in the equatorial plane and to two water molecules in the axial sites. The structure of the dicopper complex is built by centrosymmetric bpym-bridged $[Cu_2(bpym)(C_4O_4)_2(H_2O)_6]$ units, with the coordination geometry of the copper centres similar to that in (**104**). Squarate acts as a monodentate ligand in both complexes, whereas bipym exhibits chelating and bis(chelating) coordination modes in the mono- and dinuclear complexes, respectively. The intramolecular Cu···Cu distance in $[Cu_2(bpym)(C_4O_4)_2(H_2O)_6]$ of 5.542(1) Å is claimed to be the largest found in bipym-bridged copper(II) complexes. The magnetic behaviour of $[Cu_2(bpym)(C_4O_4)_2(H_2O)_6]$ has been investigated over the temperature range 10–300 K. The magnetic susceptibility data yield a singlet-triplet energy gap (J) of $-139\ cm^{-1}$ which is the smallest antiferromagnetic interaction found in bpym-bridged copper(II) complexes for which the σ in-plane exchange pathway is operative.



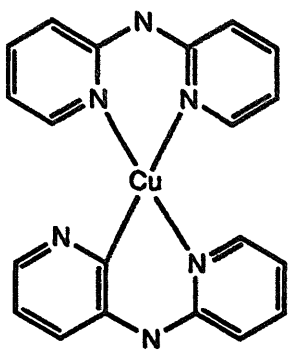
(**104**)

The synthesis and crystal structure of $Cu(Hdpa)(chp)_2$ (**105**) are reported (Hchp = 6-chloro-2-hydroxypyridine, Hdpa = dipyridylamine) [81]. The copper(II) centre is six coordinate, with Hdpa and one of the chp ligands bonding in a chelating mode. The second pyridine is bound through its nitrogen atom and with the oxygen atom taking up the sixth coordination site but is also hydrogen bonded to the Hdpa ligand of a second $Cu(hdpa)(chp)_2$ unit, forming a centrosymmetric dimer. A new (orthorhombic) phase of $[Cu(dpa)_2]$ (**106**) has been found in which the distorted tetrahedral copper(II) complexes are linked through a network of hydrogen bonds between the deprotonated dpa ligand and the C–H bonds *meta* to the pyridyl nitrogen donor.

A series of copper(II) complexes derived from tripodal ligands bearing pyridyl and phenolic arms have been synthesised as models for the active site of galactose oxidase [82]. The molecular structures of the neutral mononuclear complexes $[Cu(\mathbf{107}\text{-}H)(O_2CMe)]\cdot H_2O$ and $[Cu(\mathbf{107}\text{-}H)(SCN)]\cdot MeCO_2Et$ (**108**) [(**107**) = 2-

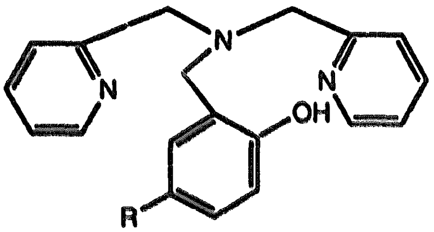


(105)

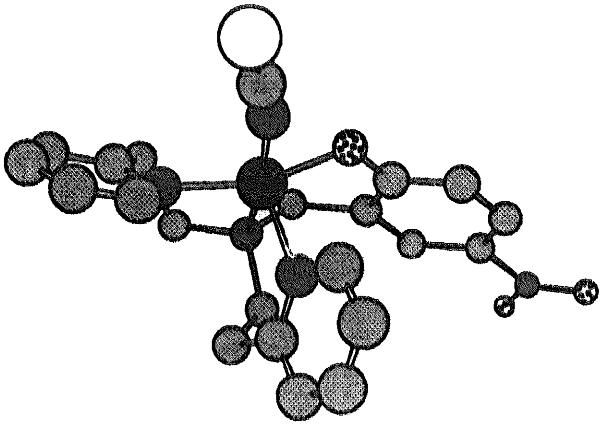


(106)

bis[2-(2-pyridyl)ethyl]aminomethyl-4-nitrophenol] were determined by X-ray diffraction. The coordination geometry around the copper atom in each is a distorted square based pyramid where one pyridyl nitrogen atom occupies the axial position. Three ligand donor atoms comprising the square plane are the same in the two complexes, while the fourth ligand is an exogenous donor atom from $MeCO_2^-$ or SCN^-, respectively. In the absence of an exogenous donor or in the presence of only weakly coordinating anions, these compounds form dimeric copper(II) complexes. In order to inhibit dimer formation and prepare the related mononuclear complexes, stronger coordinating ligands, *e.g.* acetate, have been introduced in the copper(II) coordination sphere.

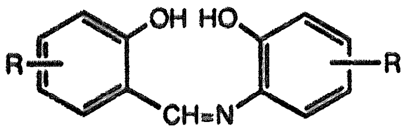


(107), $R = NO_2$, x=y=2

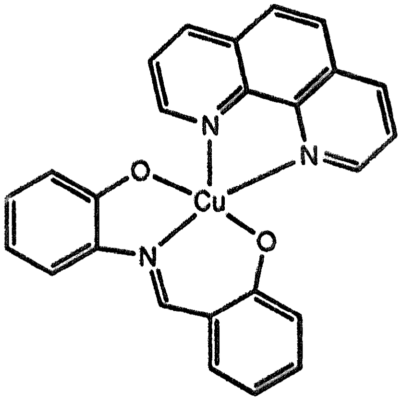


(108)

As part of the growing interest in copper complex ligands containing phenolic ligands (on account of the presence of such moieties in a number of mono-(*e.g.* galactose oxidase) or dinuclear (tyrosinase, haemocyanin) copper proteins), a study on the electrochemical oxidation of metal anodes (copper and nickel) in acetonitrile solutions of Schiff bases (**109**) (synthesised from salicylaldehydes and 2-aminophenols) has resulted in the isolation of the mononuclear complexes CuL and NiL complexes [83]. The addition of phen or bpy to the electrolytic cell resulted in the mixed complexes CuLL′ and NiLL′ (L′=phen or bpy) being obtained. The crystal structure of the copper(II) complex (**110**) was determined by X-ray diffraction and shows it to consist of monomeric molecules in which the copper atom has a distorted square pyramidal CuN_3O_2 coordination.

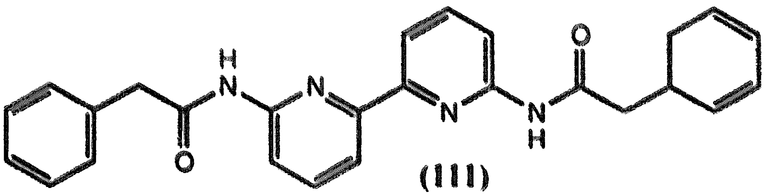


(109)



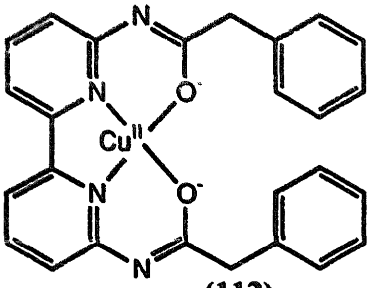
(110)

The synthesis of four 6,6′-bis(acylamino)-2,2′-bipyridine-based amino acids are described [84]. These residues when coordinated to Cu(II) are designed to replace the i+1 and i+2 residues of a β-turn. The amino acids were incorporated into several different peptides in order to evaluate their efficacy as β-sheet nucleators. Matrix-assisted laser desorption mass spectroscopy and UV spectroscopy reveal that peptides incorporating these residues bind Cu(II) ions under alkaline and acidic conditions with a 1:1 stoichiometry. In an effort to predict the geometry of the metal binding site of peptides containing β-turn mimics, three model complexes (**111**), (**112**) and (**113**), were prepared and their crystal structures determined. The crystal structure of 6,6′-bis(phenylacetamide)-2,2′-bipyridine (**111**) suggests that the bpy rings of peptides containing these residues should exist in a transoid conformation in the absence of Cu(II) ions and other stabilising forces. The crystal structures of neutral (deprotonated) Cu(II) complex (**112**) and 2^+ charged (protonated) Cu(II) complex (**113**) suggest the peptides containing the bpy residues bind Cu(II) ions under alkaline and acid conditions resulting in a cisoid bpy ring conformation with a near perfect square planar geometry about the copper centre.

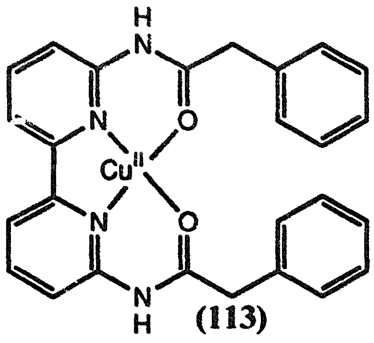


(111)

An investigation has been performed into the synthesis of an efficient model of dopamine β-hydroxylase (DβH), an enzyme that catalyses the ascorbate dependent benzylic hydroxylation of phenylethylamines such as dopamine to the corresponding norepinephrine [85]. The enzyme contains two copper atoms per catalytic unit, but

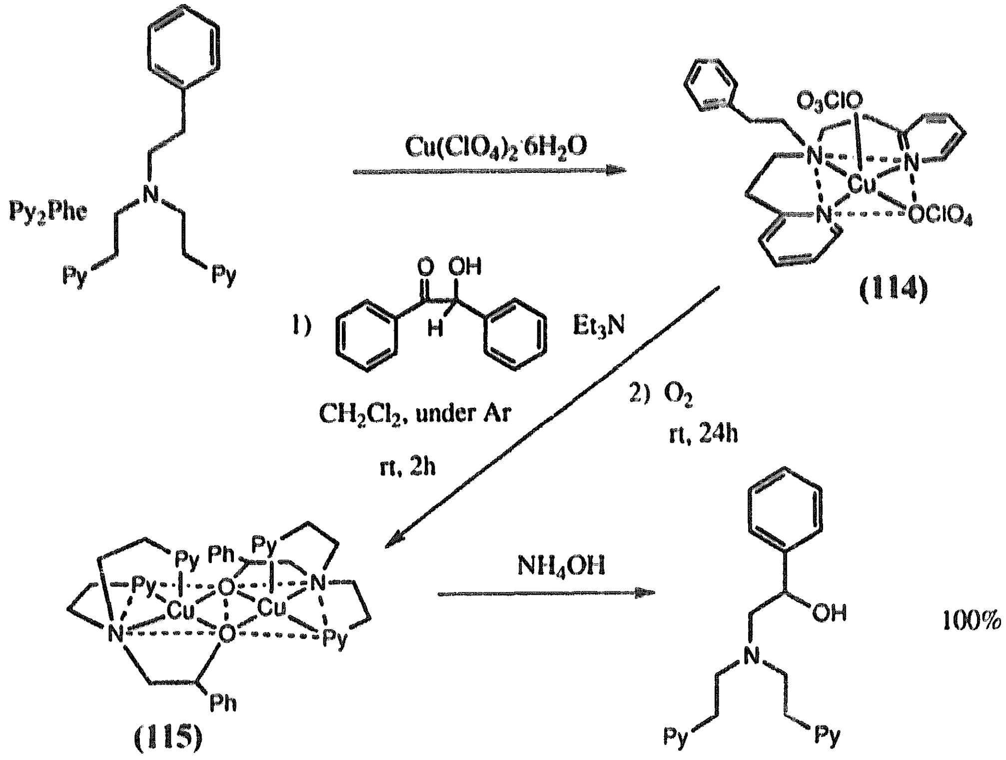


(112)



(113)

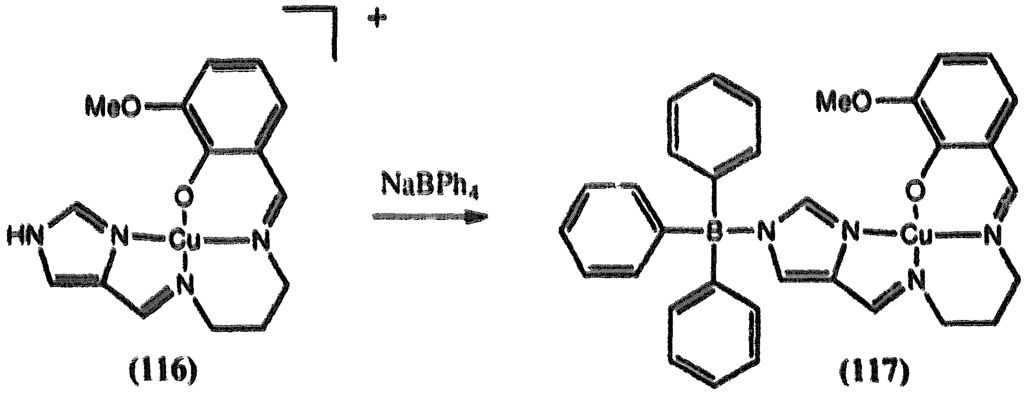
these copper centres have recently been suggested as having different roles, one (Cu_A) being an electron acceptor (ascorbate binding site) and the other(Cu_B) acting as a substrate as well as an O_2 binding site. In order to mimic the enzyme active centre, a tridentate ligand py_2Phe (*N*,*N*-bis[2-(2-pyridyl)ethyl]-2-phenylethylamine) in which a phenylethylamine (substrate) moiety is incorporated into the ligand molecule. The copper(II) complex (**114**) was prepared by the treatment of the py_2Phe ligand with $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol (Scheme 2). X-Ray crystallographic analysis of the complex shows the Cu(II) complex has a nearly square pyramidal structure and with the phenyl ring located far from the copper centre. In the enzymatic system, two electrons are supplied to the Cu_B active centre from ascorbate through the Cu_A centre during the hydroxylation reaction. Therefore, this study employed a 1,2-enediolate, derived from benzoin and a base, as a model of the electron donor, ascorbate. The Cu(II) complex (**114**) was treated with an



Scheme 2.

equimolar amount of benzoin and triethylamine in CH_2Cl_2 at room temperature for 2h under Ar and then the mixture stirred under an atmospheric pressure of O_2 for several hours. On standing, a single green crystal was obtained and its structure determined by X-ray crystallographic analysis. The product was shown to be a dinuclear copper(II) complex (**115**) in which ligand hydroxylation had occurred selectively at the benzylic position of the substrate moiety and this O^- group acts as a bridge for both copper atoms. The two copper centres have nearly square pyramidal structures. The yield of the ligand hydroxylation was 100% with the modified ligand being isolated after treating the reaction mixture with NH_4OH. When the reaction was carried out using $[Cu^I(CH_3CN)_4](PF_6)$ under O_2 rather than the Cu^{II} salt, the yield of hydroxylation was 50% based on the copper ion and the stoichiometry of $Cu{:}O_2$ was 2:1 which indicates that 2 equivalents of electrons and one equivalent of O_2 are required for the quantitative ligand hydroxylation.

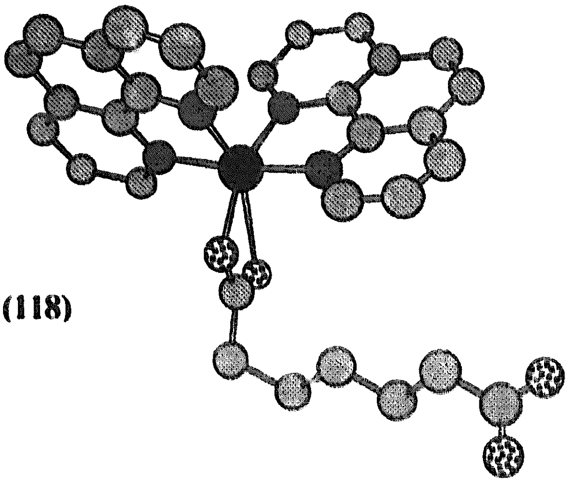
The perchlorate salt of the copper(II) complex (**116**) reacts with sodium tetraphenylborate in dmf to give an electrically neutral complex (**117**) exhibiting a B-N bond [86]. The syntheses and the crystal structures of (**116**) and (**117**) and the *N*-methylimidazole adduct of (**117**), $[Cu(LBPh_3)(N\text{-MeIm})]$ are reported. The important feature of (**117**) and its *N*-methylimidazole adduct is the presence of a B–N bond, in which the boron atom bonds to the nitrogen atom of the imidazolate moiety of the copper(II) complex and to the three carbon atoms of the phenyl groups. The B–N bond of (**117**) is rather stable towards acid and base.



(**116**) (**117**)

The copper(II) complex $[Cu(bdoa)(H_2O)_2]$ ($bdoaH_2$ = benzene-1,2-dioxyacetic acid) reacts with aniline in an ethanol-water mixture to give $[Cu(bdoa)(C_6H_5NH_2)_2]_2C_6H_5NH_2$ [87]. The X-ray crystal structure of this complex shows the asymmetric unit to contain two mononuclear $[Cu(bdoa)(C_6H_5NH_2)_2]$ units and a solvent aniline molecule. Each copper(II) atom has essentially square planar coordination and is bonded to the nitrogen atoms of two *trans* aniline molecules and a single oxygen atom from each of the two carboxylate moieties of the $bdoa^{2-}$ ligand. The ether oxygen atoms of the $bdoa^{2-}$ bond only weakly to the metal, and one of the metals also interacts weakly with the solvate aniline. Compound $[Cu(bdoa)(H_2O)_2]$ reacts with bipyridine to form the dinuclear copper(II) complex $[Cu_2(bdoa)(bpy)_4]bdoa.8.66H_2O$ the X-ray structure of which shows a discrete $[Cu_2(bdoa)(bpy)_4]^{2+}$ dication, an uncomplexed $bdoa^{2-}$ dianion and water molecules linked by O–H···O hydrogen bonding. The dication shows the copper centre to have a N_4O_2 distorted octahedral. Only one of the carboxylate oxygens is strongly bonded and the other forms a weak interaction with the metal centre.

The α,ω-dicarboxylic acids heptanedioic acid ($hdaH_2$) and octanedioic acid ($odaH_2$) reacted smoothly with $[Cu(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ in water giving the insoluble copper(II) complexes [Cu(hda)] and [Cu(oda)] [88]. These complexes reacted further with 1,10-phenanthroline giving $[Cu(\eta^2\text{-hda})(phen)_2]\cdot xH_2O$ and $[Cu(\eta^2\text{-oda})(phen)_2]\cdot xH_2O$ ($x \approx 8$), respectively. The X-ray structures of $[Cu(\eta^2\text{-hda})(phen)_2]\cdot 11.73H_2O$, **(118)**$\cdot 11.73H_2O$, and $[Cu(\eta^2\text{-oda})(phen)_2]\cdot 12H_2O$ show that for each complex the copper(II) atom lies at the centre of a distorted octahedron comprising four nitrogen atoms from two chelating phen units and two oxygen atoms from a single asymmetric chelating carboxylate function, with the remaining carboxylate group of the diacid uncoordinated.



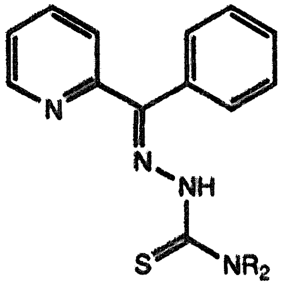
(118)

Mononuclear compounds of composition $CuX_2(py)_2(H_2O)$ and dinuclear complexes of composition $Cu_2X_4(py)_2$ (py = pyridine, X = heptanoate, octanoate, nonanoate, decanoate or dodecanoate) were prepared and analysed [89]. Generally, the complexes are unstable, the mononuclear being even less so than the dinuclear, losing pyridine in air at room temperature. The X-ray structure of the mononuclear adduct of copper(II) nonanoate with pyridine, $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$, was determined and shows the copper centre to have a square pyramidal coordination geometry with two pyridine nitrogen atoms and two oxygen atoms from unidentate nonanoato ligands forming the basal plane of the pyramid and with a water molecule coordinated at the apex.

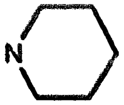
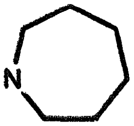
3.2.5. Nitrogen and sulfur coordination

2-Benzoylpyridine ^{4}N-substituted thiosemicarbazones (**119**) commonly coordinate as neutral tridentate ligands to give five coordinate $[Cu(HL)Cl_2]$ complexes when prepared in boiling isopropanol [90]. However, when prepared in boiling ethanol, the anion (loss of the ^{3}N-hydrogen) coordinates as a tridentate ligand to give

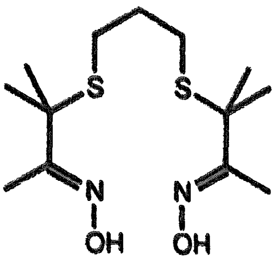
[CuLCl] complexes. The crystal structures of representatives of both stoichiometries, [Cu(HBz4P)Cl_2] and [Cu(Bzhexim)Cl], have been determined (Lhexim = the anion of 2-acetylpyridine 3-hexamethyleneiminylthiosemicarbazone). The antifungal properties of some of the complexes are described.



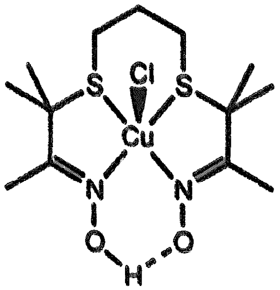
(119)

	R
HBz4M	NHMe
HBz4E	NHEt
HBz4P	NHPr
HBz4DE	NMe_2
HBz4DP	NPr_2
HBzpip	
HBzhexim	

The reaction of $CuCl_2$ with ligand (**120**) in methanol-acetone afforded the neutral five-coordinate dithiadioxime copper(II) complex (**121**) [91]. The crystal structure of Cu(LH)Cl monohydrate, $[CuCl(C_{13}H_{25}N_2S_2O_2)]\cdot H_2O$, shows the copper centre to have a square pyramidal geometry. The Cu(II) ion is coordinated in an approximately square plane by the two oxime nitrogen atoms and the two thioether sulfur atoms of the tetradentate dithiadioxime ligand and with the chlorine atom occupying the apical coordination site at a Cu–Cl distance of 2.2931(8) Å. The Cu···N distances average 1.997 Å, while the Cu···S distances average 2.3279 Å. The copper atom is displaced 0.467(1) Å above the S_2N_2 plane towards the chlorine atom. A proton bridges the two oxime oxygen atoms (O···O = 2.425(3) Å) of the complex in the fashion typical of metal complexes containing *cis*-oxime functions.

