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Copper 1996

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Contents

1. Introduction 458
2. Copper(I) 458
  2.1. Mononuclear complexes with macrocyclic ligands 458
  2.2. Mononuclear complexes with acyclic ligands 461
  2.3. Dinuclear complexes with macrocyclic ligands 470
  2.4. Dinuclear complexes with acyclic ligands 473
  2.5. Tetranuclear complexes 476
  2.6. Cluster complexes 477
  2.7. Polymeric complexes 478
  2.8. Supramolecular complexes 484
3. Copper(II) 488
  3.1. Mononuclear complexes with macrocyclic ligands 488
  3.2. Mononuclear complexes with acyclic ligands 499
    3.2.1. Nitrogen coordination 499
    3.2.2. Oxygen coordination 512
    3.2.3. Nitrogen and oxygen coordination 513
    3.2.4. Nitrogen and oxygen coordination 523
  3.3. Dinuclear complexes with macrocyclic ligands 526
  3.4. Dinuclear complexes with acyclic ligands 533
    3.4.1. Nitrogen, sulfur and oxygen coordination 533
    3.4.2. Nitrogen and sulfur coordination 541
    3.4.3. Nitrogen and oxygen coordination 542
  3.5. Trinuclear complexes 550
  3.6. Tetranuclear complexes 553
  3.7. Hexanuclear complexes 556
  3.8. Cluster complexes 557
  3.9. Polymeric complexes 558
4. Mixed valence complexes 564
References 565

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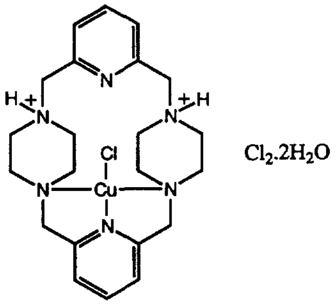
1. Introduction

This review provides an overview of the coordination chemistry of copper published in 1996. The large volume of publications arising during 1996 has made it impossible to include all papers and the method limiting the number has been to confine the search to Current Contents and then select mainly those published in major journals, although structurally characterized complexes have been given priority. Heteronuclear complexes have in general not been included. Organometallic complexes are generally not included in this article.

2. Copper(I)

2.1. *Mononuclear complexes with macrocyclic ligands*

The structure of a 2:2 macrocycle containing pyridine and piperazine subunits has been characterized [1]. This molecule lies on an inversion centre and with the piperazine subunits having the chair conformation. Upon reaction with $CuCl_2$ in methanol, this macrocycle becomes diprotonated, and the Cu^{II} is reduced to Cu^{I}. The X-ray structure of the resulting Cu^{I} complex of the diprotonated macrocyclic dication (**1**) has been determined and shows the Cu atom coordinates in an approximately linearly manner to one of the pyridine N atoms and a chloro ligand with a Cu–N distance of 1.947(3) Å, a Cu–Cl distance of 2.1331(1) Å, and an N–Cu–Cl angle of 164.5(1)°. While the piperazine subunits maintain their chair conformations, one nitrogen atom of each is protonated and turned outward. The unprotonated piperazine nitrogen atoms form long interactions of 2.488(4) and 2.508(4) Å to the Cu atom.



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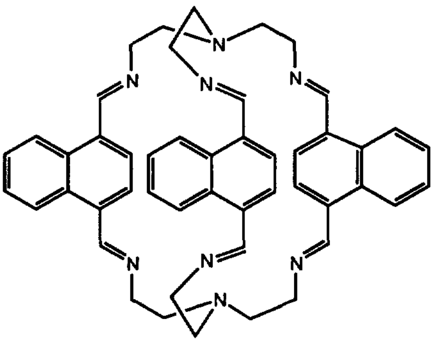