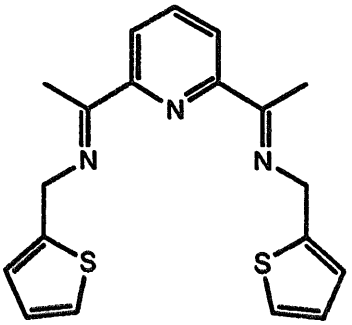


(120)



(121)

An investigation into the development of simple models towards further understanding of the structural and redox properties in copper metalloenzymes has resulted in the structure of the copper(II) complex of the Schiff base ligand (**122**) has been determined [92]. Mixing one equivalent of $Cu(ClO_4)_2\cdot 6H_2O$ and one equivalent of (**122**) afforded the complex of 1:2 Cu:(**122**) stoichiometry. The copper(II) ion is coordinated to six nitrogen atoms in an octahedral arrangement not involving the thiophene S atoms. Cyclic voltammetry in acetonitrile showed reversible behaviour for the $[Cu^{II}(122)_2]^{2+}$-$[Cu^{I}(122)_2]^{+}$ couple.



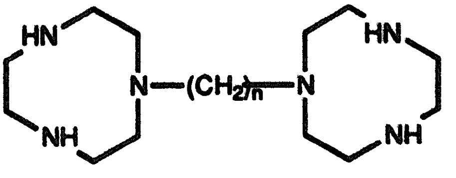
(122)

The copper(II) complex of 2-methylthiosemicarbazide (2MeTSC) was obtained to evaluate the influence of the ^{2}N-substitution on the structure and properties of thiosemicarbazide complexes. The structure of $[Cu(2MeTSC)_2(NO_3)_2]$ was determined [93]. The complex was shown to be monomeric and hexa-coordinated with a strongly tetragonally elongated octahedral structure. Two 2MeTSC groups coordinate to the metal ion as didentate ligands through the hydrazinic nitrogen and the sulfur atoms, giving a nearly square-planar coordination. The remaining two coordination sites are filled by two NO_3^- anions at a long distance from the metal (Cu···O = 2.864(3) Å). The Cu···S (2.262(1) Å) and Cu–N (1.992(3) Å) bond lengths are shorter than those observed in similar thiosemicarbazide copper(II) compounds indicating a stronger bond. The complex units link together into a 3-dimensional network through hydrogen bonding. The interest in thiosemicarbazides and thiosemicarbazones arises owing to their pharmacological activity.

3.3. Dinuclear complexes with macrocyclic ligands

Two members of a homologous series of bis(triazacyclononane) ligands, 1,3-bis(1,4,7-triaza-1-cyclononyl)propane, (**123**) and 1,4-bis(1,4,7-triaza-1-cyclononyl)-butane, (**124**), form stable 1:1 and 2:1 Cu(II)-L complexes [94]. The cation $[Cu(\mathbf{123})]^{2+}$ is more stable than $[Cu(\mathbf{124})]^{2+}$ while $[Cu_2(\mathbf{124})]^{4+}$ is slightly more stable than $[Cu_2(\mathbf{123})]^{+}$. Dinuclear complexes of both ligands have been isolated and their structures determined by X-ray crystallography. In both complexes, the copper(II) centre is 5-coordinate with two secondary amine N atoms of a [9]ane N_3 group and two Cl^- occupying sites at the base and the tertiary N atom of the same unit at the apex of a square pyramid. The structures have somewhat different conformations: the pair of chloride ions attached to the two Cu(II) are approximately *syn* for $Cu_2(\mathbf{123})Cl_4 \cdot 2H_2O$ and *anti* for $Cu_2(\mathbf{124})Cl_4$. This family of ligands allows construction of dinuclear complexes where metal-metal distances can be varied.

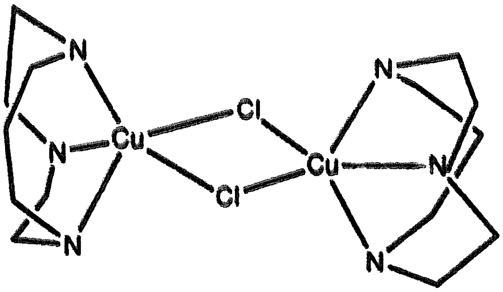
A systematic study has been carried out into the long-range exchange coupling between two unpaired electrons of two copper(II) ions in a square pyramidal ligand environment which are rigidly separated by > 10 Å by an organic spacer ligand (*e.g.*



n = 3 (123)
n = 4 (124)

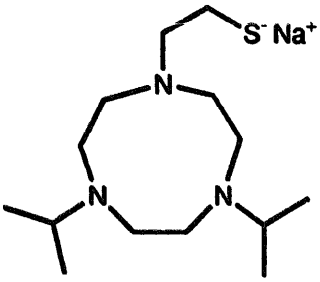
a μ-dicarboxylato ligand) [95]. The following complexes have been synthesised and characterised $[\{LCu(OH_2)\}_2(\mu\text{-terephthalao})](ClO_4)_2$ $[LCu^{II}(OH_2)(\text{benzoato})](ClO_4)$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-terephthalato})].2CH_3OH$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-4,4'-oxybisbenzoato})].3CH_3OH$, $[\{LCu^{II}(OH_2)\}_2(\text{m-tetrafluoroterephthalato})](ClO_4)_2$, $[\{LCu^{II}(OH_2)\}_2\{LCu^{II}\}_2(\mu\text{-tetrafluorobenzoato})_3](ClO_4)_2.6H_2O$, $[\{LCu^{II}(OH_2)\}_2(\mu\text{-biphenyl-4,4'-dicarboxylato})](ClO_4)_2$, $[LCu^{II}(\mu\text{-biphenyl-4,4'-dicarboxylato})]_n(H_2O)_{2n}$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-biphenyl-4,4'-dicarboxylato})]$, $[\{LCu(OH_2)\}_2(\mu\text{-}trans,trans\text{-2,4-hexadien-1,6-dicarboxylato})](ClO_4)_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). The combined crystallographic and magnetic susceptibility data from this investigation demonstrate that intramolecular antiferromagnetic exchange coupling of considerable magnitude is possible over distances >15 Å, provided that the effective magnetic orbitals are favourably aligned.

Two dichloro-bridged dimeric metal complexes of 1,4,7-triazacyclodecane (tacd) $[Cu_2(tacd)_2Cl_2](ClO_4)_2$ (**125**) and $[Zn_2(tacd)_2Cl_2](ClO_4)_2$ have been prepared and characterised by X-ray crystallographic analysis [96]. Each copper(II) atom has a highly distorted trigonal-bipyramidal N_3Cl_2 coordination geometry with the Cu-N bond lengths in the range of 2.011(4)–2.180(4) Å and the Cu–Cl bond lengths in the range 2.323(3)-2.353(1) Å. The Cu···Cu distance is 3.369(1) Å.

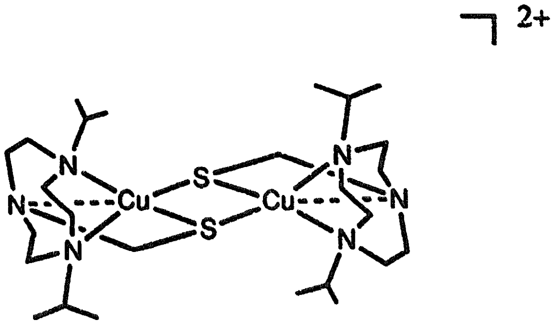


(125)

A model system for understanding the unusual spectroscopic properties of type I copper sites in proteins has been reported in a study that claims the first example of a doubly bridged $Cu^{II}_2(\mu-SR)_2$ [bis(μ-thiolato)dicopper(II)] motif by using a sterically hindered ligand (**126**) [97]. Mixing the ligand with cupric triflate in thf, followed by removal of solvent, anion exchange ($NaClO_4$ in MeOH) and recrystallisation afforded the complex $[(\mathbf{126})Cu]_2(ClO_4)_2$ (**127**) as dark green crystals. Crystallographic determination of the crystals showed the complex to consist of two symmetry-related square pyramidal Cu(II) ions linked by the thiolate arms of the ligands. The short Cu···Cu separation of 3.340(3) Å arises from the structure showing a distinct "butterfly" distortion with the axial N donors in a *cis* arrangement. Combined analytical and spectroscopic data suggest that the structure persists in a methanolic solution. X-Ray absorption spectroscopic measurements on the complex have helped to define the EXAFS signatures associated with bis(thiolate)-bridged dicopper centres. This has shown that observable Cu–Cu interactions are expected from dicopper sites with bis(thiolate) connectivity at distances well in excess of 3 Å. This result is relevant to the interpretation of the EXAFS of the Cu_A sites in proteins where the Cu···Cu distances are believed to be much shorter (2.5 Å).



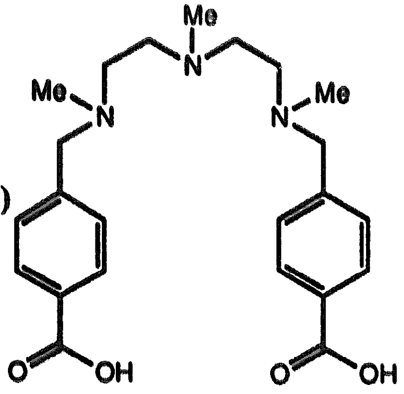
(126)

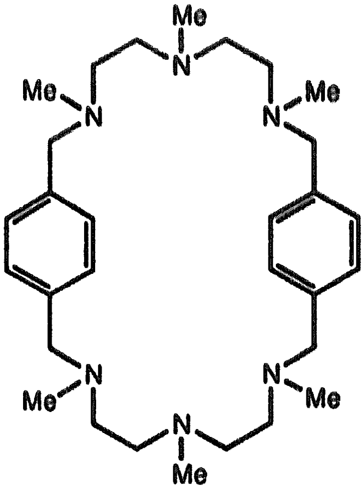


(127)

The syntheses of 1,4,7-trimethyl-1,7-bis(4-carboxybenzyl)-1,4,7-triazaheptane (**128**) and 1,4,7,16,19,22-hexamethyl-1,4,7,16,22-hexaaza[9.9]paracyclophane (**129**) are described [98]. **129** forms both mono and dinuclear complexes with Cu^{2+} in aqueous solution, but does not interact with Zn^{2+} and Cd^{2+}. The X-ray structure of crystals of $[Cu_2(\mathbf{129})Cl_2](ClO_4)(BPh_4).CH_3CN$ show the two copper(II) centres coordinated by three nitrogen atoms of the ligand and a Cl^- anion in a square coordination environment. The ligand acts as a ditopic receptor. The stability of **128** with divalent metal ions is rather low. Thermodynamic data suggest the N_3 moiety is the binding site for the Cu^{2+}.

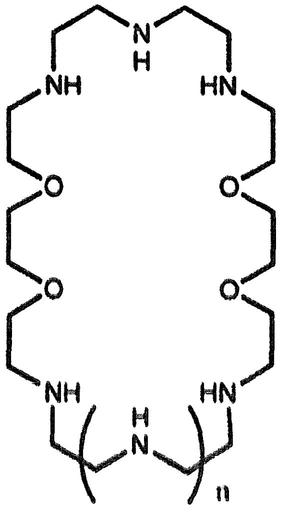
(128)





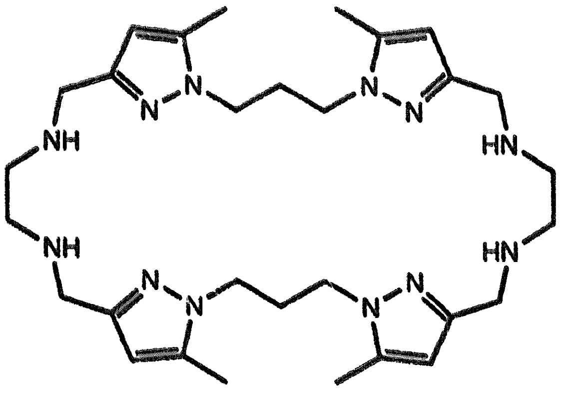
(129)

The Cu(II) complexes of two new macrocyclic ligands 1,4,7,16,19,22-hexaza-10,13,25,28-tetraoxacyclotriacontane (**130**) and 1,4,7,16,19,22,25-heptaza-10,13,28,31-tetraoxacyclotritriacontane (**131**) are reported [99]. Both ligands contain two polyamine units separated by two eight atom dioxa-bridges. Both (**130**) and (**131**) form mono- and dinuclear complexes in aqueous solution. In the mononuclear complex, the Cu(II) ion is coordinated to only one polyamine unit. The dinuclear complexes show a marked tendency to form mono- and dihydroxo species in aqueous solution. The high values for the formation constants for the addition of the first hydroxide group to the dinuclear complexes suggests that in the $[Cu_2(\mathbf{130})(OH)]^{3+}$ and $[Cu_2(\mathbf{131})(OH)]^{3+}$ species the OH^- group bridges the two metal centres. This thermodynamic result is confirmed by the crystal structure of the zinc analogue $[Zn_2(\mathbf{130})(\mu\text{-}OH)](ClO_4)_3\cdot 0.5EtOH$. In the crystal structure of $[Cu_2(\mathbf{130})(NCS)_4]$, each metal ion is coordinated to one triamine unit and by two isothiocyanate ions in a distorted square pyramidal arrangement. The Cu···Cu distance is 6.18 Å. In the structure of $[Cu_2(\mathbf{130})(NCS)_4]$.Na2S2, the copper centres exhibit a coordination geometry almost equal to that found in $[Cu_2(\mathbf{130})(NCS)_4]$, but the $[Cu_2(\mathbf{130})(NCS)_4]$ units are joined by NCS—Na^+—$(S\text{-}S)^{2-}$—Na^+ interactions giving rise to a 3-dimensional polymeric structure.



n =1 (**130**)

n =2 (**131**)

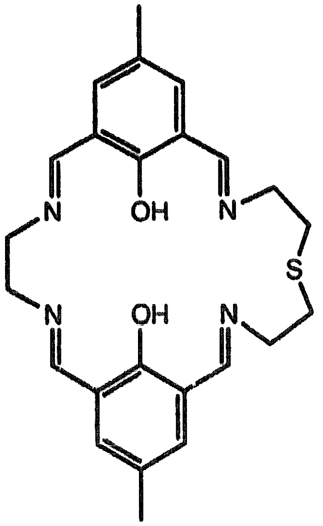


(**132**)

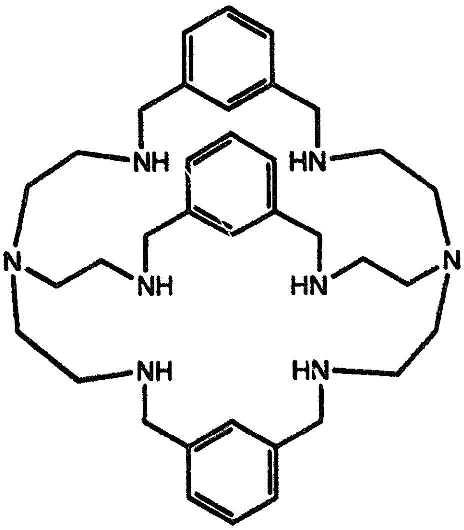
In the aim of synthesising mimics for the active site of copper proteins such as haemocyanin, tyrosinase and dopamine-β-hydroxylase the first example of a structurally characterised macrocycle containing neutral endocyclic pyrazole donors capable of coordinating two metal ions is reported [100]. The 30-membered tetrapyrazolyl macrocycle (**132**), was synthesised by the Schiff base condensation under dilute conditions between the 1,3-di(3′-formyl-5′-methyl-1′-pyrazolyl)propane precursor and ethylenediamine followed by *in situ* reduction of the (2+2) tetraimine macrocycle with $NaBH_4$. The addition of 2 equivalents of $Cu(NO_3)_2$ to a solution of (**132**) affords the dinuclear copper(II) complex. Microanalytical data are consistent with a mixed-anion composition with formula $[Cu_2(\mathbf{132})Cl_2(EtOH)_2](NO_3)_2$. The presence of the chloride ion arises from the unexpected coordination of NaCl during the isolation of the ligand. However, NaCl is only weakly bound to (**132**) and can be removed by washing a CH_2Cl_2 solution of (**132**) with water. The X-ray structure of the complex reveals the presence of two copper(II) ions, each bound in a distorted square pyramidal geometry. The absence of any bridging ligand between the copper centres results in a long Cu···Cu distance of 7.14 Å. However, the macrocycle appears to be sufficiently flexible to allow bridging of small molecules such as hydroxide anions.

A dinucleating macrocycle H_2L with two 2,6-bis(iminomethyl)-4-methylphenolate entities combined through two lateral chains, CH_2CH_2 and $CH_2CH_2SCH_2CH_2$, at the imino nitrogen atoms has been obtained as a mononuclear copper(II) complex $[Cu(\mathbf{133})](ClO_4)_2$ [101]. Reaction of this complex with a second metal ion under alkaline conditions forms the dinuclear complexes $[Cu^{II}M^{II}(\mathbf{133}\text{-}2H)(NCS)_2].H_2O$ (M = Co, Ni, Zn), $[Cu^{II}Cu^{II}(\mathbf{133}\text{-}2H)](ClO_4)_2$ and $[Cu^{II}Cu^{I}(\mathbf{133}\text{-}2H)](ClO_4)$. An antiferromagnetic spin exchange is observed in the $Cu^{II}M^{II}$ complexes with $J = -32\ cm^{-1}$ for Co, $-90\ cm^{-1}$ for Ni and $-440\ cm^{-1}$ for Cu. The cyclic voltammograms of the $[Cu^{II}Cu^{II}(\mathbf{133}\text{-}2H)](ClO_4)_2$ and $[Cu^{II}Cu^{I}(\mathbf{133}\text{-}2H)](ClO_4)$ complexes showed a reversible Cu^{II}–Cu^{I} redox couple at +0.08 V for the copper ion at the site with the $CH_2CH_2SCH_2CH_2$ lateral chain. The crystal structure of $[CuZn(\mathbf{133}\text{-}2H)(NCS)_2]\cdot dmf$ has been determined. This shows a CuZn dinuclear structure bridged by two phenolic oxygen atoms. The Cu^{II} resides at the site with the CH_2CH_2 and assumes a square pyramidal geometry with an isothiocyanato nitrogen atom at the apex. The Zn^{II} is at the site with the $CH_2CH_2SCH_2CH_2$ chain and assumes a similar square pyramidal geometry with an isothiocyanate nitrogen at the apex.

The imidazolate-bridged dinuclear copper(II) (**134**) and the imidazolate-bridged



(**133**)

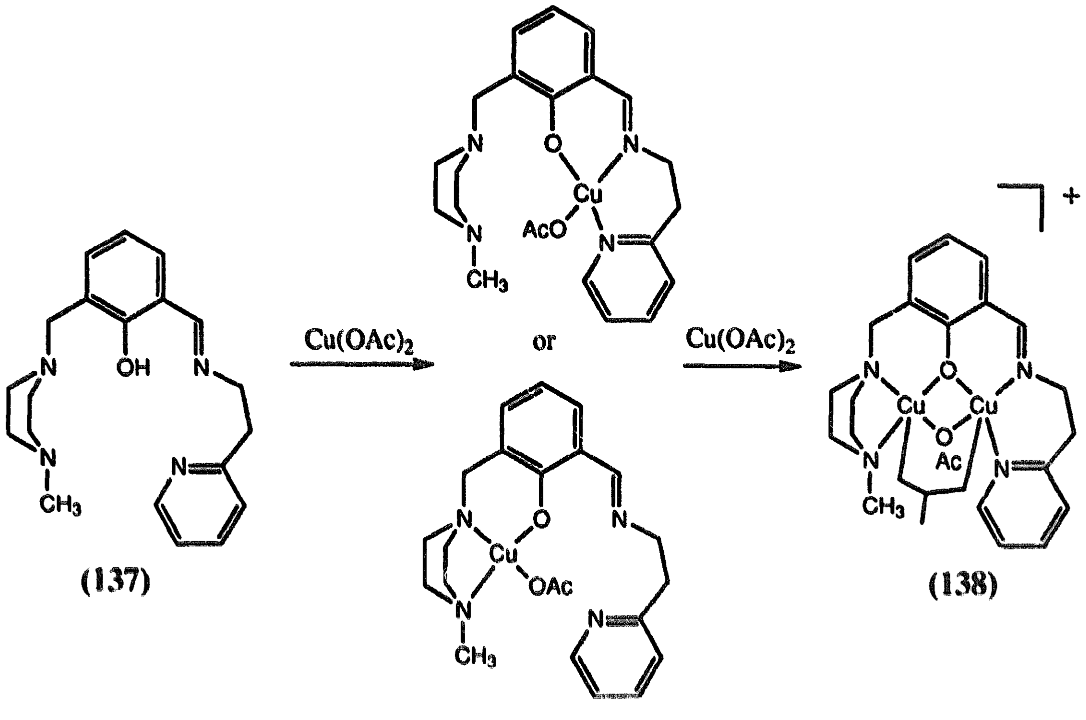


(136)

heterodinuclear copper(II)–zinc(II) (**135**) complexes of the macrobicyclic ligand (**136**) (L = 1,4,12,15,18,26,31,39-octaazapentacyclo[13.13.13.$1^{6,10}$.$1^{20,24}$.$1^{33,37}$]tetratetracontane-6,8,10,20,22,24,33,35,37-nonanene) were synthesised as possible models for superoxide dismutase (SOD) [102]. The solid state structures of both complexes show that the two ions are pentacoordinated in a coordination environment that is found to be a slightly distorted trigonal bipyramid for one metal centre and a distorted square pyramid for the other. The metal-nitrogen bond lengths range from 1.91 to 2.33 Å and with the Cu···Cu and Cu···Zn distances being 5.95 and 5.93 Å, respectively, slightly shorter than the value in the (Cu–Cu) SOD or in the (Cu–Zn) SOD. Magnetic measurements and ESR spectroscopy of the dicopper complex show an antiferromagnetic exchange to occur with a coupling constant of $-2J = 88\ \text{cm}^{-1}$. The complexes have been found from pH-dependent ESR and electronic spectroscopic studies to be stable over wide pH ranges (4.4–12 for (**134**) and 6–10.5 for (**135**)). Electrochemical studies have indicated quasi-reversible behaviour in dimethylacetamide solution for the first step of the reduction Cu^{II}_2/Cu^{I}_2 $E_{1/2}$ −0.27 V for (**134**) and $E_{1/2} = -0.31$ V for (**135**) (both *vs* SCE). Both complexes catalyse the dismutation of superoxide at biological pH and the activity survives in the presence of bovine serum albumine. All these results indicate that both (**134**) and the zinc complex act as good models for superoxide dismutase.

3.4. *Dinuclear complexes with acyclic ligands*

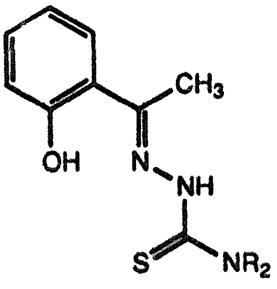
A new nonsymmetric dinuclear copper(II) complex [Cu(**137**)(OAc)$_2$](ClO$_4$) (**138**) has been synthesised as a possible mimic for active sites of type III dinuclear copper enzymes hemocyanin and tyrosinases [102]. The complex was prepared by complexation of Cu(OAc)$_2$.H$_2$O with a new nonsymmetric dinucleating ligand (**137**) which is formed *in situ* by condensation of 2-formyl-6-((4-methylpiperazin-1-yl)methyl)-phenol with 2-(aminoethyl)pyridine (Scheme 3). The crystal structure establishes the presence of a dinuclear copper core with distinct copper sites. One of the copper ions is coordinated by two sp^3 nitrogen atoms whereas the other copper is coordinated by two sp^2 nitrogen atoms. The two copper ions are bridged by a phenoxo group, by a *syn-syn* didentate acetato bridge and by a monodentate acetato group resulting in a Cu···Cu distance of 3.0293(10) Å. The copper centres are weakly antiferromagnetically coupled with $2J = -15\ \mathrm{cm}^{-1}$. Microcalorimetric and UV–VIS spectroscopic measurements establish the stepwise complexation behaviour of the ligand (**137**) with the enthalpy of formation of the first complexation step being $-8.4\ (\pm 0.2)\ \mathrm{kcal\ mol}^{-1}$ ($K = 1.8\ (\pm 0.1) \times 10^8$; and for the second step $\Delta H = -1.9\ (\pm 0.1)\ \mathrm{kcal\ mol}^{-1}$ ($K = 1.1\ (\pm 0.1) \times 10^5$) as determined by microcalorimetry.



Scheme 3.

Dinuclear copper(II) complexes with eight different 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones (**139**) have been prepared and characterised [103]. The copper(II) complex of 2-hydroxyacetophenone 3-hexamethyleneiminylthiosemicarbazone $[\mathrm{Cu(Aphexim)}]_2$ has been solved.

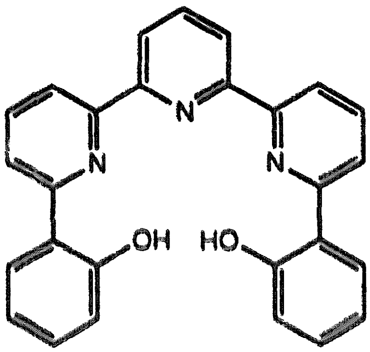
A potentially pentadentate (ONNNO donor) ligand 6,6″-bis(2-hydroxyphenyl)-2,2′:6′,2″-terpyridine (**140**) was reacted with Cu(II) resulting in the formation of $[\{\mathrm{Cu}(\mathbf{140}\text{-H})\}_2](\mathrm{PF_6})_2$ [104]. X-Ray structural analysis showed the complex to exist as centrosymmetric dimers. The monomeric unit is four coordinate $\mathrm{Cu(HL)}^+$ in which the copper(II) ion is coordinated to one phenolate oxygen and three pyridyl nitrogen atoms of (**140**-H). The remaining phenol group remains protonated and uncoordinated, but involved in hydrogen-bonding interactions with $[\mathrm{PF_6}]^-$ ions or lattice MeCN molecules. The geometry is best described as square planar. Two of these units are stacked such that the copper(II) centre of one monomeric unit is coordinated axially by the phenolate ligand of the other, forming a $\mathrm{Cu_2}(\mu\text{-O})_2$ core with (approximately) elongated square-pyramidal copper(II) centres, resulting in



(139)

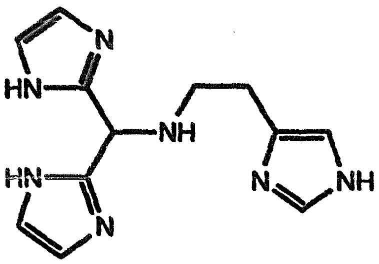
^{4}N substituent
NHMe
NHEt
NHPr
$N(Me)_2$
$N(Et)_2$
$N(Pr)_2$
$NCH_2(CH_2)_3CH_2$
$NCH_2(CH_2)_4CH_2$ H_2Aphexim

aromatic stacking between the two ligands. Low-temperature magnetic susceptibility measurements indicate a weak antiferromagnetic coupling between the metals.

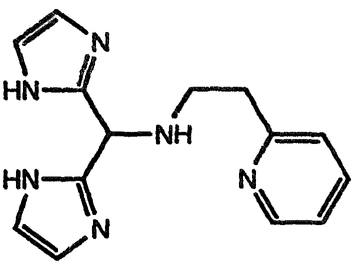


(140)

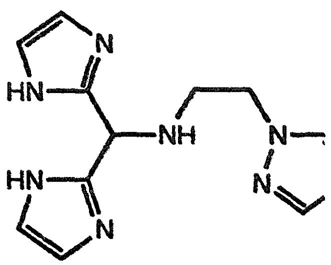
A study into the synthesis of model systems for the dinuclear type-3 site of haemocyanin in which the copper centre is bound by three imidazole nitrogens from histidine residues has been carried out [105]. The Cu···Cu distance in the oxy and deoxy form of *Limulus lyphemus* haemocyanin has been determined as ≈3.6 Å and ≈4.6 Å, respectively. Three new asymmetric tripodal imidazole-containing ligands (**141**), (**142**) and (**143**) have been designed and synthesised by the reaction of bis(imidazol-2-yl)nitromethane with histamine, 2-ethylaminopyridine and 1-ethylaminopyrazole, respectively. The reaction of (**143**) with copper(II) perchlorate in ethanol afforded the rather unusual dinuclear complex $\{[Cu_2(\mathbf{143})_2(ClO_4)_2](ClO_4)_2\}$ (**144**) which is formed by two copper ions sharing two ligand moieties. This sharing of two ligands results in the formation of a cavity between the two copper^{II} ions which may be accessible to small molecules after a slight conformational rearrangement. The two copper centres are separated by a distance of 3.42 Å and coordinated in a square pyramidal geometry, with the equatorial sites occupied by a nitrogen of the bis(imidazole) unit, the amine nitrogen atom, the nitrogen atom of the separate imidazole group and the nitrogen atom from a bis(imidazole) unit of a second ligand. The axial site is filled by a weakly coordinated perchlorate anion. The diffuse-reflectance spectrum in the VIS-NIR region shows a band at $17.7\times10^3\,\mathrm{cm}^{-1}$, which is the usual range for a square pyramidal coordinated Cu^{II} ion.



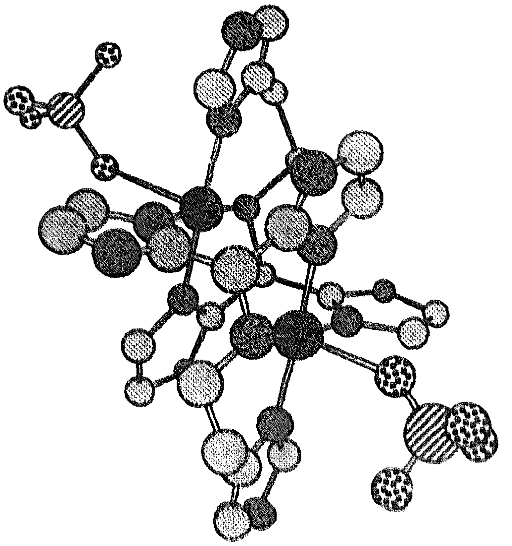
(141)



(142)



(143)



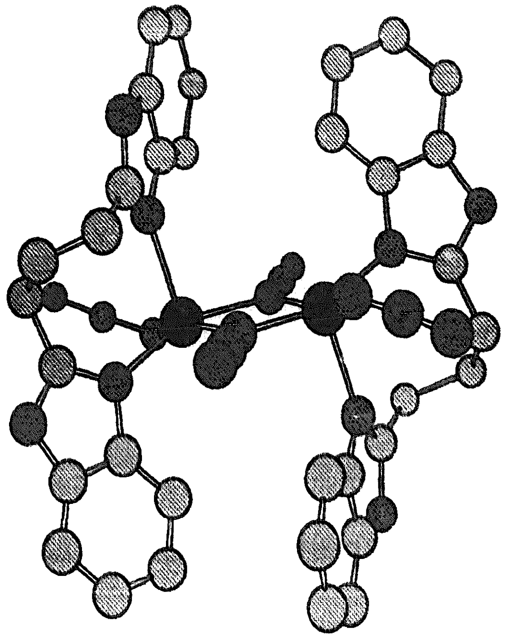
(144)

The structure of the complex $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ (L-Et = the anion of *N,N,N′,N′*-tetrakis[2-(1-ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane) has been redetermined and has been found to deviate significantly from that published earlier [106, 107]. The main difference between the two structures is the coordination geometry of the copper ions which is trigonal-bipyramidal in the current determination, but approximately square-planar in the earlier structure. This results as a consequence of a different coordination of the central carbon atom of the L–Et ligand. Magnetic measurements on the current compound shows a strong antiferromagnetic coupling ($-2J > 1200\,\mathrm{cm}^{-1}$) which is claimed to be a new lower limit for a single bridging azide in copper dimers. This study shows that a *cis* μ-1,3-bridging azide group is able to mediate strong superexchange without contribution from a second bridging ligand and indicates that a tetragonal ground state is not a necessity for strong antiferromagnetic coupling.

A group of new compounds with the general formula $Cu(L)(sol^-)(A^-)(Hsol)$, where $A = ClO_4^-$, $CF_3SO_3^-$, BF_4^- and NO_3^-, L = bis(2-benzimidazolyl)propane (tbz) and bis(2-benzimidazolyl)butane (qbz), and Hsol = methanol and ethanol, and with the formula $[Cu(tbz)(N_3^-)(Hsol)$ has been prepared and characterised structurally, magnetically and spectroscopically [108]. Three representative compounds

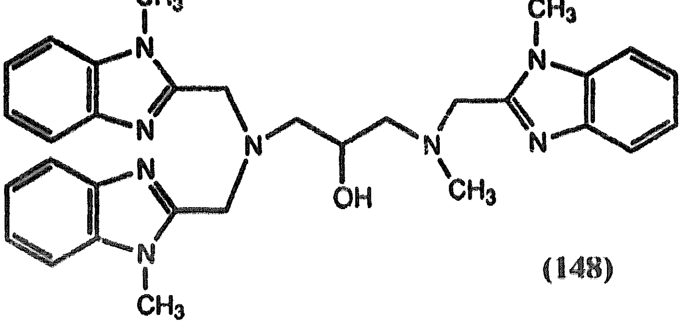
$[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$ (**145**), $[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$ (**146**) and $[Cu(tbz)_2(N_3)_2]_2(CH_3OH)_2$ (**147**) have been characterised by X-ray crystallographic analysis. The structures (**145**) and (**146**) consist of dinuclear units with bridging methoxo groups and one ligand linked to each copper *via* the nitrogen atom providing square planar CuN_2O_2 chromophores. Structure (**146**) consists of a dinuclear unit in which one of the copper atoms is linked to an oxygen atom of a nitrate ion to yield a unit with two different copper environments, one square planar and the other square pyramidal. Structure (**147**) consists of dinuclear units with the two copper centres bridged by μ-(1,1)-azido groups. Furthermore, each copper is surrounded by two nitrogen atoms of the ligand and a nitrogen atom of a non-bridging end-on μ(1,1)-azido unit resulting in a distorted square pyramidal geometry. Far infra-red spectroscopy reveals bands characteristic of the bridging $Cu_2O_2N_2$ chromophore with Cu–O vibrations found near 457 and 330 cm^{-1} for the ethoxo-bridged compounds and in the region 390 and 232 cm^{-1} for the methoxo-bridged compounds. The magnetic susceptibility measurements of the alkoxo-bridged compounds display a diamagnetic behaviour below room temperature with an estimated exchange parameter $2J$ of < -600 cm^{-1}. These dinuclear complexes are EPR silent, and only a weak signal assigned to monomeric impurities is observed. The μ-(1,1)-azido-bridged dimer shows ferromagnetic behaviour with a calculated J value of $+23$ cm^{-1} and a weak, very broad isotropic EPR signal at $g=2.14$. The results show that the ligands tbz and qbz in the presence of weakly coordinating anions in alcoholic solution form copper(II) alkoxy dimers. It appears that the ligands are sufficiently basic to dehydronate the alcohol. When stronger coordinating anions are used (*e.g.* chlorides) only monomeric species are obtained whereas with the azido anion bis-μ-(1,1)-bridging dimers are formed. Formation of the dinuclear species is related to the flexibility of the ligand; the ligand with the shorter chain between the two benzimidazole moieties (bis(2-benzimidazolyl)ethane) only forms monomeric species.

The synthesis and coordination chemistry of a new asymmetric multidentate ligand designed for modelling coordination number asymmetry at metal sites in dinuclear metalloproteins is reported [109]. A dinuclear copper complex of this ligand demonstrates proof-of-concept for inducing coordinative unsaturation at one metal of the dinuclear pair, and subsequent reaction with azide illustrates site-directed reactivity. The ligand *N,N,N'*-tris((*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propanol (**148**) reacts with copper(II) in methanol to produce a mononuclear copper complex, $[Cu(\mathbf{148})](ClO_4)_2 \cdot CH_3CN$. The X-ray structure of the complex shows that the copper ion is coordinated to the five N donor atoms in a distorted trigonal bipyramidal structure, with the hydroxo oxygen of the ligand not participating in the metal coordination. The reaction of (**148**) with 2 equivalents of Cu(II) and acetate in methanol produces the dinuclear copper complex $[Cu_2(\mathbf{148}\text{-}H)(OAc)](ClO_4)_2 \cdot 2H_2O$ (**149**). The solid state structure reveals that the two copper ions are coordinated to the aromatic and aliphatic N atoms as well as being bridged by the acetate anion and the alkoxide oxygen of the ligand. As a result of the inherent asymmetry in the ligand, one copper ion is five coordinate (distorted trigonal bipyramidal) while the other one is four coordinate (distorted

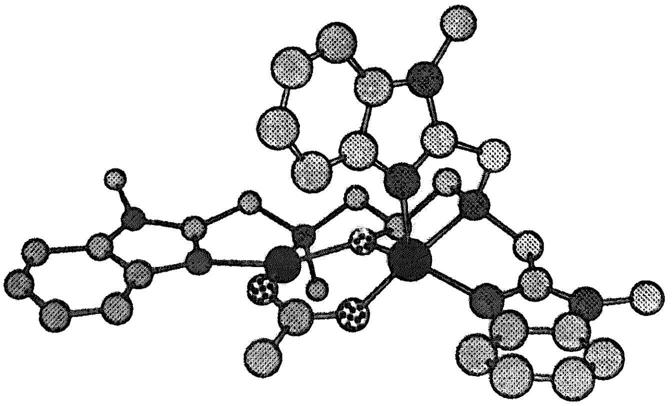


(147)

square planar). The structure also shows that in the solid state an oxygen atom from one of the perchlorate counter-ions is weakly bound to the 4-coordinate copper (≈2.6 Å), suggesting that a vacant coordination site exists at this formally 4-coordinate copper centre. The potential for site-directed reactivity at this lower coordinated copper centre was demonstrated by adding 0.5 equivalents of azide ion to the dinuclear complex in acetonitrile resulting in the formation of an azido-bridged complex of formula $\{[Cu_2(\mathbf{148}\text{-}H)(OAc)_2]N_3\}(ClO_4)_3 \cdot 8.5H_2O$. The X-ray structure of this complex shows that the two copper ions within the dinuclear unit are still bound to the ligand N atoms, the acetate and the alkoxy oxygen atom. In addition, the copper ion that was four coordinate is now bridged by azide to its neighbouring previously 4-coordinate centre in a separate dinuclear unit. As a result, both copper centres within the dinuclear unit are now 5 coordinate, one remaining distorted trigonal bipyramidal while the other adopts a square pyramidal geometry. The two dinuclear paramagnetic copper(II) complexes are only weakly magnetically coupled, but their ^1H NMR spectra show relatively sharp lines.

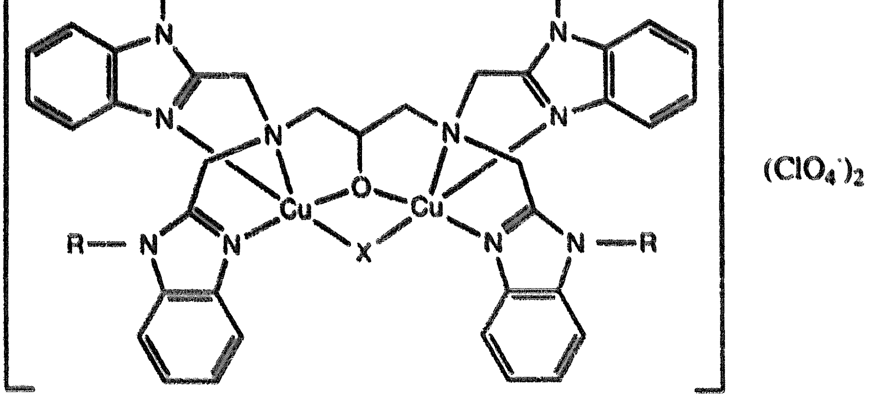


(148)



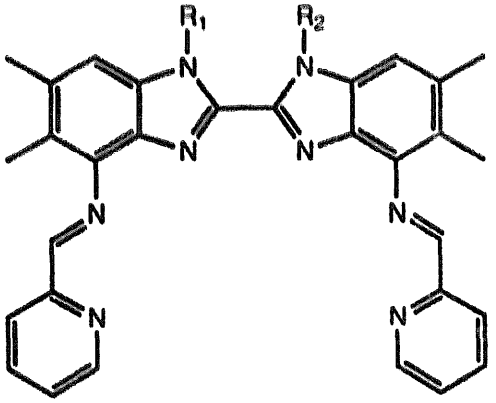
(149)

The (μ-alkoxo)(μ-X)dicopper(II) complexes [Cu_2(L-R)(X)](ClO4)$_2$ (**150**) have been prepared by two routes [110]. In the first, ethanolic solutions of the free ligand, HL-R, and two equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ were mixed to form the unbridged species [Cu_2(L-R)$(H_2O)_x$]$(ClO_4)_2$ which was then reacted with one equivalent of NaX to form the bridged species. In the second route, the free ligand, HL-Me and two equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ were added sequentially as solids to boiling methanol, followed by the addition of a methanolic solution containing two equivalents of NaX to precipitated the desired bridged complex. X-Ray structural analysis of the complexes [Cu_2(L-Me)(O_2CCH_3)]$(ClO_4)_2$ and [Cu_2(L-Me)(pz)]$(ClO_4)_2$ (with a pyrazolate bridge in place of the acetate bridge) have been obtained. The ^{1}H NMR spectra of the complexes in acetonitrile-d_3 are reasonably sharp and isotropically shifted signals are observed over the 250 to 1.5 ppm chemical shift range for the acetate-bridged complex and between 180 and 1.5 ppm for [Cu_2(L-Me)(pz)]$(ClO_4)_2$ which have been assigned. Hence this study shows that ^{1}H NMR spectroscopy can be used to characterise dinuclear complexes with magnetic coupling that ranges from weakly ferromagnetic (acetate) to strongly antiferromagnetic (pz).



(150)

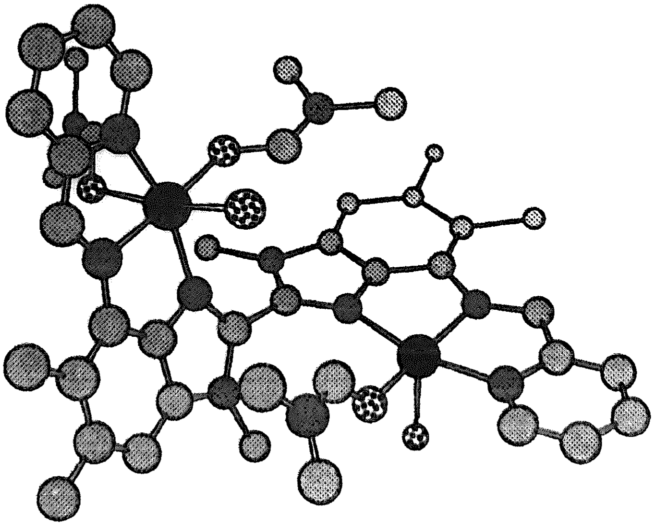
4,4′-Bis(2-picolinimino)-2,2′-dibenzimidazoles derived from 1,1′-disubstituted 4,4′-diamino-2,2′-bibenzimidazoles and 2-pyridinecarboxaldehyde were developed as models for type 3 sites of the copper proteins hemocyanin and tyrosinase [111]. These hollow, ditopic ligands can hold two metal ions face to face at distances of 3.15 Å or larger. The metal···metal distance can be restricted (tuned) to a given value *via* a corresponding polymethykene bridge in the backbone of the ligand. The complex $[Cu^{II}_2($*151*$)(dmf)_3(H_2O)_2](F_3CSO_3)_4$ (**153**) of the unrestricted ligand 1,1′,5,5′,6,6′-hexamethyl-4,4′-bis(picolinimino)-2,2′-bibenzimidazole (**151**) has been characterised by X-ray crystallography and shows an open conformation with discrete (4+2) copper environments, where two dmf molecules occupy the fourth positions of the equatorial CuN_3O squares (Cu–N=2.02 Å, Cu–O=1.95 Å). Two water molecules, a dmf and one of the triflate anions are coordinated to the four axial sites (Cu–O=2.28–2.74 Å). The two halves of the ligand are rotated out of the *cis*-coplanar conformation by 115.7° resulting in a relatively long Cu···Cu distance of 6.16 Å. In acetonitrile, the complex shows two irreversible Cu^{II}/Cu^{I} redox potentials at 0.60 and 0.30 V(vs NHE). Two oxygenation products of the dicopper(I) complex of the restricted ligand 1,1′-trimethylene-5,5′,6,6′-tetramethyl-4,4′-bis(2-picolinimino)-2,2′-bibenzimidazole (**152**), which best approaches the geometry of a type 3 site were isolated in the crystalline state. The first product, $[Cu^{II}_4(H_2(\mathbf{152})O_2^{2-})_2](ClO_4)_4$, is a tetranuclear copper(II) cluster, best described as a symmetric Cu_4O_4 eight membered ring (Cu···Cu distances are 3.05, 3.50 and 6.30 Å), attached to two (**152**) molecules, with the four oxy anions covalently linked to the azomethane carbons. The second oxygenation product $[Cu^{I}_2(L3')_2](ClO_4)_2$ is a dinuclear copper(I) complex of a degradation product of (**152**), carrying a free amino group on one side. The copper ions are in a bis(diimine) type, distorted tetrahedral environment (dihedral angle 79.1°) with a Cu···Cu distance of 4.59 Å.