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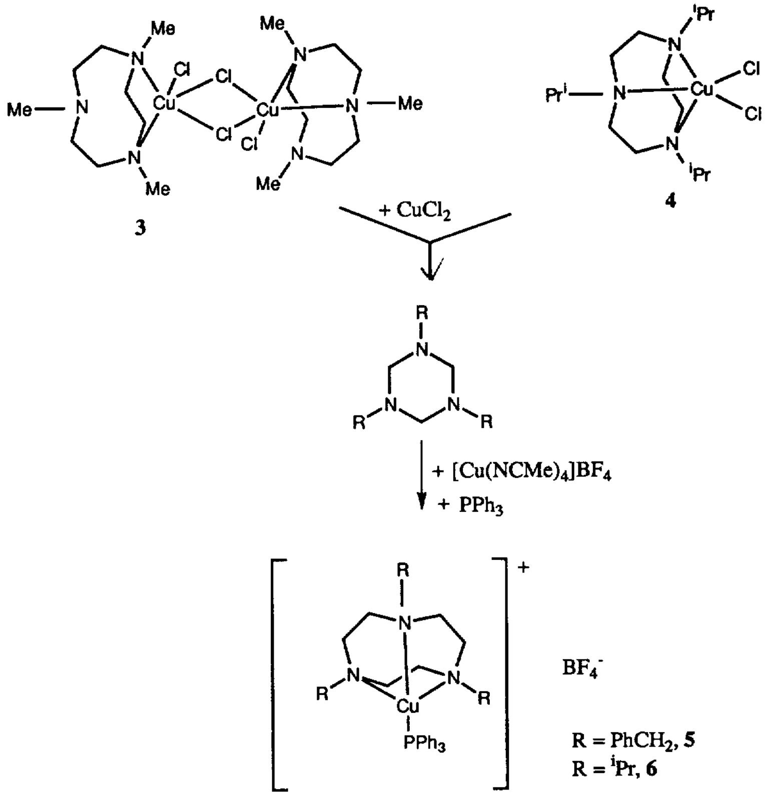
A study has been carried out that demonstrates that the conformation of a cryptand can be modified by the choice of the metal ion encapsulated in its cavity [2]. A new hexaimino cryptand containing two tris(2-aminoethyl)amine moieties bridged by three naphthalene groups (**2**) and its copper(I) and silver(I) complexes have been synthesized and characterized. The solid state structures of the cryptand and cryptates have been determined by X-ray diffraction, unveiling three different conformations. The macrobicyclic ligand has an anti conformation in the cryptand, but has a sym form in each cryptate. Although the Ag^+ cryptates have a symmetric structure on the three arms, one of the three arms in the Cu^+ complex shows remarkable bending. The bent conformation is intrinsic to the Cu^+ complex, as indicated by X-ray analyses and MM2 calculations. The temperature dependence of the ^1H NMR spectra has also been investigated, revealing fluxional behaviour of the ligand in each complex.

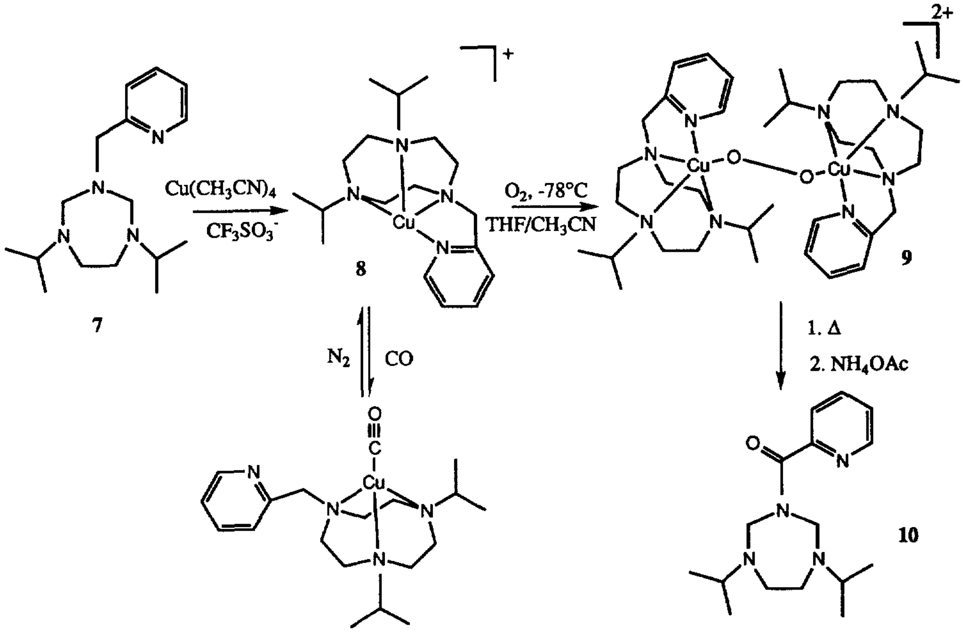
The synthesis of η^3-1,3,5-triazacyclohexane (R_3TAC) complexes of copper(I) and copper(II) have been reported (Scheme 1) and the complexes $[\{(Me_3TAC)CuCl_2\}_2]$ (**3**), $[(^iPr_3TAC)CuCl_2]$ (**4**), $[\{PhCH_2)_3TAC\}Cu(PPh_3)](BF_4)$ (**5**) and $[(^iPr_3TAC)Cu(PPh_3)](BF_4)$ (**6**) characterized by X-ray crystallographic analysis [3]. The highly strained and bent Cu–N bonds are longer than in the corresponding complexes of other amine ligands. One methylene carbon atom of the ring comes close to the copper atom (2.55–2.65 Å). However, investigation of