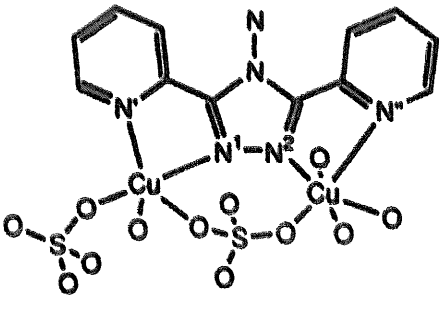
(**151**) $R_1 = R_2 = CH_3$
(**152**) R_1-$R_2 = (CH_2)_3$

The structure of (μ-4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole-*N′*,*N*^{1},*N*^{2},*N″*)(μ-sulfato-*O*,*O′*)[(sulfato-*O*)aquacopper(II)]triaquacopper(II)hydrate, $[Cu_2(abpt)(SO_4)_2(H_2O)_4]\cdot H_2O$ (**154**) in which abpt=4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole, has been determined [112]. The structure consists of asymmetric dinuclear units in which the copper(II) ions are linked by an *N*^{1},*N*^{2} bridging chelating abpt ligand and a didentate bridging sulfate anion resulting in the Cu-O distances being very short (1.937(4)-1.908(5) Å) and with a Cu···Cu distance is 4.415(1) Å. The

(153)

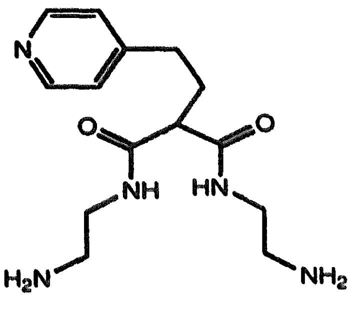


compound is claimed to represent the first example of a dinuclear copper(II) compound having a single N^1N^2 1,2,4-triazole bridge. Both Cu(II) ions have four short equatorial distances to the bridging sulfate, the bridging 1,2,4-triazole, the pyridyl group and a monodentate sulfate or a water molecule. One of the copper centres has one additional apical water molecule while the second copper has two additional axial water molecules. Hydrogen bonding appears to play an important role in the stabilisation of the complex. The study has shown that the anisotropic exchange *via* a single 1,2,4-triazole bridge is comparable to that *via* a double 1,2,4-triazole bridge. However, the isotropic exchange *via* the single N^1,N^2 1,2,4-triazole bridge is found to be about four times smaller than that *via* a double N^1,N^2 1,2,4-triazole bridge. These exchange effects arise from different mechanisms and so cannot be correlated.

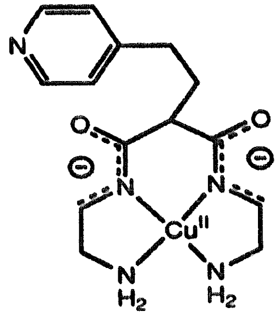


(154)

The ethylpyridino functionalised N,N′-bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)-malondiamide ligand (**155**) has been prepared and its protonation and complexation properties (toward Cu^{II}) have been studied in aqueous solution [113]. The ligand can coordinate one Cu^{II} ion with the diamino-diamido binding unit to form complex (**156**) after the release of two protons. This complex still has a free, outward pointing pyridine unit capable of coordinating to a second metal centre. Two molecules of (**156**) have been joined through their pyridine nitrogen atom *via* the kinetically inert *cis*-Cl_2Pt^{II} unit. This complex is able to release the peripheral Cu^{II} when the pH of the solution becomes acidic and to re-form the original complex when basicity is restored. The crystal and molecular structure show the solid state structure to consist of "head-to-tail" dimers, *i.e.* **(156)**$_2$. In the dimeric complex, each dianion acts as a tetradentate tris(chelate) ligand, through the two amino and the two amido groups. The coordination sphere of the copper centre is completed by the pyridine of the second complex giving a distorted square pyramidal geometry. The roughly planar N_4 donor set (two mutually *cis* *N*-amino and two mutually *cis* *N*-amido atoms) is distorted toward a very flattened tetrahedron and with the metal centre displaced from the N_4 donor set by 0.34 Å toward the vertex of the pyramid. The pyridine rings interact with each other by "head-to-tail" type overlap leaving an interplanar separation of 3.52 Å between the pyridine rings. Electrochemical studies revealed that both in the separate component and in the assembled system the Cu^{II} centres are reversibly oxidisable to Cu^{III}.



(155)



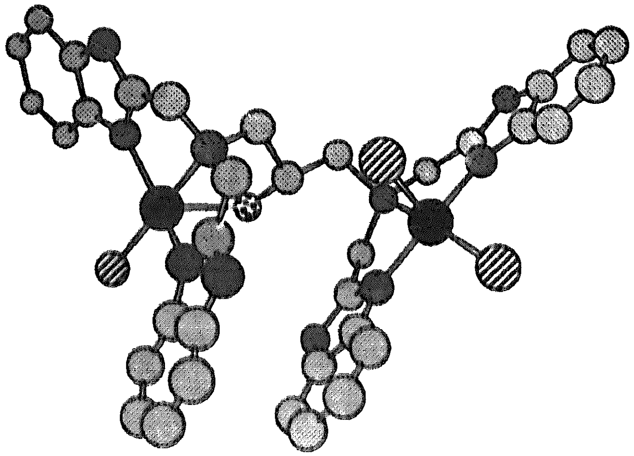
(156)

The structures of four dicopper complexes of the dinucleating ligand HL-H (*N*,*N*,*N'*,*N'*-tetrakis[(2-benzimidazolyl)methyl-2-hydroxy-1,3-diaminopropane) with chloride counter ions were investigated by X-ray diffraction studies [114]. In $Cu_2(HL\text{-}H)Cl_4 \cdot 2H_2O \cdot Et_2O \cdot CH_3OH$ **(157)**, one chloride is not coordinated and a square pyramidal geometry is found for both the CuN_3Cl_2 and CuN_3OCl coordination sites. In $Cu_2(HL\text{-}H)Cl_4 \cdot 5H_2O \cdot 2CH_3OH \cdot 0.5CH_3CN$ **(158)**, which was obtained from the same reaction as that for **(157)** on addition of sodium azide, the basic coordination environments of the two copper ions are the same as in **(157)** with CuN_3Cl_2 and CuN_3OCl in square pyramidal geometries. Complexes **(157)** and **(158)** are rotational isomers. In $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2 \cdot 1.5Et_2O \cdot CH_3OH$ the complex exists as a dimer with the two monomeric units connected by two bridging chloride ions. The basic coordination environments of the two copper centres are square pyramidal CuN_3Cl_2 and CuN_3OCl. In the fourth complex, $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2 \cdot 5H_2O \cdot Et_2O \cdot C_2H_5OH$ the coordination of both copper centres is CuN_3OCl with hydroxy bridges between the two copper centres. The coordination geometries of the two copper centres are quite distinct, however, with one being square pyramidal while the other is distorted trigonal bipyramidal. The Cu···Cu distances in the four complexes are in the range of 4.9–7.2 Å. The endogenous hydroxy groups in these complexes do not deprotonate and are claimed to be the first structurally-characterised examples of the coordination of nondeprotonated alcoholic hydroxy groups to Cu(II) in dicopper complexes.

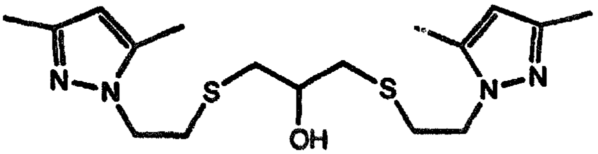
A ligand that was originally designed to form mononuclear 4- or 5-coordinate

(157)

(158)



nickel compounds as model systems for hydrogenases has in fact turned out to be a powerful dinucleating ligand, which yields complexes that may be mimics for several enzymes with two metal ions in the active site, such as urease and tyrosinase [115]. The synthesis and characterisation of transition metal coordination complexes of the new pentadentate ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol (**159**) are described. Most of the compounds are of the general formula $[M_2(bdnol)X_3]\cdot n(solvent)$ with $M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} and $X = Cl^-$, Br^-, NO_3^- and NCS^-. Additionally, a polymeric copper(I) compound of the formula $[Cu_2(\mathbf{159})(NCS)_2]$ has been isolated. In all the complexes, (**159**) acts as a pentadentate ligand with the alcohol group generally deprotonated and bridging between the metal ions, except in the case of the copper(I) complex, where the alcohol group is non-coordinating. X-Ray structures of $[Cu_2(\mathbf{159}\text{-H})NO_3]$ and $[Cu_2(\mathbf{159})(NCS)_2]$ are reported. In the former, the geometry of the two metal centres is significantly different from each other with the ligand folded in a facial way around one copper centre, but in a meridional fashion around the other. Both centres have an elongated octahedral geometry, but formed in different ways. The alcohol group is deprotonated and bridges the two copper centres, which are separated by a distance of 3.308 Å. In $[Cu_2(\mathbf{159})(NCS)_2]$ each copper(I) has a distorted tetrahedral geometry. As the copper ions are not bridged by the alcohol group of the ligand, the Cu···Cu distance is quite large at 7.42 Å. Shorter Cu···Cu distances are obtained through the thiocyanate bridges between neighbouring units of 5.95 and 5.85 Å.



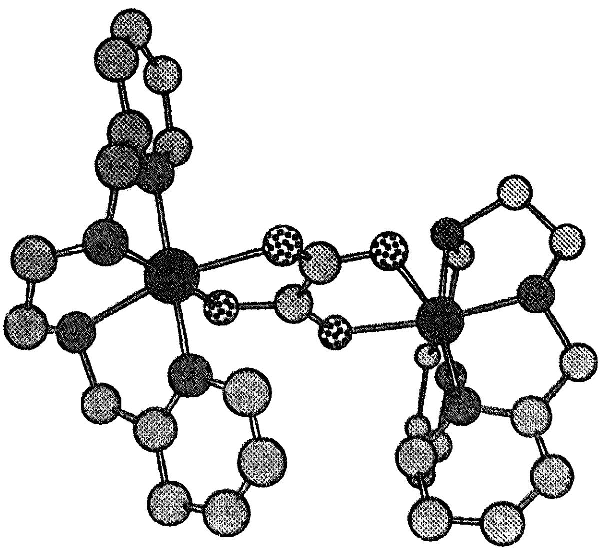
(159)

The mixed-ligand dinuclear complex $[Cu(phen)(Sa)(ClO_4)]_2$ (where phen = 1,10-phenanthroline and Sa = salicylaldehyde) has been synthesised and characterised as part of a study to elucidate further the biological-potential of Cuphen complexes [116]. The solid state structure consists of a dimer of two $[Cu(phen)(Sa)(ClO_4)]$ units linked by two oxygen atoms from two phenolate groups with the coordination of the copper atom being an elongated octahedron. The Cu···Cu separation is 3.379(2) Å. Magnetic susceptibility measurements obeyed the Curie–Weiss law with $\theta = -10$ K.

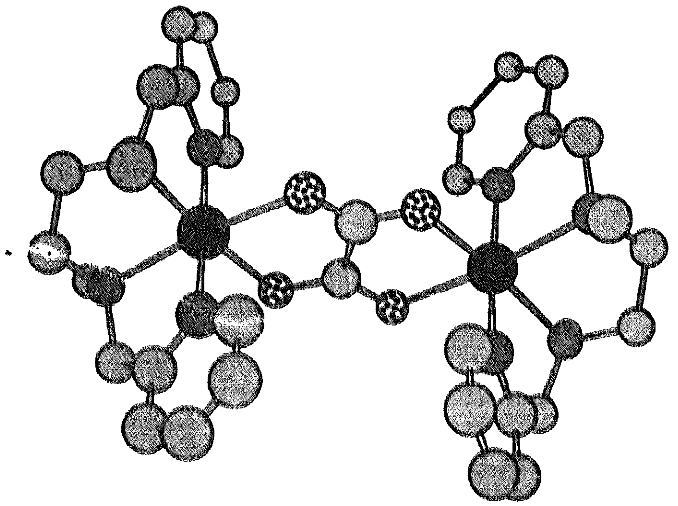
An investigation of the magnetic interaction through oxalato bridges has resulted in the syntheses and characterisation of a series of dinuclear μ-oxalato complexes of the type $[(N)_4M(C_2O_4)M(N_4)]^{2+}$, where M = Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) are described [117]. The ligands $(N)_4$ represent the tetradentate ligands *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine (L1), *N,N′*-bis(2-pyridylmethyl)-1,3-propanediamine, and *N,N′*-bis(2-pyridylmethyl)-*N,N′*-dimethyl-1,2-ethanediamine (L2). The structures of $[(L1)Cu(C_2O_4)Cu(L1)](ClO_4)_2$ (**160**) $[(L2)Cu(C_2O_4)Cu(L2)](ClO_4)_2$ (**161**) have been determined. Both complexes contain six-coordinate metal centres bridged by planar bis-didentate oxalate groups. For the copper complexes, there is only a small magnetic interaction between the two metal centres, with $J = 2\ cm^{-1}$.

A systematic study has been carried out into the long-range exchange coupling between two unpaired electrons of two copper(II) ions in a square pyramidal ligand environment which are rigidly separated by > 10 Å by an organic spacer ligand (*e.g.* a μ-dicarboxylato ligand) [118]. The following complexes have been synthesised and characterised $[\{LCu(OH_2)\}_2(\mu\text{-terephthalao})](ClO_4)_2$, $[LCu^{II}(OH_2)(\text{benzoato})](ClO_4)$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-terephthalato})]\cdot 2CH_3OH$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-4,4'-oxybisbenzoato})]\cdot 3CH_3OH$, $[\{LCu^{II}(OH_2)\}_2(\text{m-tetrafluoroterephthalato})](ClO_4)_2$, $[\{LCu^{II}(OH_2)\}_2\{LCu^{II}\}_2(\mu\text{-tetrafluorobenzoato})_3](ClO_4)_2\cdot 6H_2O$, $[\{LCu^{II}(OH_2)\}_2(\mu\text{-biphenyl-4,4'-dicarboxylato})](ClO_4)_2$, $[LCu^{II}(\mu\text{-biphenyl-4,4'-dicarboxylato})]_n(H_2O)_{2n}$, $[\{LCu^{II}(NCS)\}_2(\mu\text{-biphenyl-4,4'-dicarboxylato})]$, $[\{LCu(OH_2)\}_2(\mu\text{-}trans,trans\text{-2,4-hexadien-1,6-dicarboxylato})](ClO_4)_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). The combined crystallographic and magnetic susceptibility data from this investigation demonstrate that intramolecular antiferromagnetic exchange coupling

(160)

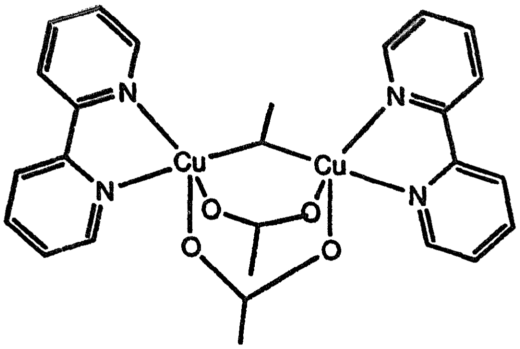


(161)



of considerable magnitude is possible over distances >15 Å, provided that the effective magnetic orbitals are favourably aligned.

A series of complexes containing the cations $[Cu_2(\mu\text{-}OR)(\mu\text{-}O_2CMe)_2(bpy)_2]^+$ (R = Me, Et, Pr^n) have been prepared [119]. Treatment of $Cu_2(O_2CMe)_4(H_2O)_2$ with 2 equivalents of bpy and 1 equivalent of NaOH in anhydrous EtOH followed by the addition of $[Bu^n_4N][PF_6]$ in MeCN gave the highly crystalline blue complex $[Cu_2(OEt)(O_2CMe)_2(bpy)_2](PF_6)$ (**162**) in ≈70% yield. The corresponding reaction in dry MeOH–MeCN led to green crystals of the methoxy analogue $[Cu_2(OMe)(O_2CMe)_2(bpy)_2](PF_6)$ (**163**), also in ≈70% yield. The structures of the two complexes were shown to consist of triply-bridged pairs of copper(II) atoms. Two of the bridging groups are *syn,syn* $\eta^1{:}\eta^1{:}\mu_2$ acetate groups, with the third being the OR^- ion. A terminal bpy unit completes the five coordination at each copper centre which in (**162**) is best described as square pyramidal, while in (**163**) it is best described as trigonal bipyramidal. The Cu···Cu distance are 3.093(1) and 3.230(1) Å for (**163**) and (**162**), respectively.

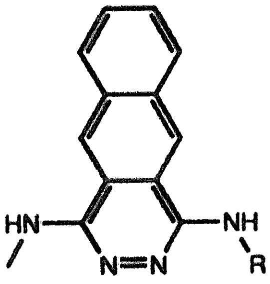


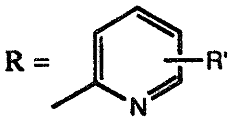
(163)

Two dinuclear copper(II) complexes, $[Cu_2(bpm)(H_2O)_8](SO_4)_2 \cdot 2H_2O$ (**164**) and $[Cu_2(bpm)(H_2O)_4(SO_4)_2] \cdot 3H_2O$ (**165**) and (bpm = 2,2′-bipyrimidine) have been synthesised and characterised by X-ray crystallographic analysis [120]. The structure of (**164**) is composed of non-centrosymmetric dinuclear $[Cu_2(bpm)(H_2O)_8]^{4+}$ cationic units, uncoordinated sulfate anions and waters of crystallisation with both copper centres having distorted octahedral geometries; one being compressed and the other elongated. The structure of (**165**) consists of a 2D-array of copper(II) ions bridged by bis-didentate bpm groups and bis-unidentate sulfate groups. Each copper centre has an elongated octahedral CuN_2O_4 geometry with two water molecules and two nitrogen atoms from a bpm molecule forming the basal plane and with two sulfate oxygen atoms occupying the axial sites. The 2D-structure is held together by hydrogen bonding. Both (**165**) and (**164**) exhibit antiferromagnetic coupling which is relatively strong in (**165**) ($J = -159\ cm^{-1}$) but is weak in (**164**) ($J = -24\ cm^{-1}$).

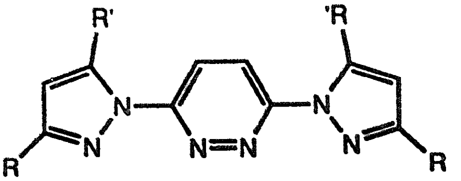
Dinuclear copper(II) complexes involving a combination of μ_2-1,2-diazine (pyridazine or phthalazine) and a μ_2-1,1-azide bridge have been shown to exhibit net antiferromagnetism with the azide contributing to the total spin exchange as an antiferromagnetic bridge [121]. X-Ray structures of the complexes $[Cu_2(\mathbf{166})(\mu_2\text{-}N_3)Br_3] \cdot CH_2Cl_2$, $[Cu_2(\mathbf{167})(\mu_2\text{-}N_3)(\mu_2\text{-}Br)Br_2] \cdot 1.68H_2O$, $[Cu_2(\mathbf{167})(\mu_2\text{-}N_3)(\mu_2\text{-}H_2O)NO_3](NO_3) \cdot 0.75CH_3OH$, $[Cu_2(\mathbf{168})(\mu_2\text{-}N_3)(\mu_2\text{-}NO_3)(NO_3)_2]$ $CH_3OH \cdot CH_3CN$, and $[Cu_2(\mathbf{169})(\mu_2\text{-}N_3)Br_3(CH_3OH)$. These show azide bridge angles in the range 108.7–122.5°. Very strong net antiferromagnetic coupling ($-2J > 780\ cm^{-1}$) is observed for complexes with large azide bridge angles while complexes having much smaller azide bridge angles exhibit much weaker net antiferromagnetism. In all cases, both the azide and diazine appear to act in a complementary manner with both parallel, magnetically active bridge groups (N_3, diazine), contributing to the total exchange in an antiferromagnetic sense.

An investigation into the synthesis of new electrical-conducting molecular materials has resulted in the synthesis of a fully conjugated, 2-thioxo-1,3-4,5-dithiolate (dmit) capped, tetrathiooxalate-bridged, copper(II) acceptor complex [122]. The crystal structure shows two Cu(dmit) units bridged by the side on coordination of the tetrathiooxalate ligand with all the Cu–S (2.269(1) Å to the tetrathiooxalate bridging ligand being equivalent, thus indicating a fully conjugated system. The coordination geometry around the copper centre is square planar with a slight





R' = H (**166**)
R' = 6Me (**167**)
R' = H (**168**)



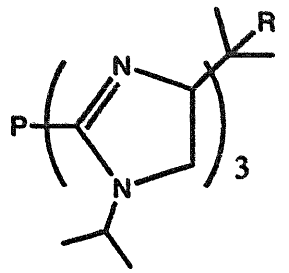
R = R' =H (**169**)

tetrahedral distortion. The crystal packing consists of sheets of anionic chains separated by sheets of isolated cations. The complex is insulating with single-crystal conductivities of $<10^{-10}$ S cm^{-1}. Reaction of the complex with varied amounts of NaI/I_2 in acetone afforded black powders with pressed pellet conductivities of up to 10^{-2} S cm^{-1}.

Copper complexes of sterically demanding tris(pyrazolyl)hydroborate ligands have found application as synthetic analogues for cuproprotein active sites and this has led to the synthesis of copper(I) complexes of the new tripodal ligands tris[2-(1,4-diisopropylimidazolyl)phosphine (**170**) and tris[2-1-isopropyl-4-*tert*-butylimidazolyl)]phosphine (**171**) [123]. The dioxygen reactivity of the pseudotetrahedral complexes [Cu(**170**)CH_3CN](BF_4) and [Cu(**171**)CH_3CN](BF_4) has been examined. The former complex forms a violet peroxo-dicopper(II) species upon reaction with O_2 at low temperature; the electronic absorption spectrum ($\lambda = 343$ nm, $\epsilon = 19500$ M^{-1} cm^{-1}; $\lambda = 549$ nm, $\epsilon = 790$ M^{-1} cm^{-1}) and O–O stretching frequency ($\nu_{(O-O)} = 750$ cm^{-1}) of the adduct approximate those of oxyhaemocyanin. Warming a mixture of the peroxide complex and triphenylphosphine at room temperature affords [Cu(**170**)PPh_3](BF_4) and produces no O=PPh_3. In methanol at −78°C, the peroxide complex is unreactive towards acid, carbon dioxide, hex-1-ene and triphenylphosphine. Thermal decomposition of the dioxygen adduct in the presence of water yields a bis(hydroxo)-bridged dicopper(II) dimer [Cu(**170**)$]_2(OH)_2(BF_4)_2$ which further reacts with atmospheric CO_2 to produce the carbonate-bridged complex [{Cu(**170**)}$_2CO_3$](BF_4)$_2$ which has been characterised by X-ray crystallographic analysis. The structure of a prototypical mononuclear 5-coordinate complex [Cu(**170**)OAc](BF_4) has also been determined. The geometry about the Cu(II) in both structures is near square pyramidal indicating that (**170**) can accommodate side-on binding of oxygen to the copper centres. The more sterically hindered Cu(I) complex [Cu(**171**)CH_3CN](BF_4) is inert to O_2, but reacts readily with CO to form the isolable adduct [Cu(**171**)CO](BF_4).

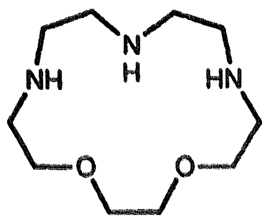
3.5. *Trinuclear complexes*

The complexation of the macrocyclic ligand [15]aneN_3O_2, (**172**), with Cu^{II} and Zn^{II} in aqueous solution has been studied [124]. In the case of copper, the species present in alkaline solution are the mono- and dihydroxo complexes [Cu(**172**)(OH)]$^+$ and [Cu(**172**)$(OH)_2$]. When a solution containing the copper

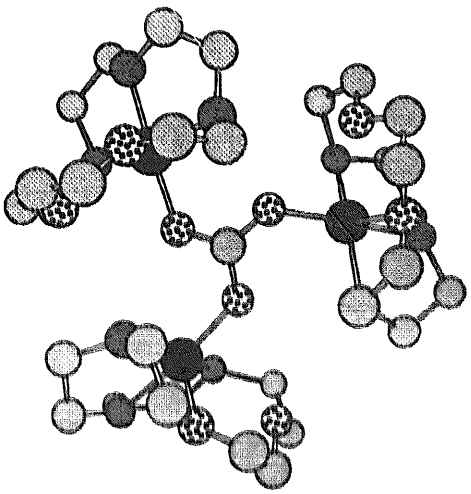


R = (170)
R = (171)

complex of the macrocycle is exposed to air, CO_2 is rapidly absorbed (15–30 mins) forming the product $[\{Cu(\mathbf{172})\}_3(\mu_3\text{-}CO_3)](ClO_4)_4$, $[(\mathbf{173})](ClO_4)_4$, in good yield. The solid-state structure of the complex shows the $\mu_3-CO_3^{2-}$ anion bridging the three metal ions through the three oxygen atoms of the carbonate group. The metal ions are five-coordinate having a distorted square pyramidal geometry, being bound to the three nitrogen atoms and one oxygen atom of the macrocycle and by one oxygen atom of the carbonate group. The copper centres are displaced by 0.294(1) Å from the carbonate plane. A similar structure is observed for the zinc structure.



(172)



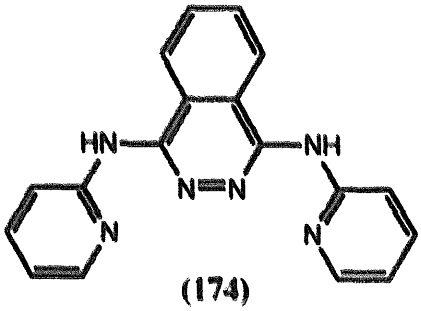
(173)

A systematic study of the products of the reaction of pyridazine with copper(II) nitrate in ethanol has revealed conditions for obtaining four distinct products, one $[\{Cu(pdz)_3(NO_3)_3\}_2Cu]$ contains both bridging and terminal pyridazine ligands while the other three, $[Cu(pdz)_3(NO_3)_2]$, $[Cu(pdz)_4(NO_3)_2]$ and $[Cu(pdz)_4(NO_3)](NO_3)$ contain only terminal ligands [125]. No evidence for an extended chain structure is observed as exists for pyrazine in $Cu(pyz)(NO_3)_2$. The trimetallic complex $[\{Cu(pdz)_3(NO_3)_3\}_2Cu]$ is claimed to be the first example of a structurally and magnetically characterised complex in which both terminal and bridging pyridazines are present and in which the metals are doubly bridged by pyridazine. The magnetic susceptibility measurements determined $J = -139\ cm^{-1}$, a value which is much greater than that observed in pyrazine complexes and shows the greater efficiency of the two atom pathway at mediating magnetic exchange. The other three complexes have nonmetallic structures and are magnetically dilute. $[\{Cu(pdz)_3(NO_3)_3\}_2Cu]$ appears to be indefinitely stable, while the other three complexes showed visible signs of decomposition over time. This has been interpreted in terms of molecular rearrangements in the solid state possibly involving changes in pyridazine coordination yielding $Cu(pdz)_3(NO_3)_3]_2Cu$ and conversion of some of the coordinated pyridazine to lattice pyridazine.

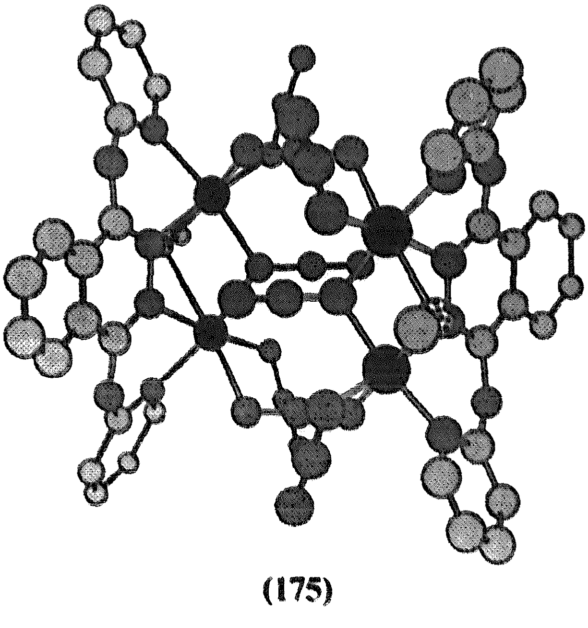
The structure of the complex $[Cu^{II}Br_2(Hae)_2][Cu_2^{II}(ae)_2Br_2]$ (Hae = 2-aminoethanol) containing a neutral mononuclear copper unit bridged by a μ_4-bromide ion and hydrogen bonds to a dinuclear copper(II) unit has been determined [126]. The bridging bromide ion is unique; it links two copper(II) ions in the dinuclear unit and a Cu^{II} centre in the mononuclear unit forming a chain-type of structure. Hydrogen bonding stabilises the formation of the chains and links the chains together. Magnetic susceptibility studies have shown that the dinuclear unit exhibits a weakly antiferromagnetic exchange interaction, while the mononuclear unit behaves as a paramagnetic centre.

3.6. Tetranuclear complexes

The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with the N_4 diazine ligand (**174**) followed by the addition of a slight excess of NaN_3 dissolved in water has led to the formation of green crystals of $[Cu_4(\mathbf{174})_2(\mu\text{-}1,1\text{-}N_3)_2(\mu\text{-}1,3\text{-}N_2)_2(\mu\text{-}MeOH)_2(N_3)_4]$ (**175**) [127]. The crystal structure shows three different bonded azide groups to be present. Each pair of six coordinate copper(II) centres, which are bonded to one ligand, are bridged equatorially by an intramolecular μ-1,1-azide with a bridge angle of 107.9(5)°. Two μ-1,3-azide bridges link the two *anti*-dinuclear complex units *via* axial interactions and four terminal azide ligands fill the remaining equatorial coordination sites. A distant bridging methanol completes the coordination sphere. The intradinuclear copper-copper separation (3.207(3) Å) is smaller than the interdinuclear separations [5.517(4), 6.382(3) Å]. Magnetic measurements have shown the copper centres to be weakly antiferromagnetically coupled.

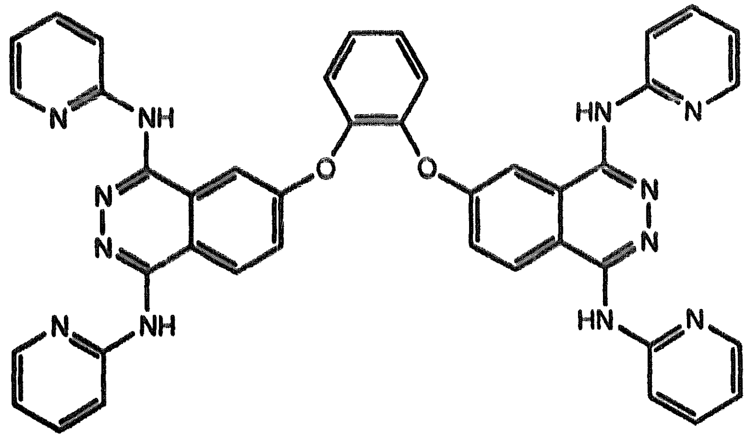


(**174**)



(**175**)

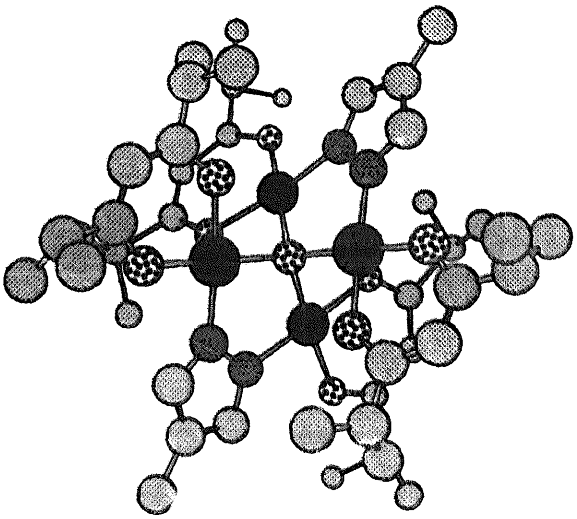
The generation of dendritic, polypodal ligands with the capacity to coordinate large numbers of metal centres and produce nanometer-sized complexes has been demonstrated using a simple reaction involving poly(alcoholic) substrates 4-nitro-1,2-dicyanobenzene to give poly(phthalonitriles), which are further functionalised to produce polyisoindolines and poly(aminophthalazines) [128]. The poly(aminophthalazine) ligands involving two (N_8) connected phthalazine groups produce tetranuclear, hexanuclear and octanuclear copper(II) complexes, which contain repeating arrays of spin-coupled, dinuclear centres.The ligands 6,6′-(1,2-phenylenedioxy)bis[1,4-bis(2′-pyridylamino)phthalazine] (**176**) and 6,6′-oxybis[1,4-bis(2′-pyridylamino)phthalazine] (**177**) bind four copper(II) ions in two well-separated dinuclear pairs in one molecular entity in the derivatives $[Cu_4(\mathbf{176})(\mu_2\text{-OH})_2(\mu_2\text{-NO}_3)_2(H_2O)_2(NO_3)_2](NO_3)_2\cdot 4H_2O$ (**178**) and $[\{Cu_4(\mathbf{177})(\mu_2\text{-OH})_2(\mu_2\text{-NO}_3)_2(H_2O)_7\}(\mu_2\text{-NO}_3)](NO_3)\cdot 6H_2O$ (**179**). Variable-temperature magnetic studies indicate strong local antiferromagnetic coupling in these hydroxide-bridged compounds, with non-existent coupling across the ligand framework itself. The solid state structure of (**176**), shows two chemically identical, but structurally slightly different, tetranuclear species exist per unit cell. Pairs of square-pyramidal copper centres are bridged equatorially by hydroxides and phthalazine diazine units with Cu–OH–Cu angles in the range 110.4–116.7° and Cu···Cu separations in the range 3.122–3.188 Å. In (**177**), pairs of six coordinate copper centres are bridged equatorially by hydroxides and phthalazine groups with comparable dinuclear centre dimensions to (**176**). Two tetranuclear complexes are linked by a didentate nitrate bridge to form an octahedral species.



(**176**)

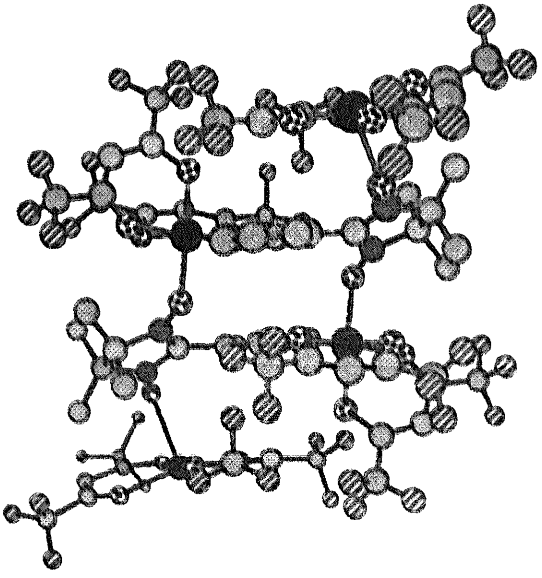
When $[Cu(L1))_2]$ (HL1 = aliphatic β-diketone with branched alkyl groups) and $[Cu(L2))_2$ (HL2 = aliphatic β-diketone with linear alkyl groups) were allowed to react with 1H-pyrazoles (Hpz1), tetranuclear complexes $[Cu_4(\mu_4\text{-O})(L1)_4(\mu\text{-pz1})_2]$ and dinuclear complexes $[Cu_2(L2)_2(\mu\text{-pz1})_2]$ were produced, respectively [129]. However, the reactions of $[Cu(L3)_2]$ (HL3 = aroyl- or heteroaroylacetone) with 1H-pyrazole (Hpz) gave coordination polymers $[\{Cu(L3)(\mu\text{-pz})\}_n]$ and/or adducts $[Cu(L3)_2(Hpz)_n]$ (n = 1 and/or 2). The structure of one of the tetranuclear products $[Cu_4(\mu_4\text{-O})(dibm)_4(\mu\text{-4-mpz})_2]$ (**180**) (Hdibm = 2,6-dimethylheptane-3,5-dione; 4-Hmpz = 4-methyl-1H-pyrazole) has been determined. The four copper centres have an approximately tetrahedral arrangement, with each copper centre having an approximate square-planar geometry, being linked to the central oxygen atom, two oxygen atoms from a didentate dibm ligand and a nitrogen atom from a didentate 4-mpz ligand.

(180)



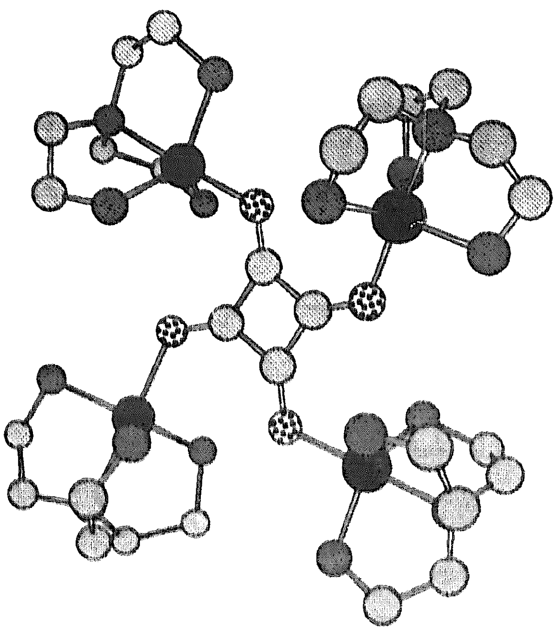
The nitroxide free radical 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide (L) reacts with Cu(hfac)$_2$, leading to a complex of formula [Cu(hfac)$_2$]$_4$L$_2$ (**181**) [130]. This complex has a cyclic molecular structure where two copper ions are bridged by the free radicals. The two remaining metal centres are exocyclic. Both oxygen atoms of the nitronyl nitroxide ligand are axially bound to both types of copper(II) ions at room temperature, while at 50 K, coordination of the NO group to the intracyclic metal ion is equatorial. The magnetic behaviour is strongly correlated to the change of coordination. While at room temperature the complex observes a Curie law corresponding to six independent $S=1/2$ spins, at low temperature only two $S=1/2$ spins are observed.

(181)

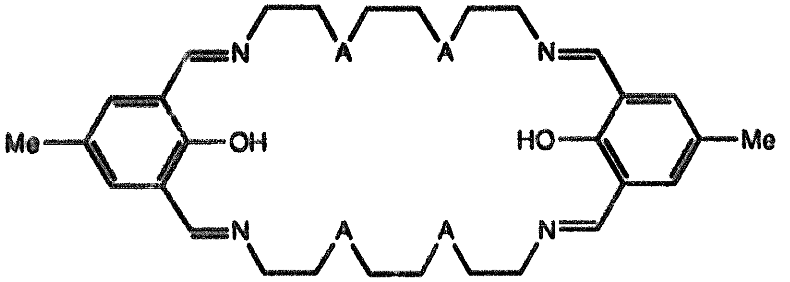


The crystal structure of $[\mathrm{Cu_4(tren)_4(C_4O_4)}](\mathrm{ClO_4})_6$ (**182**) (where tren is tris(2-aminoethyl)amine and $[\mathrm{C_4O_4}]^{2-}$ is the dianion of 3,4-dihydroxycyclobutenedione) has been determined [131]. The structure consists of tetranuclear $[\mathrm{Cu_4(tren)_4(C_4O_4)}]^{6+}$ cationic units and uncoordinated perchlorate anions. The copper centres have trigonal bipyramidal coordination geometry with tren nitrogen atoms occupying the equatorial positions and with the axial sites filled by the tren central nitrogen atom and a squarate oxygen atom. The squarato group acts as a tetra-monodentate ligand. The X-ray structure of this complex is claimed to be the first example of a tetrameric transition metal complex with the four metal cations being bridged by a single squarato ligand in a μ-1,2,3,4-coordination mode. Magnetic susceptibility studies have shown the complex to be antiferromagnetic and the value of $J = -19.0\,\mathrm{cm}^{-1}$ for the interaction through the OCCO fragment is the largest found in a structurally characterised squarato-bridged copper(II) complex.

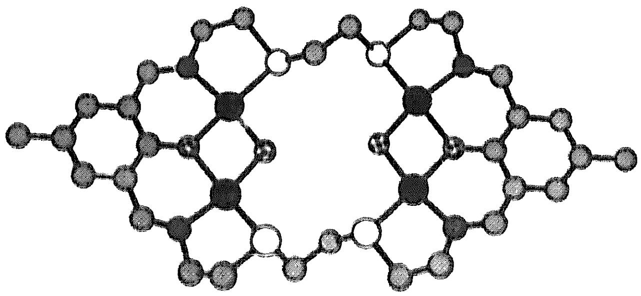
(182)



Macrocyclic tetranuclear copper(II) complexes of the general formula $[\mathrm{Cu_4L(OH)_2}][\mathrm{X}]_2[\mathrm{Y}]_2$ (L = (**183**), X = Y = $\mathrm{ClO_4^-}$ or X = $\mathrm{MeCO_2}$, Y = $\mathrm{PF_6}$; L = (**184**), X = Y = $\mathrm{ClO_4}$ or X = Y = $\mathrm{PF_6^-}$) have been obtained by template reactions, where L denotes the macrocycles formed by the [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 3,6-diazaoctane-1,8-diamine (L = (**183**)) or 3,6-dithiaoctane-1,8-diamine (L = (**184**)) [132] In the complex $[\mathrm{Cu_4}(\mathbf{183})(\mathrm{OH})_2][\mathrm{MeCO_2}]_2(\mathrm{PF_6})_2\cdot 4\mathrm{MeCN}\cdot 2\mathrm{Pr^iOH}$, the tetranuclear cation $[\mathrm{Cu_4}(\mathbf{183})(\mathrm{OH})_2(\mathrm{Pr^iOH})_2(\mathrm{MeCN})_2]^{4+}$ contains two dinuclear $\mathrm{Cu_2^{II}}$ units in a 'dimer-of-dimers' arrangement. In each unit two copper(II) ions are bridged by an endogenous phenolic oxygen of $(\mathbf{183})^{2-}$ and an endogenous hydroxide oxygen with a Cu···Cu separation of 2.949(4) Å. A propan-2-ol molecule resides on the axial site of one of the copper ion and an acetonitrile molecule on the axial site of the other copper ion, affording a square-pyramidal geometry about both copper centres. The two dinuclear skeletons are nearly coplanar and the two bridging $\mathrm{OH^-}$ groups are facing each other with an O···O separation of 3.32(2) Å. In the complex $[Cu_4(\mathbf{184})(OH)_2](PF_6)_4$, the centrosymmetric cation $[Cu_4(\mathbf{184})(OH)_2(MeCN)_4]^{4+}$ (**185**) assumes a similar 'dimer-of-dimers' structure with two facing OH^- groups where an acetonitrile molecule coordinates at the axial site of each copper(II) ion. The Cu···Cu separation in the dinuclear unit is 2.976(2) Å and the O···O separation between the two facing OH^- groups is 3.80(1) Å. In all the tetranuclear complexes the two dinuclear units are magnetically isolated from each other and a significant antiferromagnetic interaction operates within each Cu_2^{II} unit ($-J = 229$–$357\ cm^{-1}$).