Scheme 1.

the ring deuterated complexes by IR and X-ray crystallography showed no clear evidence for attractive C–H–Cu interactions.

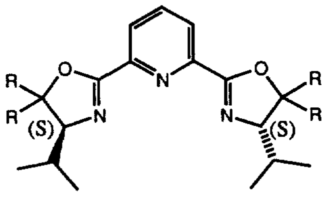
A study relevant to biological and catalytic hydrocarbon oxidations mediated by copper active sites has been carried out [4]. The Cu(I) starting material [7Cu]CF_3SO_3 **8** was isolated in 95% yield from the reaction of the Cu(I) salt with **7**, a sterically hindered tetradentate tripodal ligand (Scheme 2) which X-ray crystallographic analysis shows has a trigonal-bipyramidal coordination geometry. The reaction of **8** with CO (1 atm) caused a bleaching of the 360 nm absorption feature and growth of a ν_{CO} absorption at 2067 cm^{-1}, consistent with binding of CO concomitant with displacement of the pyridyl arm to yield [η^3-7CuCo]CF_3SO_3. Purging with N_2 cleanly reversed the process to regenerate **8**. Oxygenation of a solution of **8** in thf/CH_3CN (10:1) at −78 °C yielded a deep purple solution with spectroscopic properties indicating a *trans*-1,2-peroxodicopper(II) complex having tetradentate ligand coordination, $[(7Cu)_2(O_2)](CF_3SO_3)_2$ **9**, which is EPR silent. Although **9** was found to be stable for weeks at −78 °C, it decomposes on warming, both in the presence or absence of O_2, to yield a blue solution. Extraction of copper ions from this solution with NH_4OH yielded a mixture of **7** and a new modified ligand **10** in a 4:1 ratio. With **9**–^{18}O, derived from the reaction of $^{18}O_2$ with **8** was allowed to decompose, ^{18}O was incorporated into **10** (>95% by GCMS). This conversion (**7**–**10**) represents a four electron hydrocarbon oxidation. Preliminary mechanistic experiments implicate a kinetically complex pathway for the four electron oxidative transformation which the authors suggest involves a unimolecular isomerization of the peroxodicopper core as an initial step.



Scheme 2.

2.2. Mononuclear complexes with acyclic ligands

The synthesis of optically active allylic benzoates using chiral copper bis(oxazolinyl)pyridine complexes has been studied [5]. The Cu(I) catalyst was prepared by the reaction of bis(oxazolinyl)pyridine (**11**) with $Cu(Otf)_2$ in acetonitrile followed by reduction of the subsequent blue–green copper(II) complex with phenylhydrazine. Reaction of a variety of olefins with *tert*-butylperbenzoate in the presence of a catalytic amount of the chiral copper(I) complexes afforded optically active allylic benzoates with a maximum of 81% *ee* obtained during this asymmetric oxidation reaction, the highest to date for this kind of reaction. The use of copper(II) catalyst was found to lower the enantioselectivity of the reaction.