(183) A = NH
(184) A = S



(185)

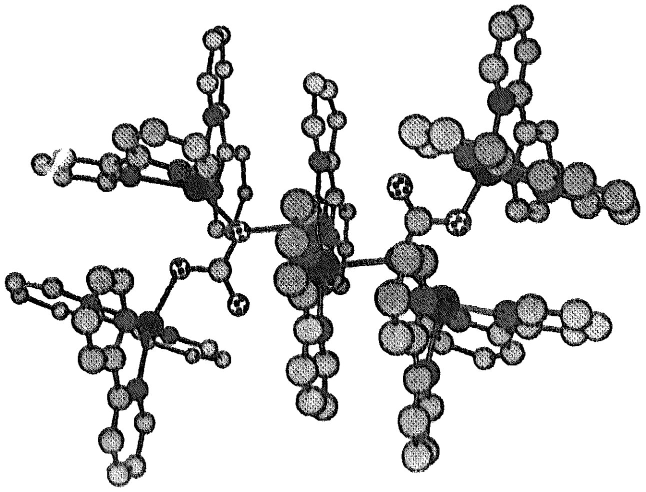
Reaction of $CuCl_2.2H_2O$ or $CuBr_2$ with the tridentate ligand 4-methyl-2,6-bis(pyrrolidin-1-yl-methyl)phenol (Hmbpp) in methanol yielded two copper(II) complexes $[Cu_4OCl_4(mbpp)_2].2MeOH$ and $[Cu_4OBr_4(mbpp)_2]$ [133]. Both structures were characterised by X-ray crystallographic analysis and both are shown to consist of a tetrahedron of copper atoms centred by a μ_4-bridging oxygen atom. Magnetic susceptibility data indicate a significant antiferromagnetic coupling between the copper(II) centres with $J_{12} = -275(1)\ cm^{-1}$ and $J_{13} = -27.8(5)\ cm^{-1}$ for $Cu_4OCl_4(mbpp)_2]\cdot 2MeOH$ and $J_{12} = -261(1)\ cm^{-1}$ and $J_{13} = -21.6(5)\ cm^{-1}$ for $[Cu_4OBr_4(mbpp)_2]$, where J_{12} and J_{13} describe the intra- and inter-dimer exchange phenomena respectively. By comparison with similar μ_4-oxo-bridged copper(II) complexes, a linear relationship between the magnetic intradimer coupling constant and the mean Cu–O–Cu angle is obtained.

3.7. *Higher nuclear complexes*

A hexanuclear copper(II) complex $[Cu_6(bpy)_{10}(\mu\text{-}CO_3)_2(\mu\text{-}OH)_2](ClO_4)_6\cdot 4H_2O$ (**186**), has been characterised [134]. The structure consists of discrete centrosymmetric hexanuclear units in which a central bis(μ-hydroxo)copper(II) bipyridine moiety contains two *cis*-Cu(bpy) fragments attached *via* carbonate bridging groups, *trans*-

axially to the central Cu atoms. The bpy rings are arranged in a parallel fashion due to π–π interactions. Detailed magnetic studies on the complex show that ferromagnetic coupling of the spins on each copper(II) centre occurs leading to a $S=3$ ground state. The J value for the central $Cu_2(OH)_2$ moiety was determined as $+24\,cm^{-1}$ and three J values for the three identifiable $Cu_2(\mu\text{-}CO_3)$ pathways were determined to lie in the range $+2.75$ to $+3.3\,cm^{-1}$. A second complex was formed on recrystallisation of the $[PF_6]^-$ salt of (**186**) from dmf. This structure is dinuclear with the formula $[Cu_2(bpy)_4(\mu\text{-}CO_3)](PF_6)_2.2dmf$ and has an *anti–anti* mode of carbonate bridging with the two square-pyramidally coordinated copper atoms separated by 5.26 Å. This complex displays antiferromagnetic coupling with $J=-70.2\,cm^{-1}$.

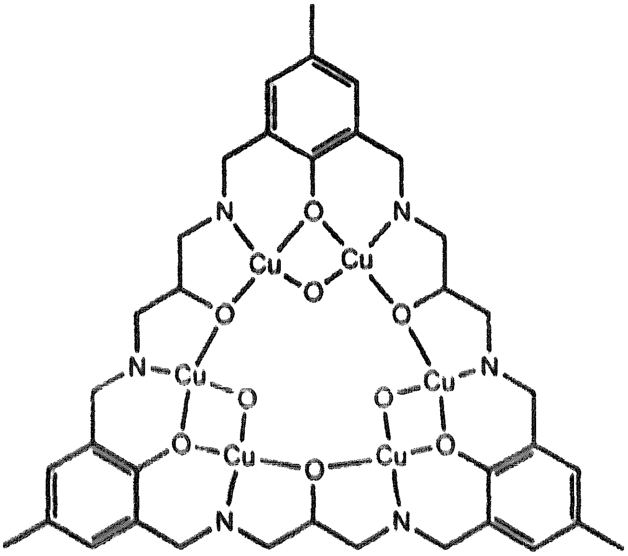
(186)



A series of octanuclear Cu(II) complexes has been prepared containing carboxylate and 2-pyridonate ligands [135]. The complexes have the general formula $[Cu_8(O)_2(O_2CR)_4L_8]$, where R = Me, Ph or CF_3, and L = 6-chloro-, 6-bromo- or 6-methyl-2-pyridonate. X-Ray structural analyses of the acetate complexes show the compounds to have an edge-sharing Cu_6O_2 bitetrahedral core, surrounded by two $[CuL_4]$ units. The Cu···Cu distances within the core vary from 2.92 to 3.58 Å, depending on the ligand bridging the Cu–Cu vector. Two routes to these complexes have been investigated; the first involving the reaction of the preformed copper pyridonate complexes with copper carboxylates and the second involving the reaction of copper carboxylates with molten HL. DSC and TGA studies reveals (ii) to proceed *via* formation of copper pyridonate complexes. The ^1H NMR spectra of the octanuclear complexes show the resonances of both the pyridonate and carboxylate ligands to be paramagnetically shifted. Magnetic studies of $Cu_8(O)_2(O_2CMe)_4L_8]$ (L = 6-chloro- and 6-bromo-2-pyridonate) show largely antiferromagnetic exchange coupling within the Cu_6O_2 core. The structure of the complexes and the magnitude of the couplings lead to spin-frustrated systems, with subtle differences between the two complexes studied. These results demonstrate the degree to which the magnetic properties of a complex can be altered (a change of $\approx 10\,cm^{-1}$ in one of the exchange coupling terms) by seemingly trivial changes in structure (a 2° change in a bond angle at a bridging ligand) which at present can neither be predicted or controlled.

The template condensation of 2,6-diformyl-4-(R)phenol (R = methyl, *tert*-butyl) with 1,3-diamino-2-hydroxypropane in the presence of Cu(II) or Ni(II) salts and base results in the formation of hexacopper(II) and hexanickel(II) complexes of the 30-membered, 3:3 macrocyclic ligands (H_6MME, H_6MTB) [136]. The macrocyclic rings contain pseudohexagonal "benzene-like" arrangements of metal centres, which are linked by alternating double (μ_2-phenoxide, μ_2-hydroxide) and single (μ_2-alkoxide) bridges within each ring: $[Cu_6(L)(\mu_2\text{-}OH)_3]X_6 \cdot yH_2O$ (L = MME, X = NO_3, y = 10 (**187**); X = ClO_4, y = 6; X = BF_4, y = 8. L = MTB: X = ClO_4, y = 8 (**188**); X = BF_4, y = 14. The two complexes (**187**) and (**188**) exist as dimers in the solid state, with the hexagonal fragments linked by axial interactions, forming dodecanuclear species. The addition of NCS to the mother liquor from the preparation of (**188**) led to the formation of a 2:2 macrocyclic complex $[Cu(H_2MTB)(NCS)_2]_n$. Magnetic susceptibility data for the copper complexes show the presence of intra-ring and inter-ring antiferromagnetic interactions

(187)

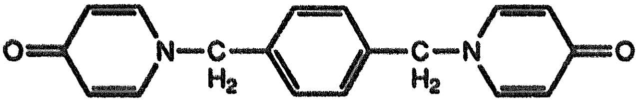


The concentration of an aqueous solution of the composition LiOH:Cu(OH)2:D-sorbitol in the molar ratio 1:2:1 resulted in the isolation of blue crystals of the D-sorbitol-copper complex $Li_8[Cu_{16}(\text{D-Sorb}_{-6})_4(\text{D-Sorb}1,2,3,4H_{-4})_4] \cdot \approx 46H_2O$ [137]. In the structure, half of the D-sorbitol ligands are completely deprotonated η^6,μ_5-hexaanions while the other half are present as μ_3-tetraanions in which four neighbouring hydroxy groups have been deprotonated. The eight polyolate ions are the sole ligands in the resulting hexadecanuclear cuprate. The hexadecacuprate ion is toroidal in structure with an oval cross-section. Magnetic susceptibility measurements indicate a weak antiferromagnetic coupling between the copper centres.

3.8. *Polymeric complexes*

The reaction of ligand (**189**) with copper(II) nitrate in a mixture of methanol and acetonitrile afforded the polymeric species $[Cu(\mathbf{189})_3(NO_3)_2](NO_3)_2 \cdot 2H_2O$

[138]. The X-ray structure shows the presence of dinuclear Cu_2O_2 units in which pyridone oxygen atoms bridge pairs of copper ions. The Cu_2O_2 units are linked by (**189**) bridges to produce a complex array of 68-membered rings 'threaded' by interwoven (**189**) strands. Each copper centre adopts a distorted square-pyramidal geometry with bridging *p*-(**189**) oxygen atoms occupying both axial and basal positions and with the remaining coordination sites occupied by two pyridone oxygen atoms and the oxygen atom of a unidentate nitrate group. The transannular Cu···Cu distance is 3.34 Å. This close approach of the copper centres results in Cu···Cu spin coupling and an $S=1$ type EPR spectrum.


(**189**)

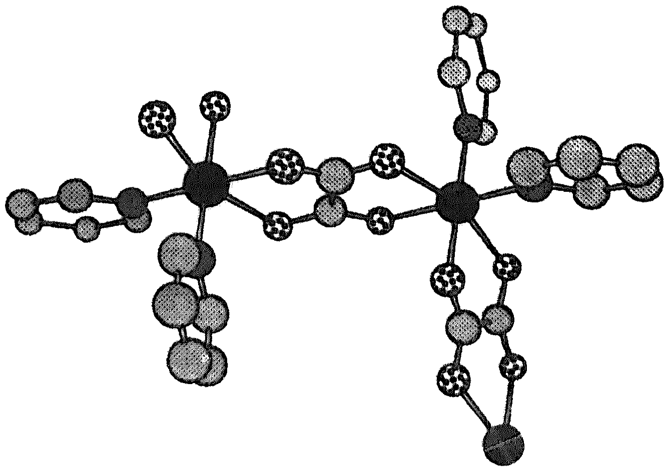
The crystal structures of $[Cu(C_{13}H_{13}N_3)Cl](PF_6)$ and $[Cu(C_{13}H_{13}N_3)Br](PF_6)$ where $C_{13}H_{13}N_3$ = pepci = *N*-(2-2-pyridylethyl)pyridine-2-carbaldimine, have been determined at room temperature [139]. Both structures consist of $[Cu(pepci)X]^+$ (X = Cl, Br) cations which stack in a chain structure with $[PF_6]^-$ anions sited in spaces between the chains. Within the stack, two successive copper complexes are in alternating orientation giving a zigzag, mono(μ-halide) chain structure. There are four independent $[Cu(pepci)X](PF_6)$ units in the unit cell, repeated four times. The magnetic properties of the complexes have been investigated down to 4K. The chloro complexes exhibit weak antiferromagnetic interactions while the bromo complex is ferromagnetic.

The compound $[Cu(ox)(py)_2]$ (**190**) (ox = oxalate, py = pyridine) was obtained as a breakdown oxidised product of $[Cu(epgly)_2]$ (Hepgly = *N*-ethylphenylglycine) and has been characterised by means of structural and magnetic measurements [140]. The structure of the complex consists of $[Cu(py)_2]^{2+}$ units bridged sequentially by centrosymmetric oxalate anions to form zig-zag polymeric chains with a Cu···Cu distance of 5.463(1) Å. The copper centre has a distorted octahedral geometry with the equatorial sites occupied by two nitrogen atoms from two pyridine molecules and two oxygen atoms from two oxalate molecules. Two weaker axial bonds are formed from the two oxalate molecules. From magnetic susceptibility data, the complex is found to exhibit a weak ferromagnetic exchange interaction ($J = 0.67\ cm^{-1}$) between nearest-neighbour copper(II) ions.

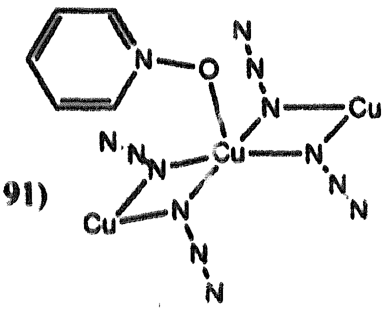
The synthesis and characterisation of two new complexes of copper(II) azide, 1:1 with pyridine *N*-oxide (**191**) and 1:2 with 3-acetylpyridine (**192**) are described [141]. The polymeric structure of (**191**) features five coordinate copper centres in distorted tetragonal pyramidal environments with two μ(1,1) bridging azido ligands in the basal sites and the oxygen atom of the pyridine *N*-oxide occupying the apical site. The dimeric structure (**192**), contains both terminal and μ(1,1) bridging azido groups. Each copper(II) centre is further coordinated by two nitrogen atoms from 3-acetylpyridine molecules to give a distorted square pyramidal geometry.

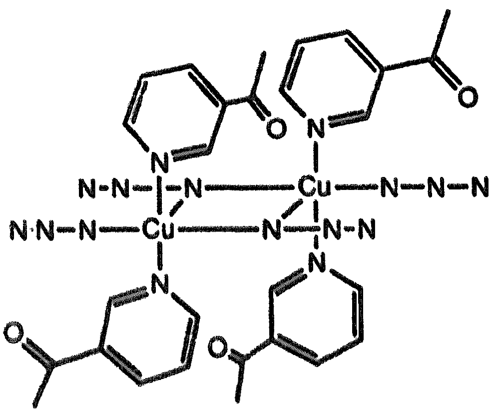
A new modification of the polymeric $[Cu(pyridine)_2(N_3)_2]_n$ complex has been synthesised and characterised by spectroscopic and X-ray crystallographic methods

(190)



(191)





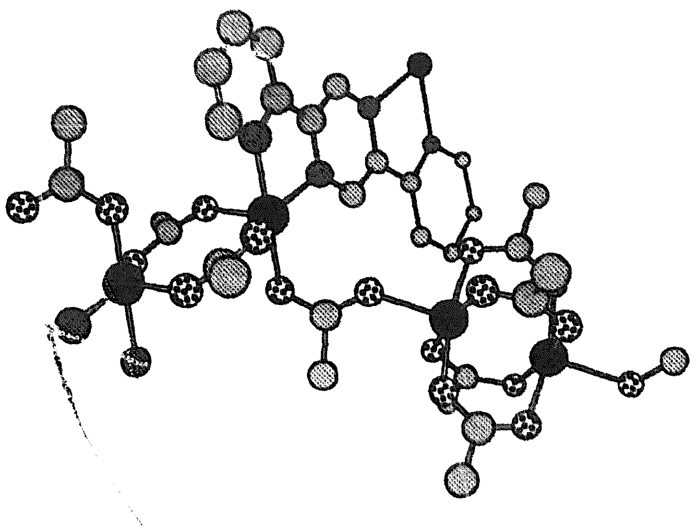
(192)

[142]. The copper centres are six coordinate and simultaneously bridged by $\mu(1,1)$ and $\mu(1,3)$ azido ligands. The $\mu(1,3)$ bridging azido ligand is symmetrical whereas the $\mu(1,1)$ group is asymmetric but both are almost linear [178.5(5) and 176.4(5)°, respectively]. The presence of two azido ligand environments was also evident in the IR spectrum.

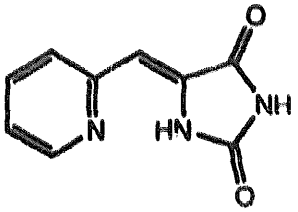
The reaction of 1 equivalent of 2,5-bis(2-pyridyl)pyrazine (bppz) with 4 equivalents of $Cu(OAc)_2 \cdot H_2O$ in acetonitrile afforded an insoluble green precipitate which was characterised as *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II) [143]. The structure consists of symmetrical [Cu_2(bppz)] dinuclear units linked by two acetate groups coordinating in the *syn-syn* mode so forming a one-dimensional chain. These 1-D chains are further linked to the copper acetate dimer by an acetate anion coordinating in a *syn-anti* mode so forming a 2-dimensional network (**193**). The polymer sheets in the solid state structure are separated by 6.6 Å and the pyridine rings of neighbouring sheets overlap almost perfectly with a separation of 4.07 Å. The shortest interplane Cu···Cu distance is 6.287 Å while the intraplane Cu···Cu distances are 3.941 and 5.167 Å.

A new synthesis of 5-(2-pyridylmethylene)hydantoin (**194**) and the first transition metal complexes (nickel(II) and copper(II)) are reported [144]. The addition of an aqueous solution of $CuCl_2 \cdot 6H_2O$ to a methanolic solution of (**194**) gave a green

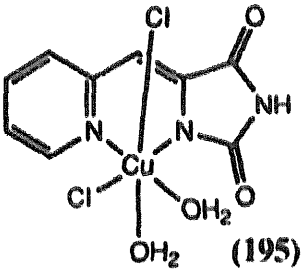
(193)



precipitate that analysed correctly for [CuCl(**194**-H)(OH_2)]. X-Ray crystallographic analysis shows the complex to consist of a polymeric structure based on distorted octahedral coordination centres linked through asymmetric double chloro- and aqua-bridges. Each linear polymeric chain of copper complexes is cross-linked *via* intermolecular hydrogen bonds involving the Cu–O–Cu bridging aqua oxygen atoms in one chain and one of the hydantoin carbonyl oxygen atoms in another. Hydantoins substituted at the C-5 position exhibit a wide range of pharmacological activities including anticonvulsant, antidepressant and platelet aggregation inhibitory activities. Hence the coordination complexes that incorporate the hydantoin fragment could have significant biological uses.



(194)



(195)

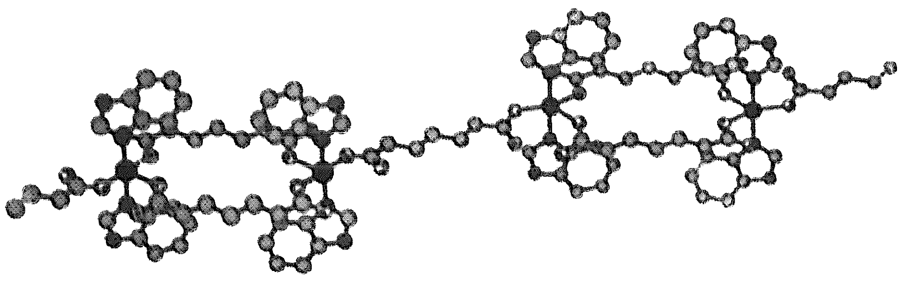
A study into one-dimensional magnetic systems has resulted in the preparation and characterisation of four 2,2′-bipyrimidine-containing (bpm = 2,2′-bipyrimidine) copper(II) complexes of formula [Cu_2(bpm)$_2$(H_2O)$_2$(OH)$_2$(NO_3)$_2$]·4H_2O (**196**), [Cu_2(bpm)(OH)$_2$(NO_3)$_2$]·2H_2O (**197**), [Cu_2(bpm)(H_2O)$_2$(OH)$_2$](NO_3)$_2$ (**198**), and [Cu_2(bpm)(H_2O)$_2$(OH)$_2$(NO_3)$_2$]·2H_2O (**199**) [145]. The structure of (**196**) consists of discrete, centrosymmetric bis(μ-hydroxo) copper(II) dimers with bpm as terminal ligand, weakly coordinated water molecules, monodentate nitrate anions and molecules of water of crystallisation. The copper centre is in a distorted octahedral geometry with two bridging hydroxo groups and two nitrogen atoms of the bpm building the equatorial plane whereas two oxygen atoms from water and nitrato groups occupy the axial sites. The Cu–OH–Cu bridging angle is 95.7° and the Cu···Cu distance is 2.881(1) Å. The structures of (**197**)-(**199**) consist of cationic one-dimensional chains of copper(II) ions alternately bridged by bpm and two hydroxo groups. Electroneutrality is achieved the nitrate groups in (**197**) and (**199**) binding in a monodentate fashion and being uncoordinated in (**198**). The metal environment in (**197**) and (**198**) is square pyramidal, whereas in (**199**) it is best described as distorted octahedral. The copper atoms in (**197**)–(**199**) bond to two nitrogen atoms of bpm and two oxygen hydroxo groups in the equatorial plane while the axial sites are filled by oxygen atoms of nitrate (**197**), of water (**198**) and of both ligands (**199**). The angles of the hydroxo bridge vary in the range 95.0(1)–96.1(2)°. The metal–metal separations through the double-hydroxo bridge [2.886(1) (2), 2.854(1) (3) and 2.860(1) Å (4)] are much shorter than through the bis-chelating bpm [5.471(1) and 5.474(1) (2), 5.461(3) and 5.452(2) Å (4)]. A strong intramolecular ferromagnetic coupling (114 cm^{-1} for the singlet-triplet energy gap) is observed in (**196**). Alternating antiferromagnetic ($-J = 145$–$135\ cm^{-1}$) interactions through the bpm bridge and ferromagnetic ($\alpha J = 160$–$97.5\ cm^{-1}$) interactions through the hydroxo bridges are obtained for (**197**)-(**199**).

The preparation, X-ray structure and optical and magnetic properties of a polymeric 2-dimensional μ-2,2′-bipyrimidine (bpm), μ-oxalato-bridged ($C_2O_4^{2-}$, ox) and μ-chloro-bridged copper(II) network of formula $[Cu_2(bpm)(ox)Cl_2]_n$ is reported [146]. The structure consists of alternating μ-bpm- and μ-ox bridged copper(II) chains which are again connected through mono (μ-chloro) ligands forming a corrugated 2-dimensional framework. The temperature dependence of the magnetic susceptibility is explained with an alternating chain model, taking into account the strong intramolecular antiferromagnetic interaction through the μ-bpm- and μ-ox bridges with the exchange parameters of $J = -189(1)\ cm^{-1}$ for the μ-ox link and $\alpha J = -76(1)\ cm^{-1}$ for the μ-bpm link which corresponds to an alternation parameter of $\alpha = 0.40(2)$.