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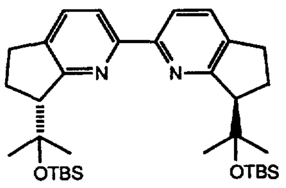

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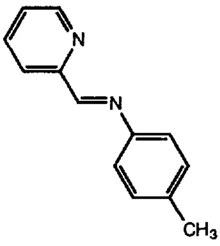
The copper(I) complex of (7*R*,7′*R*)-7,7′-di(1-*tert*-butyldimethylsiloxy-1-methylethyl)-6,6′,7,7′-tetrahydro-5*H*,5′*H*-2,2′-bi-1,1′-pyrindine (**12**) has been shown to catalyse the enantiospecific ring expansion of oxetanes to tetrahydrofurans with diazoacetic acid ester [6]. The results from this study suggest that the chirality of the catalyst regulates the steric course of the reaction. This is demonstrated by the reaction of (*R*)-2-phenyloxetane of 89% *ee* and *tert*-butyl diazoacetate with the Cu complex as a catalyst giving (2*S*,3*R*)-*tert*-butyl-3-phenyltetrahydrofuran-2-carboxylate of 92% *ee* as a major product, whereas that of (*S*)-2-phenyloxetane of 85% *ee* provided (2*S*,3*S*)-*tert*-butyl-3-phenyltetrahydrofuran-2-carboxylate of 93% *ee* as the major product.

A series of new copper(I) complexes of chiral didentate, *N*,*N*′-ligands of general formula $[Cu(CH_3CN)(L\text{–}L)]X$ ($X = PF_6$, ClO_4) has been synthesized [7]: (*S*)-2-t-butylaminocarbonylpyrrolidine, (*S*)-1,2-(bis-t-butylaminocarbonyl)pyrrolidine; (*S*)-1-t-butylaminocarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine; (*S*)-1-t-butylaminocarbonyl-2(1-naphthylaminomethyl)pyrrolidine; (2*S*,4*S*)-1,2-(bis-t-butylaminocarbonyl)-4-aminopyrrolidine. These complexes catalyse the cyclopropanation of styrene, used as a model for monosubstituted olefins, with ethyl diazoacetate to yield a mixture of *cis*/*trans* ethyl 2-phenylcyclopropan-1-carboxylates with up to 30% *ee*. A study of azaalkanes has indicated that the stabilization of a Cu^I centre by tertiary amine ligands in aqueous solutions requires at least four nitrogen atoms in the ligand [8].

The photophysical properties of the mononuclear copper(I) complexes CuL_4 (L = pyridine (py), 4-methylpyridine, 4-phenylpyridine, or acetonitrile), $Cu(lut)_3^+$ (lut = 2,6-lutidine) and $Cu(lut)_2^+$ have been reported [9]. Each of these compounds as their solid PF_6^- salts displays a relatively long-lived (> 1 μs) visible range emission at both ambient temperature and at 77 K, but not in fluid solutions. Also reported are the results for *ab initio* calculations to probe the natures of lower energy excited states of the hypothetical species CuL_n^+ ($L = NH_3$, CH_3CN, or py; $n = 1$–4). These results point to an assignment of the lowest energy, luminactive excited states as being largely metal centred, d→s in character for each of the above complexes with the possible exception of the CuL_4^+ species, where L is py or a substituted analogue. In the case of $Cu(py)_4^+$ the *ab initio* calculations indicate a metal-to-ligand charge transfer (MLCT) to be the lowest energy Franck–Condon state, although the similarities of emission band shapes, energies, and lifetimes among the various complexes suggest a common d→s assignment.

A direct synthetic route, based on silver(I)-assisted metal exchange reaction, to cationic bis-ligand complexes of copper(I) involving *N*-aryl-pyridine-2-aldimines has been studied [10]. These complexes are obtained as their perchlorate salts. The X-ray structure of $[Cu(\mathbf{13})_2]ClO_4$, where **13** is *N*-*p*-tolyl-pyridine-2-aldimine is reported. There are two crystallographically independent molecules in the asymmetric unit. The ligand **13** coordinates in a didentate manner providing a highly distorted tetrahedral geometry about the copper centre. The complexes show highly resolved symmetrical ^1H NMR spectra and intense MLCT absorptions are observed in the visible range. The moderately high positive potential of $E_{1/2} \approx 0.35$ V *vs* SCE at 298 K for the $Cu\mathbf{13}^{2+}/Cu\mathbf{13}^+$ couple in methanol arises from the distortion in the geometry of $Cu(\mathbf{13})^{2+}$.



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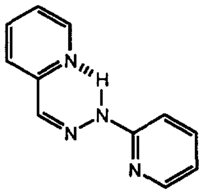

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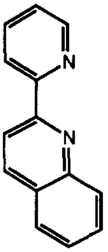
The copper(I) linkage isomers of pyridine-2-carbaldehyde 2′-pyridylhydrazone (**14**), $[Cu(PPh_3)_2(Z\text{-}\mathbf{14})]ClO_4$ and $[Cu(PPh_3)_2(E\text{-}\mathbf{14})[ClO_4$, have been prepared by the reaction of $[Cu(PPh_3)_2(CH_3CN)_2]ClO_4$ with the *Z*- and *E*-forms of **14** [11]. The complexes have been characterized by spectroscopic methods and single crystal X-ray diffraction analysis. In the solid state $[Cu(PPh_3)_2(Z\text{-}\mathbf{14})]ClO_4$ consists of discrete monomers of distorted tetrahedral geometry, with the metal atom coordinating to the imino nitrogen and one of the pyridyl nitrogen atoms (Cu–N, 2.070(7), 2.117(5) Å). The second pyridyl nitrogen is involved in an intramolecular hydrogen bond with the hydrogen atom of the hydrazono moiety. The related isomer $[Cu(PPh_3)_2(E\text{-}\mathbf{14})]ClO_4$ crystallizes with two non-equivalent molecules within the asymmetric unit. The first has a distorted tetrahedral geometry with regular copper–nitrogen distances (Cu–N, 2.141(4), 2.130(6) Å), whereas in the second the copper atom is five-coordinate with a distorted trigonal-bipyramidal stereochemistry and exhibits long axial copper–nitrogen distances of 2.371(5) and 2.767(5) Å. The ^2H and $^{13}C(^1H)$ NMR spectra of $[Cu(PPh_3(_2(E\text{-}\mathbf{14})]ClO_4$ show that in solution there is no isomerization about the imino carbon–nitrogen bond and that the five-coordinate nature of the complex is retained.

Photocatalytic reduction of methyl viologen (1,1′-dimethyl-4,4′-bipyridinium mv^{2+}) was efficiently carried out with copper(I) complexes $[Cu(dmphen)L_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline, $L = PPh_n(C_6H_4OMe\text{-}p)_{(3-n)}$, $n = 0$–3) upon irradiation of the MLCT band at around 360 nm [12]. The quantum yield for reduction increases considerably in the order $L = PPh_3 \ll PPh_2(C_6H_4OMe\text{-}p)$, $PPh(C_6H_4OMe\text{-}p)_2 < P(C_6H_4OMe\text{-}p)$, i.e. in increasing order of the phosphine donation ability with the best quantum yield being 0.1 for $[Cu(dmphen)\{P(C_6H_4OMe\text{-}p)_3\}_2]^+$. Kinetic analysis and measurement of the lifetime of the excited copper(I) complex revealed that the quantum yield for reduction increases as the phosphine donation ability increases because the excited state becomes longer-lived and the charge-separation step becomes easier with increasing donation ability.

Per-chlorinated derivatives of the common α-diimine chelate ligands 2,2-′-bipyridine and 1,10-phenanthroline were synthesized and tested for their coordination behaviour towards metal ions [13]. Octachloro-1,10-phenanthroline (ocp) was obtained via chlorination with PCl_5 under pressure (300 °C, 18 h). It fails to form stable complexes with, for example, divalent metal ions, but yields complex cations $[M(ocp)_2]^+$ with M = Cu. The crystal structure analysis of the red tetrafluoroborate salt of the copper(I) complex cation reveals a distorted tetrahedral coordination at the metal with a slight tendency towards the trigonal-pyramidal arrangement; two essentially planar ligands with small bite angles intersect at almost right angles. Relative to conventional bis(1,10-phenanthroline)copper(I) complexes with similar structures, $[Cu(ocp)_2]^+$ has oxidation and reduction potentials shifted positively by about 1 V which leaves the energy of the main MLCT absorption features little changed. In contrast to ocp, octachloro-2,2′-bipyridine showed no detectable complexation with Cu and a very negative reduction potential, which is explained as a consequence of its inability to exhibit a low-energy coplanar conformation.