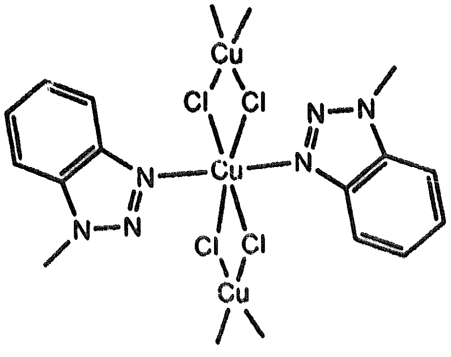
Copper(II) bis(carboxylato) benzimidazole complexes of the type $Cu(Hbim)_2$-(A) and $Cu(Hbim)_2(A)_{1/2}(HA)$ (where Hbim = benzimidazole and A and HA = the dianion and monoanion of a dicarboxylic acid) have been synthesised [147]. The X-ray structure of $\{[Cu_2(Hbim)_4(pim)(Hpim)_2]\cdot 8H_2O\}_n$ (**200**) (where pim and Hpim stand for the di- and mono-deprotonated forms of pimelic acid) has been determined and show a polymeric chain structure in which single dianionic and double monoanionic bridge the metal centres with each carboxylate or carboxylic group acts as a monodentate moiety. The Cu^{II} ions are five coordinate with a square-pyramidal CuN_2O_2O chromophore.

The 1:2 and 1:1 reactions of $CuCl_2$ with 1-methylbenzotriazole in

(**200**)



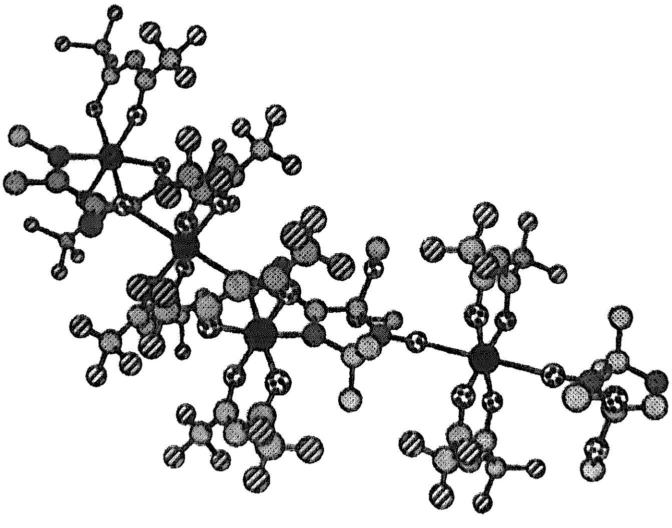
EtOH-CH(OEt)$_3$ gave the doubly chloro-bridged dimer $[Cu_2Cl_4(C_7H_7N_3)_4]$ and the alternating linear-chain polymer $[\{Cu_2Cl_4(C_7H_7N_3)_2\}_n]$ (**201**), respectively [148]. The crystal structure of $[Cu_2Cl_4(C_7H_7N_3)_4]$ consists of isolated dinuclear molecules with two bridging chloro ligands with Cu_2Cl_2 unit planar. The geometry of the copper centres is square pyramidal and with a Cu···Cu separation of 3.438(1) Å. The $C_7H_7N_3$ groups in the *syn* positions are nearly parallel with the angle between their mean planes being 4.3°. There appears to be intradimer stacking between these ligands which are separatedby 3.50 Å. The crystal structure of (**201**) is composed of linear, well separated polymeric chains of Cu^{II} atoms bridged asymmetrically by two chloro ligands. A regular alternation of two non-equivalent copper centres occurs in the chain, with one copper centre surrounded by four chlorides in an almost perfect square planar environment, while the other copper centre exhibits a *trans*-octahedral environment. The Cu···Cu distance is 3.556(1) Å. Magnetic susceptibility studies show that complex $[Cu_2Cl_4(C_7H_7N_3)_4]$ possesses intramolecular ferromagnetic coupling, while complex (**201**) shows intrachain ferromagnetic coupling. However, the one-dimensional chains are coupled antiferromagnetically.



(**201**)

Imidazolium bis(oxalato)cuprate(II) has been synthesised and its structure determined [149]. In the solid state the compound exists in a chain-like structure with an asymmetric one atom weak oxalate bridge joining adjacent copper(II) centres. Of the two oxygen atoms of each coordinated oxalate, only one participates in bridging, thus each oxalate ultimately achieves three-point coordination. Each of the imidazolium ions participates in two hydrogen bonds through the two N–H moieties. The compound exhibits a weak antiferromagnetic interaction ($J = -0.40\ cm^{-1}$). The EPR spectra reveal that the triplet state is appreciably populated at both room and liquid nitrogen temperature.

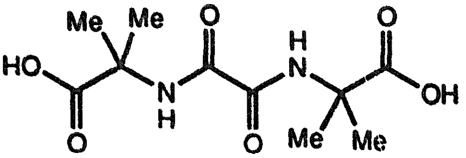
The reaction of copper hexafluoroacetylacetonate with the stable nitroxide 4-amido-2,2-dimethyl-5,5-dimethoxy-3-imidazoline-1-oxyl (L) in a 2:1 ratio in hexane afforded the Cu(hfac)$_2$-saturated coordination chain polymer of composition $[Cu(hfac)_2]_2L$ (**202**) [150]. In this polymer, half of the Cu(hfac)$_2$ molecules coordinate L in a didentate fashion by the amide-group oxygen and the imine nitrogen of the heterocycle, while the other Cu(hfac)$_2$ molecules arrange the previously described {Cu(hfac)$_2$L} fragments in polymer chains by alternate coordination of either the N–O group or the amide oxygen atoms of two {Cu(hfac)$_2$L} fragments to axial positions. This results in the polymer consisting of three copper ions with coordination number six and with different coordination environments. The magnetic properties of the complex are described in terms of an exchange cluster model with ferromagnetic intracluster exchange interactions.

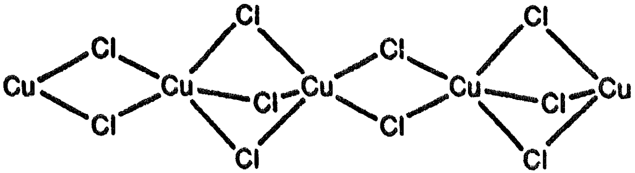


(202)

The new coordination polymer $[Cu_2(\mu\text{-ox})_2(\mu\text{-pyz})(pyz)_2]_n$ (ox = oxalate, pyz = pyrazine) has been synthesised and characterised [151]. The solid state structure of the complex shows it to consist of an extended sheet structure of copper(II) ions bridged by oxalate anions and pyrazine. The repeating unit of $[Cu_2(\mu\text{-ox})_2(\mu\text{-pyz})(pyz)_2]$ contains two types of 4+2 coordination environments with O_4N_2, which are characteristic of pyz coordination; one of the two copper atoms has only terminally coordinated pyz molecules while the other is linked by bridging pyz molecules. The Cu–ox–Cu- sequence appears as a pleated ribbon and planes of Cu–ox–Cu form a boat conformation. The magnetic susceptibilities were measured to 2K and coupling constants of $J = -20.4$ cm^{-1} and $\alpha = 0.85$ determined.

One study has shown that C_2 symmetric core oxalo retro-bispeptides show a unique property of self assembly with Cu(II) ions using the core –NH–CO–CO–NH– unit as the anchor leading to the formation of highly organised, rigid, two-dimensional molecular arrays interlinked *via* the terminal carboxylate units [152]. Addition of Cu(II) salts with the core oxalo retro-bispeptide dicarboxylic acid (**203**) resulted in the formation of a blue–violet coloured complex. The X-ray crystal structure of this complex revealed a two-dimensional structure arising from modular self-assembly. The structure consists of layers separated by 6.4 Å with a nearest contact of 3.3 Å and with the layers held together by van der Waals forces. The solid state structure shows that the interconnection of the units results in the formation of voids of 6.3-6.6 Å diameter. The Cu···Cu distance in each module of 5.155 Å and the Cu···Cu distance between proximate modules in the network of 4.551 Å permits both intramodular, as well as intermodular exchange couplings to occur. An antiferromagnetic coupling constant of $2J = -531.9\,\mathrm{cm}^{-1}$ has been observed.


(203)


(204)

The crystal structure of $(Et_2Me_2N)_3[Cu_4Cl_{11}]$ has been shown to consist of tribridged $[Cu_4Cl_{11}]^{3-}$ units that are linked into infinite chains through the formation of dibridged Cu_2Cl_2 groups (**204**) [153]. Magnetic susceptibility measurements in the range 4–100 K revealed the presence of dominant ferromagnetic coupling at high temperature with the onset of substantially weaker antiferromagnetic coupling at lower temperature. The data are consistent with ferromagnetic coupling within the tetrameric units ($J/K \approx 50$ K). The ground states of these units ($S = 2$) are essentially fully occupied before the antiferromagnetic interactions become significant. These interactions ($J/K = -2.6$ K) link the units into an effective $S = 2$ antiferromagnetic chain.

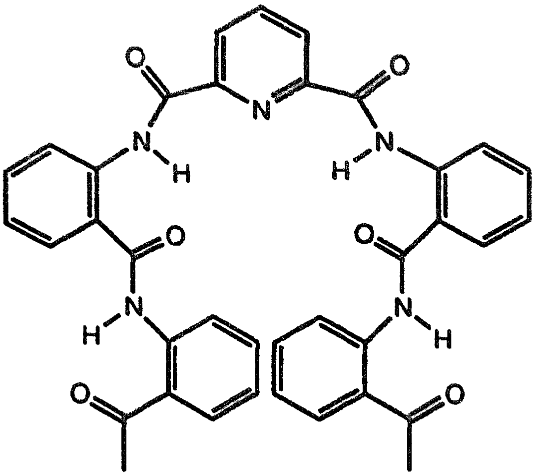
The syntheses, crystal structures and powder magnetic studies of several new quasi-planar bridged $Cu_nX_{2n+2}^{2-}$ oligomers ($n = 3,4,6$ and 7; X = Cl or Br) are reported, based on the 1-methylpyridinium $(C_6H_8N)^+$ and 1,2-dimethylpyridinium $(C_7H_{10}N)^+$ cations [154]. These include $(C_7H_{10}N)_2Cu_3Br_8$, $(C_6H_8N)_2Cu_4Cl_{10}$, $(C_7H_{10}N)_2Cu_6Cl_{14}$ and $(C_7H_{10}N)_2Cu_7Br_{16}$. A common feature of the structures is the existence of oligomers containing quasi-planar symmetric dibridged finite chains of edge-sharing CuX4 (X = halide) monomeric units. The $n = 3$ oligomers aggregate into chains through the formation of asymmetric dibridged linkages between terminal copper ions on adjacent trimers. In the $n = 4$ salt, the oligomers aggregate into stacks in which pairs of the copper ions extend their coordination sphere by forming a long, semicoordinate bond to a halide ion from a neighbouring oligomer. For both the $n = 3$ and $n = 4$ salts, the pyridinium cations lie parallel to and directly above and below the anionic oligomers separating the chains. In the $n = 6$ and $n = 7$ salts, the stacks formed in this manner interdigitate, forming two-dimensional slabs. The slabs are separated by the organic cations. The magnetic properties of the compounds are dominated by antiferromagnetic intraoligomer interactions. While the $n = 4$ and $n = 6$ salts depopulate into singlet ground states at low temperature, the $n = 3$ and $n = 7$ oligomers have $S = 1/2$ ground states. At low temperature, the $n = 3$ oligomer exhibits ferromagnetic behaviour.

3.9. Supramolecular complexes

As part of a study of synthetic metallohelices which use hydrogen bonds, π-stacking and weak metal-ligand interactions as the predominant forces that determine secondary structure the solution and solid state structures of a series of metallohelices of the multidentate ligand (**205**) have been prepared [155]. The ligand contains two aryl moieties that are held rigidly through hydrogen bonds and linked covalently to a pyridyl diamide tridentate chelate. In the solid state the ligand has a helical structure which results mainly from bifurcated hydrogen bonds between the pyridyl nitrogen atom, the amide protons and the adjacent acyloxygen atoms. The two termini overlap with a stacking distance of 3.27 Å. Deprotonation of the pyridyl amide groups gives a tridentate chelate that becomes planar on coordination to a metal centre. The acyl oxygen atoms are disposed to donate additional electron density to the metal centre. However, since these donors are relatively weak Lewis bases their interactions depend on the stereochemical requirements of the metal centres and not on the geometric requirements of the ligand. Two Cu(II) complexes, one green and one red, have been isolated and characterised by X-ray crystallography. The green Cu(II) complex crystallises with two crystallographically independent, but virtually identical molecules. The Cu(II) centre has a distorted square pyramidal geometry and the helical nature of the structure arises from unsymmetrical $Cu–O_{amide}$ interactions. This results in the helix having an unsymmetrical twist as is evident from the torsion angles 0.0 and 5.3°. In the red complex, the Cu(II) centre has a four coordinate geometry and with much shorter Cu–N and Cu–O bond lengths. The main difference between the two Cu(II) complexes is the absence, in the red complex, of the weakly coordinating amide group found in the green complex. This absence of apical ligation in the red complex results in a much more compact helix compared to that found in the green form with the pitch of the helix reduced by 1.445 Å and the radius of the helix reduced by 0.739 Å. The consequence of the difference in pitch of the two helical structures is seen in their crystal lattice structures. Whereas the green form has a microporous lattice, with the pores formed *via* parallel aryl ring π-stacking (3.40 Å) between the termini of the ligand, the red complex forms extended helices in the solid state. Each extended helix consists of alternating right- and left-handed helical monomers that assemble through intermolecular π-stacking interactions. Within an extended helix two intermolecular Cu···Cu distances (5.504 and 9.131 Å) are observed and this close arrangement of the molecules lead to crystals that are significantly more dense (1.137 g cm^{-3}) than those found for the more porous green isomer (1.505 g cm^{-3}).

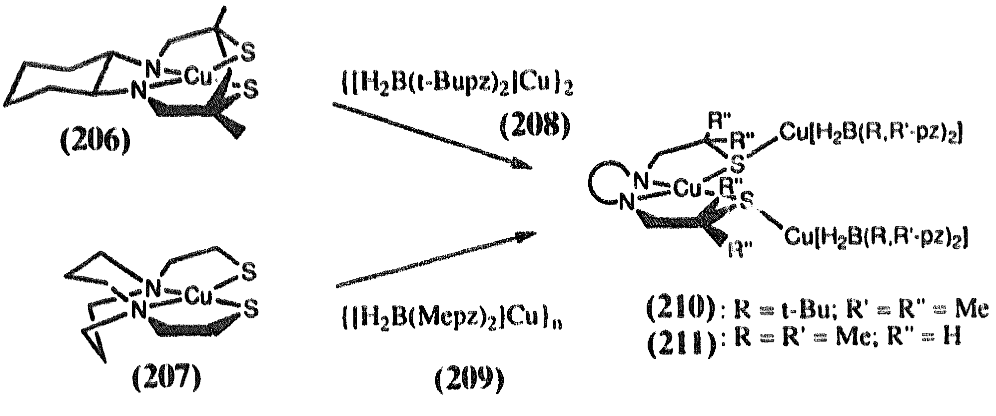
4. Mixed valence complexes

The synthesis and characterisation of a mixed valence tricopper(I,II,I) complex with thiolate bridges as a mimic to N_2OR or Cu_A active sites for example in nitrous oxide reductase (N_2OR) has been reported [156]. The assembly of the mixed valence complexes involved the combination of monomeric copper(II) dithiolates L^1Cu^{II}



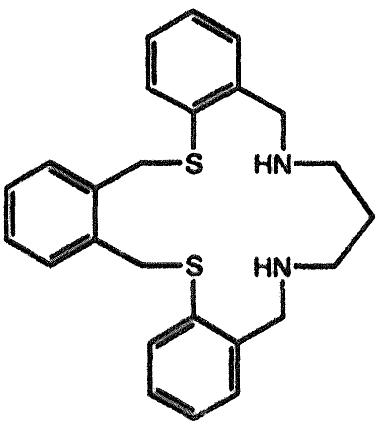
(205)

(206) or L^2Cu^{II} **(207)** with either of the copper(I) bis(pyrazolyl)dihydroborates $[\{H_2B(3,5\text{-}R,R'pz)_2\}Cu]_n$ (**(208)**: R = ^{t}Bu, R′ = H, n = 2; **(209)**: R = R′ = Me, n = unknown) (Scheme 4). The addition of colourless CH_2Cl_2 solutions of the copper(I) complexes to solutions of purple **(206)** or burgundy **(207)** induced colour changes to dark green. Monitoring the reaction by UV–VIS absorption spectroscopy indicated that 1 equivalent (*i.e.* two Cu^I ions) was needed for one equivalent of **(206)** or **(207)** to reach the reaction end-point. This was confirmed by X-ray crystallographic analysis of the dark green products $[L^1Cu\{H_2B(^tBupz)_2\}Cu_2]\cdot C_7H_{16}$ **(210)**$\cdot C_7H_{16}$, and $[L^2Cu\{H_2B(Mepz)_2\}Cu_2]\cdot C_7H_8$ **(211)**$\cdot C_7H_8$. The structures both contain two symmetry-related three-coordinate planar Cu^I ions linked via thiolate sulfur atoms to the central four-coordinate Cu^{II} ion. The $Cu^I\cdots Cu^{II}$ distances are 3.163(5) and 2.996(5) Å in **(210)** and **(211)** respectively. Preliminary EPR spectroscopic studies support the presence of localised mixed valence formulations in the tricopper complexes.

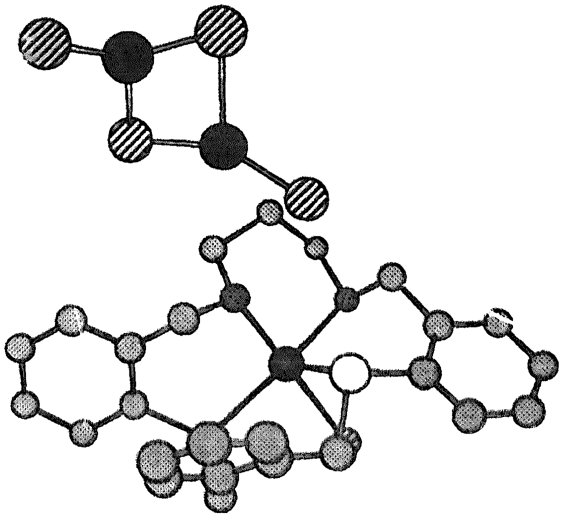


Scheme 4.

In another study, a mimic of the electron-transfer site "CuA" has been synthesised by a Cu(I) template method followed by Ag^+ oxidation [157]. The X-ray crystallographic study of the complex confirms the close approach of the copper nuclei



(212)



(213)

within the cryptate ligand cage with a Cu–Cu distance of 2.419(1) Å. Comparison of the electronic spectra of the complex with related cryptate systems have enabled the spectra to be assigned to transitions within a manifold of mainly d orbitals delocalised over the Cu_2^{3+} dimer.

A doubly complex salt containing the atypical non-planar Cu^I dimeric anion $[Cu_2Cl_4]^{2-}$ and a Cu^{II} containing macrocyclic cation has been synthesised starting from $CuCl_2.2H_2O$ and a new N_2S_2 type macrocycle 7,9-diaza-3,14-dithiatetracycle[15,4,0,$0^{4,5}$,$0^{13,14}$]nonacosa-1(17),18,20,4(22),23,25,13(26),-27,29-nonaene (**212**) [158]. The complex $[Cu(\mathbf{212})Cl]_2[Cu_2Cl_4].2CH_3OH$ (**213**) is a dark blue air-stable complex which X-ray diffraction analysis shows contains both copper^{II}, $[Cu(\mathbf{212})Cl]^+$, cations and copper^I $[Cu_2Cl_4]^{2-}$ anions.

References

[1] D.R. Smith, Coord. Chem. Rev., (1997) in press

[2] A.K. Burrell, D.L. Officer, D.C.W. Reid, Angew. Chem. Int. Ed. Engl. 34 (1995) 900.

[3] D.A. Bradwell, A.M.W. Cargill Thompson, J.C. Jeffery, E.E.M. Tilley, M.D. Ward, J. Chem. Soc., Dalton Trans., (1995) 835.

[4] C. Pettinari, G.G. Lobbia, G. Sclavi, D. Leonesi, M. Colapietro, G. Portalone, Polyhedron 14 (1995) 1709.

[5] A.J. Pallenberg, K.S. Koenig, D.M. Barnhart, Inorg. Chem. 34 (1995) 2833.

[6] D.J. Darensbourg, M.W. Holtcamp, B. Khandelwal, K.K. Klausmeyer, J.H. Reibenspies, Inorg. Chem. 34 (1995) 2389.

[7] D.J. Darensbourg, M.W. Holtcamp, E.M. Longridge, B. Khandelwal, K.K. Klausmeyer, J.H. Reibenspies, J. Am. Chem. Soc. 117 (1995) 318.

[8] V.W.-W. Yam, K.K.-W. Lo, K.-K. Cheung, Inorg. Chem. 34 (1995) 4013.

[9] B.J. Reedy, N.N. Murthy, K.D. Karlin, N.J. Blackburn, J. Am. Chem. Soc. 117 (1995) 9826.

[10] G. Speier, A.M. Whalen, J. Csihony, C.G. Pierpont, Inorg. Chem. 34 (1995) 1355.

[11] I. Haiduc, R. Cea-Olivares, R.A. Toscano, C. Silvestru, Polyhedron 14 (1995) 1067.

[12] G.P. Voutsas, S.C. Kokkou, C.J. Cheer, P. Aslanidis, P. Karagiannidis, Polyhedron 14 (1995) 2287.

[13] C.L. Doel, A.M. Gibson, G. Reid, C.S. Frampton, Polyhedron 14 (1995) 3139.

[14] P. Cecchi, B. Bovio, G.G. Lobbia, C. Pettinari, D. Leonesi, Polyhedron 14 (1995) 2441.

[15] C.J. Harding, Q. Lu, J.F. Malone, D.J. Marrs, N. Martin, V. McKee, J. Nelson, J.Chem. Soc., Dalton Trans., (1995) 1739.

[16] S. Kitagawa, M. Kondo, S. Kawata, S. Wado, M. Maekawa, M. Munakata, Inorg. Chem. 34 (1995) 1455.

[17] M.J. Begley, P. Hubberstey, P.H. Walton, J. Chem. Soc., Dalton Trans., (1995) 957.

[18] H.G. Raubenheimer, S. Cronje, G.J. Kruger, P.J. Olivier, Polyhedron 14 (1995) 2389.