In a detailed investigation, the quenching of photoexcited $Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by a series of ferrocene derivatives with varying numbers of methyl substituents has been studied [14]. When the ferrocenes have relatively positive reduction potentials, the quenching rate is consistently around $10^8\ M^{-1}\ s^{-1}$ due to an energy-transfer process. For the strongest reducing agents, the quenching rate constants are larger, but electron-transfer quenching does not become dominant until the driving force is about 0.3 V. An inner sphere reorganizational energy requirement of the copper system inhibits reductive quenching such that the effective self-exchange rate of the system is about $10^5\ M^{-1}\ s^{-1}$. In contrast, with oxidative quenchers the corresponding rate constant is about $10^{10}\ M^{-1}\ s^{-1}$.

The first 1:2 metal complexes of 2-(2′-pyridyl) quinoxaline (**15**) have been isolated [15]. The physical and spectroscopic characteristics of the compounds $[MCl_2(\mathbf{15})_2]$ (M = Ni, Cu, Cd) and $[Cu^I\mathbf{15}_2](PF_6)$ are described. The solid state structure of the copper(I) complex shows that the ligand **15** acts as a didentate chelate, the ligated atoms being the pyridine nitrogen and the nearest quinoxaline nitrogen. The structure of $[Cu(\mathbf{15})_2]^+$ consists of a distorted tetrahedral arrangement around the copper(I) atom with Cu–N bond lengths of 2.023(6) and 2.059(5) Å, and the N–Cu–N angle of the chelating ligand equal to 80.6(2)°. A monomeric trans pseudo-octahedral stereochemistry is assigned for the $[MCl_2(\mathbf{15})_2]$ complexes.



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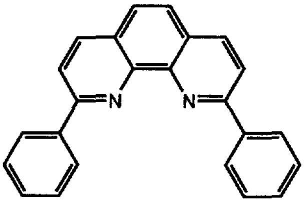

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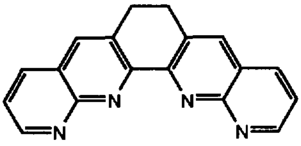
Copper phenanthroline excited states are known to be MLCT in nature, having lifetimes of ~70–250 ns in dichloromethane solution if methyl or phenyl substituents are placed in the 2- and 9-positions of the phenanthroline ligand, and the rate and efficiency of energy transfer to anthracene or to viologens have been reported [16]. The cage escape efficiency of $[Cu(\mathbf{16})_2^{2+}, MV^+]$, where **16** is 2,9-diphenyl-1,10-phenanthroline and MV = methyl viologen, is close to unity within experimental error. Back electron transfer to ground state products occurs at the diffusion limit $2 \times 10^{10}\ M^{-1}\ s^{-1}$. The unsubstituted cuprous compound $Cu(phen)_2(PF_6)$ is non-emissive under these conditions, and the excited state lifetime is <20 ns.

The electrochemical and spectral properties of some copper(I) polypyridyl complexes based on 6,7-dihydrodibenzo-[b.j][1,10]phenanthroline, (**17**), and 6,7-dihydrodipyrido[2,3,-b:3′,2′-j][1,10]phenanthroline, (**18**), have been reported [17]. These complexes are: $[Cu(\mathbf{17})_2]^+$; $[Cu(\mathbf{17})(PPh_3)_2]^+$; $[Cu(\mathbf{18})_2]^+$; $[Cu(\mathbf{18})(PPh_3)_2]^+$. $[Cu(\mathbf{18})_2]^+$ and $[Cu(18)(PPh_3)_2]^+$ may be reduced to form ligand-based radical anion species. Reduction processes for $[Cu(\mathbf{17})_2]^+$ and $[Cu(\mathbf{17})(PPh_3)_2]^+$ are irreversible. For $(Cu(\mathbf{17})_2]^+$, the electronic spectral changes arising from reduction suggest demetallation of the complex. The structure of $[Cu(\mathbf{17})_2][BF_4] \cdot CH_2Cl_2$ was determined by single-crystal X-ray diffraction and shows the geometry of the Cu centre is significantly distorted from tetrahedral on account of the small bite angle of the ligands. The ligands show significant distortion from planarity, with a dihedral angle of 21.30(9)° between the quinazoline rings. This is attributed largely to the geometric requirements of the ethylene linkage.