[19] S.-C. Sheu, M.J. Tien, M.-C. Cheng, T.I. Ho, S.-M. Peng, Y.-C. Lin, J. Chem. Soc., Dalton Trans., (1995) 3503.

[20] S. Ramaprabhu, E.A.C. Lucken, G. Bernardinelli, J. Chem. Soc., Dalton Trans., (1995) 115.

[21] D.J. Darensbourg, M.W. Holtcamp, B. Khandelwal, J.H. Reibenspies, Inorg. Chem. 34 (1995) 5390.

[22] D. Gudat, M. Schrott, M. Nieger, J. Chem. Soc., Chem. Commun., (1995) 1541.

[23] P. Strauch, W. Dietzsch, L. Golic, J. Sieler, A. Franke, I. MŸnzberg, K. TrŸenbach, R. Kirmse, J. Reinhold, E. Hoyer, Inorg. Chem. 34 (1995) 763.

[24] P. Hubberstey, C.E. Russell, J. Chem. Soc., Chem. Commun., (1995) 959.

[25] A.J. Blake, C.M. Grant, S. Parsons, R.E.P. Winpenny, J. Chem. Soc., Dalton Trans., (1995) 1765.

[26] M.K. Davies, P.R. Raithby, M.-A. Rennie, A. Steiner, D.S. Wright, J. Chem. Soc., Dalton Trans., (1995) 2707.

[27] W. Xu, J.J. Vittal, R.J. Puddephatt, J. Am. Chem. Soc. 117 (1995) 8362.

[28] Q. Liu, Y. Yang, L. Huang, D. Wu, B. Kang, C. Chen, Y. Deng, J. Lu, Inorg. Chem. 34 (1995) 1884.

[29] A.P. Purdy, C.F. George, Polyhedron 14 (1995) 761.

[30] T. Kuroda-Sowa, M. Munakata, M. Miyazaki, M. Maekawa, Polyhedron 14 (1995) 1003.

[31] X.-F. Yu, F.-K. Zheng, L.R. Huang, Polyhedron 14 (1995) 3599.

[32] C.W. Liu, T. Stubbs, R.J. Staples, FacklerJ.P., Jr., J. Am. Chem. Soc. 117 (1995) 9778.

[33] X. Gan, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Misaki, Polyhedron 14 (1995) 1343.

[34] X. Gan, M. Munakata, T. Kuroda-Sowa, M. Maekawa, M. Yamamoto, Polyhedron 14 (1995) 1647.

[35] M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota, S. Kitagawa, Inorg. Chem. 34 (1995) 2705.

[36] O.N. Kataeva, I.A. Litvinov, V.A. Naumov, L.I. Kursheva, E.S. Batyeva, Inorg. Chem. 34 (1995) 5171.

[37] G.A. Bowmaker, R.D. Hart, B.E. Jones, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans., (1995) 3036.

[38] O.M. Yaghi, H. Li, J. Am. Chem. Soc. 117 (1995) 10401.

[39] F. Bodar-Houillon, T. Humbert, A. Marsura, J.-B. Regnouf de Vains, O. Dusausoy, N. Bouhmaida, N.E. Ghermani, Y. Dusausoy, Inorg. Chem. 34 (1995) 5205.

[40] T. Kuroda-Sowa, M. Munakata, H. Matsuda, S. Akiyama, M. Maekawa, J. Chem. Soc., Dalton Trans., (1995) 2201.

[41] M.A.S. Goher, T.C.W. Mak, Polyhedron 34 (1995) 2587.

[42] H. Sleiman, P. Baxter, J.-M. Lehn, K. Rissanen, J. Chem. Soc., Chem. Commun., (1995) 715.

[43] R. Ziessel, D. Matt, L. Toupet, J. Chem. Soc., Chem. Commun., (1995) 2033.

[44] P. Comba, A. Fath; T.W. Hambley, D.T. Richens, Angew. Chem. Int. Ed. Engl. 34 (1995) 1883.

[45] O. Schlager, K. Wieghardt, B. Nuber, Inorg. Chem. 34 (1995) 6449.

[46] P.V. Bernhardt, R. Bramley, L.M. Englehardt, J.M. Harrowfield, D.C.R. Hockless, B.R. Korybut-Daszkiewicz, E.R. Krausz, T. Morgan, A.M. Sargeson, B.W. Skelton, A.H. White, Inorg. Chem. 34 (1995) 3589.

[47] M.J.L. Tendero, A. Benito, J. Cano, J.M. Lloris, R. Martinez-Máñez, J. Soto, A.J. Edwards, P.R. Raithby, M.A. Rennie, J. Chem. Soc., Chem. Commun., (1995) 1643.

[48] X.H. Bu, D.L. An, Y.T. Chen, M. Shionoya, E. Kimura, J. Chem. Soc., Dalton Trans., (1995) 2289.

[49] G. Ricciardi, A. Bavosa, A. Rosa, F. Lelj, Y. Cizov, J. Chem. Soc., Dalton Trans., (1995) 2385.

[50] P. Comba, T.W. Hambley, M.A. Hitchman, H. Stratemeier, Inorg. Chem. 34 (1995) 3903.

[51] E.R. Birnbaum, J.A. Hodge, M.W. Grinstaff, W.P. Schaefer, L. Henling, J.A. Labinger, J.E. Bercaw, H.B. Gray, Inorg. Chem. 34 (1995) 2625.

[52] M. Munakata, L.P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, J. Chem. Soc., Dalton Trans., (1995) 3215.

[53] C.A. Salhi, Q. Yu, M.J. Heeg, N.M. Villeneuve, K.L. Juntunen, R.R. Schroeder, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 34 (1995) 6053.

[54] G. Wei, C.C. Allen, T.W. Hambley, G.A. Lawrence, M. Maeder, J. Chem. Soc., Dalton Trans., (1995) 2541.

[55] C.F. Martens, A.P.H.J. Schenning, M.C. Feiters, H.W. Berens, J.G.M. van der Linden, G. Admiraal, P.T. Beurskens, H. Kooijman, A.L. Spek, R.J.M. Nolte, Inorg. Chem. 34 (1995) 4735.

[56] C.-C. Su, K.-Y. Hwang, J.H. Chen, S.-L. Wang, F.-L. Liao, J.-C. Horng, Polyhedron 14 (1995) 3011.

[57] K.J. Catalan, S. Jackson, J.D. Zubkowski, D.L. Perry, E.J. Valente, L.A. Feliu, A. Polanco, Polyhedron 14 (1995) 2165.

[58] C.-C. Su, S.-P. Wu, C.-Y. Wu, T.-Y. Chang, Polyhedron 14 (1995) 267.

[59] Z. Wang, J. Reibenspies, R.J. Motekaitis, A.E. Martell, J. Chem. Soc., Dalton Trans., (1995) 1511.

[60] T. Astley, P.J. Ellis, H.C. Freeman, M.A. Hitchman, F.R. Keene, E.R.T. Tiekink, J. Chem. Soc., Dalton, Trans., (1995) 595

[61] G.A. McLachlan, G.D. Fallon, R.L. Martin, L. Spiccia, Inorg. Chem. 34 (1995) 254.

[62] C. Chuang, K. Lim, Q. Chen, J. Zubieta, J.W. Canary, Inorg. Chem. 34 (1995) 2562.

[63] D.A. Bardwell, J.C. Jeffery, P.L. Jones, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Dalton Trans., (1995) 2921.

[64] M. Palaniandavar, T. Pandiyan, M. Lakshminarayanan, H. Manohar, J. Chem. Soc., Dalton Trans., (1995) 455.

[65] M.J. Young, D. Wahnon, R.C. Hynes, J. Chin, J. Am. Chem. Soc. 117 (1995) 9441.

[66] A. Marzotto, A. Ciccarese, D.A. Clemente, G. Valle, J. Chem. Soc., Dalton Trans., (1995)

[67] C. Price, M.R.J. Elsegood, W. Clegg, A. Houlton, J. Chem. Soc., Chem. Commun., (1995) 2285.

[68] A. Garcia-Raso, A. Terron, J.F. Fiol, E. Molins, C. Miravitlles, Polyhedron 14 (1995) 2537.

[69] M. Fettouchi, L. Ouahab, M. Hagiwara, E. Codjovi, O. Kahn, H. Constant-Machado, F. Varret, Inorg. Chem. 34 (1995) 4152.

[70] A. Charlton, A.E. Underhill, A. Kobayashi, H. Kobayashi, J. Chem. Soc., Dalton Trans., (1995) 1285.

[71] H.O. Davies, R.D. Gillard, M.B. Hursthouse, A. Karaulov, J. Chem. Soc., Dalton Trans., (1995) 2333.

[72] C.S. Bruschini, M.G.B. Drew, M.J. Hudson, K. Lyssenko, Polyhedron 14 (1995) 3099.

[73] J.A.P. Nash, S.C. Thompson, D.F. Foster, D.J. Cole-Hamilton, J.C. Barnes, J. Chem. Soc., Dalton Trans., (1995) 269

[74] J. Pinkas, J.C. Huffman, M.H. Chisholm, K.G. Caulton, Inorg. Chem. 34 (1995) 5314.

[75] Y. Kobuke, K. Kokubo, M. Munakata, J. Am. Chem. Soc. 117 (1995) 12751.

[76] G. Pilloni, G. Valle, C. Corvaja, B. Longato, B. Corain, Inorg. Chem. 34 (1995) 5910.

[77] H. Adams, N.A. Bailey, D.E. Fenton, G. Papageorgiou, J. Chem. Soc., Dalton Trans., (1995) 1883.

[78] N.V. Gerbeleu, S.S. Palanciuc, Y.A. Simonov, A.A. Dvorkin, P.N. Bourosh, M.T. Reetz, V.B. Arion, K. Töllner, Polyhedron 14 (1995) 521.

[79] M. Mitsumi, J. Toyoda, K. Nakasuji, Inorg. Chem. 34 (1995) 3367.

[80] I. Castro, J. Sletten, L.K. Glaerum, J. Cano, F. Lloret, J. Faus, M. Julva, J. Chem. Soc., Dalton Trans., (1995) 3207.

[81] A.J. Blake, S. Parsons, J.M. Rawson, R.E.P. Winpenny, Polyhedron 14 (1995) 1895.

[82] H. Adams, N.A. Bailey, C.O. Rodriguez de Barbarin, D.E. Fenton, Q.-Y. He, J. Chem. Soc., Dalton Trans., (1995) 2323.

[83] E. Labisbal, J.A. Garcia-Vazquez, J. Romero, S. Picos, A. Sousa, A. Castiñeiras, C. Maichle-Mössmer, Polyhedron 14 (1995) 663.

[84] J.P. Schneider, J.W. Kelly, J. Am. Chem. Soc. 117 (1995) 2533.

[85] S. Itoh, T. Kondo, M. Komatsu, Y. Ohshiro, C. Li, N. Kanehisa, Y. Kai, S. Fukuzumi, J. Am. Chem. Soc. 117 (1995) 4714.

[86] T. Nozaki, N. Matsumoto, H. Okawa, H. Mijasaka, G. Mago, Inorg. Chem. 34 (1995) 2108.

[87] M. McCann, J.F. Cronin, M. Devereux, V. McKee, G. Ferguson, Polyhedron 14 (1995) 3617.

[88] M. McCann, J.F. Cronin, M. Devereux, G. Ferguson, Polyhedron 14 (1995) 2379.
[89] M. Petric, I. Leban, P. Segedin, Polyhedron 14 (1995) 983.
[90] D.X. West, J.S. Ives, J. Krejci, M.M. Salberg, T.L. Zumbahlen, G.A. Bain, A.E. Liberta, J. Valdes-Martinez, S. Hernandez-Ortiz, R.A. Toscano, Polyhedron 14 (1995) 2189.
[91] S.-P. Wey, M. Ibrahim, M.A. Green, P.E. Fanwick, Polyhedron 14 (1995) 1097.
[92] C. Beguin, P. Chautemps, A. El Marzouki, J.-L. Pierre, S.M. Refaif, G. Serratrice, E. Saint-Aman, P. Rey, J. Chem. Soc., Dalton Trans., (1995) 1939.
[93] J. Valdés-Martínez, R.A. Toscano, J. Ramirez-Ortiz, Polyhedron 14 (1995) 579.
[94] X. Zhang, W.-Y. Hsieh, T.N. Margulis, L.J. Zompa, Inorg. Chem. 34 (1995) 2883.
[95] X.-M. Chen, Y.-X. Yao, Z.-T. Xu, K.-L. Shi, Y.-J. Xu, Polyhedron 14 (1995) 1195.
[96] R.P. Houser, J.A. Halfen, YoungV.G., Jr., N.J. Blackburn, W.B. Tolman, J. Am. Chem. Soc. 117 (1995) 10745.
[97] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti, A. Stefani, B. Valtancoli, Inorg. Chem. 34 (1995) 552.
[98] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti, G. Piccardi, B. Valtancoli, Inorg. Chem. 34 (1995) 5262.
[99] J.E. Bol, W.L. Driessen, J. Reedijk, J. Chem. Soc., Chem. Commun., 1995, 1365.
[100] S. Ohtsuka, M. Kodera, K. Motoda, M. Ohba, H. Okawa, J. Chem. Soc., Dalton Trans., (1995) 2599.
[101] J.-L. Pierre, P. Chautemps, S. Refaif, C. Beguin, A. El Marzouki, G. Serratrice, E. Saint-Aman, P. Rey, J. Am. Chem. Soc. 117 (1995) 1965.
[102] M. Lubben, R. Hage, A. Meetsma, K. BOma, B.L. Feringa, Inorg. Chem. 34 (1995) 2217.
[103] D.X. West, Y. Yang, T.L. Klein, K.I. Goldberg, A.E. Liberta, J. Valdes-Martinez, R.A. Toscao, Polyhedron 14 (1995) 1681.
[104] J.C. Jeffery, J.P. Maher, C.A. Otter, P. Thornton and M.D. Ward, J. Chem Soc., Dalton Trans., (1995) 819.
[105] G.J.A.A. Koolhaas, W.L. Driessen, J. Reedijk, H. Kooijman, A.L. Spek, J. Chem. Soc., Chem. Commun., (1995) 517.
[106] F. Tuczek, W. Bensch, Inorg. Chem. 34 (1995) 1482.
[107] V. McKee, M. Zvagulis, J.V. Dagdigan, M.G. Patch, C.A. Reed, J. Am. Chem. Soc. 106 (1984) 4765.
[108] G.A. van Albada, M.T. Lakin, N. Veldman, A.L. Spek, J. Reedijk, Inorg. Chem. 34 (1995) 4910.
[109] SatcherJ.H., Jr., M.W. Droegg, T.J.R. Weakley, R.T. Taylor, Inorg. Chem. 34 (1995) 3317.
[110] SatcherJ.H., Jr., A.L. Balch, Inorg. Chem. 34 (1995) 3371.
[111] E. Müller, G. Bernardinelli, J. Reedijk, Inorg. Chem. 34 (1995) 5979.
[112] P.J. Van Koningsbruggen, D. Gatteschi, R.A. G de Graaff, J.G. Haasnoot, J. Reedijk, C. Zanchini, Inorg. Chem. 34 (1995) 5175.
[113] G. De Santis, L. Fabbrizzi, A.M. Manoti Lanfredi, P. Pallavicini, A. Perotti, F. Ugozzoli, M. Zema, Inorg. Chem. 34 (1995) 4529.
[114] W.F. Zeng, C.P. Cheng, S.M. Wang, M.-C. Cheng, G.-H. Lee, Y. Wang, Inorg. Chem. 34 (1995) 728.
[115] E. Bouwman, P. Evans, R.A.G. de Graaff, H. Kooijman, R. Poinsot, P. Rabu, J. Reedijk, A.L. Spek, Inorg. Chem. 34 (1995) 6302.
[116] M. Li, J.-Z. Zou, Z. Xu, X.-Z. You, X.-Y. Huang, Polyhedron 14 (1995) 639.
[117] J. Gleruo, P.A. Goodson, D.J. Hodgson, K. Michelson, Inorg. Chem. 34 (1995) 6255.
[118] K.S. Bürger, P. Chaudhuri, K. Wieghardt, B. Nuber, Chem. Eur. J. 1 (1995) 583.
[119] S.P. Perlepes, J.C. Huffman, G. Christou, S. Paschalidou, Polyhedron 14 (1995) 1073.
[120] G. De Munno, M. Julve, F. Lloret, J. Cano, A. Caneshi, Inorg. Chem. 34 (1995) 2048.
[121] L.K. Thompson, S.S. Tandon, M.E. Manuel, Inorg. Chem. 34 (1995) 2356.
[122] J. Piotraschke, A.E. Pullen, K.A. Abboud, J.R. Reynolds, Inorg. Chem. 34 (1995) 4011.
[123] T.N. Sorrell, W.E. Allen, P.S. White, Inorg. Chem. 34 (1995) 952.
[124] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti, B. Valtancoli, J. Chem. Soc., Chem. Commun., (1995) 1555.
[125] T. Otieno, S.J. Rettig, R.C. Thompson, J. Trotter, Inorg. Chem. 34 (1995) 1718.
[126] S. Myllyviita, R. Sillanpää, J.J.A. Kolnaar, J. Reedijk, J. Chem. Soc., Dalton Trans., (1995) 2209.
[127] S.S. Tandon, L.K. Thompson, D.O. Miller, J. Chem. Soc., Chem. Commun., (1995) 1907.

[128] Y. Zhang, L.K. Thompson, J.N. Bridson, M. Bubenik, Inorg. Chem. 34 (1995) 5870.

[129] T. Kogane, T. Yamamoto, M. Hayashi, R. Hirota, C.A. Horiuchi, Polyhedron 14 (1995) 2475.

[130] F. Lanfranc de Panthou, E. Belorizky, R. Calemczuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek, P. Rey, J. Am. Chem. Soc. 117 (1995) 11247.

[131] I. Castro, J. Sletten, M.L. Calatayud, M. Julve, J. Cano, F. Lloret, A. Caneschi, Inorg. Chem. 34 (1995) 4903.

[132] K. Motoda, H. Sakiyama, N. Matsumoto, H. Okawa, D.E. Fenton, J. Chem. Soc., Dalton Trans., (1995) 3419.

[133] J. Reim, K. Grieser, W. Haase, B. Krebs, J. Chem. Soc., Dalton Trans., (1995) 2649.

[134] P.E. Kruger, G.D. Fallon, B. Moubaraki, K.J. Berry, K.S. Murray, Inorg. Chem. 34 (1995) 4808.

[135] A.J. Blake, C.M. Grant, C.I. Gregory, S. Parsons, J.M. Rawson, D. Reed. R.E.P. Winpenny, J. Chem. Soc., Dalton Trans., (1995) 163.

[136] S.S. Tandon, L.K. Thompson, J.N. Bridson, C. Benelli, Inorg. Chem. 34 (1995) 5507.

[137] P. Klüfers, J. Schuhmacher, Angew. Chem. Int. Ed. Engl. 34 (1995) 2119.

[138] D.M.L. Goodgame, S. Menzer, A.M. Smith, D.J. Williams, J. Chem. Soc., Chem. Commun., (1995) 1975.

[139] R. Cortés, L. Lezama, J.I. Ruiz de Larramendi, G. Madariaga, J.L. Mesa, F.J. Zu-iga, T. Rojo, Inorg. Chem. 34 (1995) 778.

[140] J. Suarez-Varela, J.M. Dominguez-Vera, E. Colacio, J.C. Avila-Rosón, M.A. Hidalgo, D. Martín-Ramos, J. Chem. Soc., Dalton Trans., (1995) 2143.

[141] M.A.S. Goher, F.A. Mautner, Polyhedron 14 (1995) 1751.

[142] F.A. Mautner, M.A.S. Goher, Polyhedron 14 (1995) 1809.

[143] A. Neels, H. Stoeckli-Evans, A. Escuer, R. Vicente, Inorg. Chem. 34 (1995) 1946.

[144] M.M. Chowdhry, A.D. Burrows, D.M.P. Mingos, A.J.P. White, D.J. Williams, J.Chem. Soc., Chem. Commun., (1995) 1521.

[145] G. De Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi, Inorg. Chem. 34 (1995) 157.

[146] S. Decurtins, H.W. Schmalle, P. Schneuwly, L.-M. Zheng, J. Ensling, A. Hauser, Inorg. Chem. 34 (1995) 5501.

[147] G.A. van Albada, J.G. Haasnoot, J. Reedijk, M. Biagini-Cingi, A.M. Manotti-Lanfredi, F. Ugozzoli, Polyhedron 14 (1995) 2467.

[148] K. Skorda, E.G. Bakalbassis, J. Mrozinski, S.P. Perlepes, C.P. Raptopoulou, A. Terzis, J. Chem. Soc., Dalton Trans., (1995) 2317.

[149] S.K. Chattopadhyay, T.C.W. Mak, B.-S. Luo, L.K. Thompson, A. Rana, S. Ghosh, Polyhedron 14 (1995) 3661.

[150] A.B. Burdukov, V.I. Ovcharenko, R.Z. Sagdeev, A.V. Podoplelov, N.V. Pervukhina, V.N. Ikorskii, I.A. Grigoriev, Polyhedron 14 (1995) 501.

[151] S. Kitagawa, T. Okuba, S. Kawata, M. Kondo, M. Katada, H. Kobayashi, Inorg. Chem. 34 (1995) 4790.

[152] D. Ranganathan, N.K. Vaish, G.V.R. Chandramouli, B. Varghese, R.B. Muthukumaran, P.T. Manoharan, J. Am. Chem. Soc. 117 (1995) 1643.

[153] Y. Fujii, Z. Wang, R.D. Willett, W. Zhang, C.P. Landee, Inorg. Chem. 34 (1995) 2870.

[154] M.R. Bond, H. Place, Z. Wang, R.D. Willett, Y. Liu, T.E. Grigereit, J.E. Drumheller, G.F. Tuthill, Inorg. Chem. 34 (1995) 3134.

[155] T. Kawamoto, O. Prakash, R. Ostrander, A.L. Rheingold, A.S. Borovik, Inorg. Chem. 34 (1995) 4294.

[156] R.P. Houser, W.B. Tolman, Inorg. Chem. 34 (1995) 1632.

[157] J.A. Farrar, V. McKee, A.H.R. Al-Obaidi, J.J. McGarvey, J. Nelson, A.J. Thomson, Inorg. Chem. 34 (1995) 1302.

[158] L. Escriche, N. Lucena, J. Casabó, F. Teixidor, R. Kivekäs, R. Silanpää, Polyhedron 14 (1995) 649.