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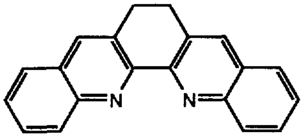
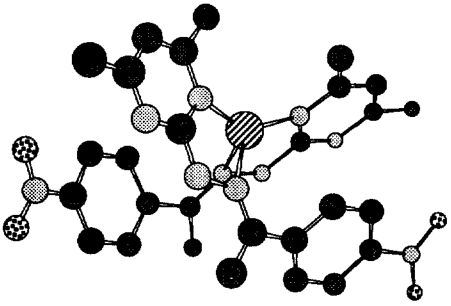


(18)

The bis-(*p*-nitroacetophenone-4,6-dimethyl-2-pyrimidyl hydrazone) copper(I) perchlorate complex of a substituted pyrimidyl hydrazone has been synthesized and characterized by X-ray diffraction [18]. The structure of the complex (**19**) has been shown to contain one central Cu atom bonded to four N atoms in a tetrahedral geometry with two hydrazinic N atoms and two pyrimidyl ring N atoms. The structure also proves that the pyrimidine ring and the phenyl ring of the acetophenone moiety are linked by an azomethine linkage.



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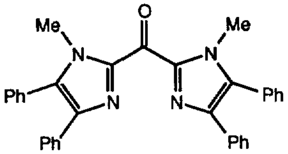
The new diimidazole ligand, bis(1-methyl-4,5-diphenylimidazol-2-yl)ketone (**20**), has been synthesized, characterized and shown to form four-coordinate bis(diimidazole) Cu^I and Cu^{II} complexes in the salts $[Cu(\mathbf{20})_2][PF_6]$ and $[Cu(\mathbf{20})_2][BF_4]_2$, the structures of which have been determined by X-ray crystallography [19]. The cations of these salts have a very similar geometry: Cu^I–N_{av} = 1.999 Å and Cu^{II}–N_{av} = 1.949 Å and the N–Cu–N interbond angles are constrained by the bite angle of the ligand **20** to $94 \pm 2°$ and the interligand steric interactions; this leads to dihedral angles of the intraligand CuN_2 planes of 74.9° for Cu^I and 68.2° for Cu^{II}—i.e. the complexes have a CuN_4 geometry intermediate between tetrahedral and square-planar. The X-band EPR spectrum for the powdered Cu^{II} compound is typical of an approximately D_2 CuN_4 centre possessing a d_{xy} ground state. The UV–VIS spectra are dominated by charge-transfer bands, and both the Cu^{II} and Cu^I systems are intensely coloured. The EPR and electronic spectra indicate that these cations have a very similar structure in the solid state and in solution: the potential of the $[Cu(\mathbf{20})_2]^{2+}/[Cu(\mathbf{20})_2]^+$ couple is 0.59 V *vs* SCE in MeCN and 0.80 V *vs* SCE in CH_2Cl_2, and the electron self-exchange constant in MeCN is $1.9 \times 10^4\ M^{-1}\ s^{-1}$. Comparisons of the properties of the $[Cu(\mathbf{20})_2]^{2+/+}$ centres and related Cu centres in chemical and biological systems reinforce the view that a $[Cu(His)_4]$ centre should not be precluded from consideration in biological electron transport.



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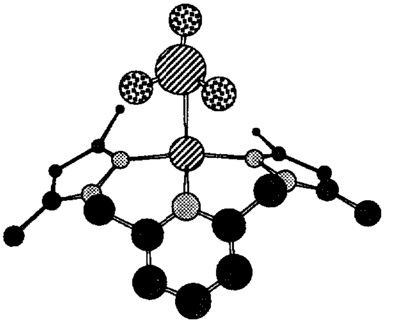
Two mononuclear copper(I) complexes of a tripodal ligand, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L), have been prepared [20]. A new route to the ligand is also proposed. The crystal structures of the complexes $[CuL(ClO_4)]\cdot CH_2Cl_2$ **21** and $[CuL(PPh_3)]ClO_4$ **22** have been determined. In **21** the perchlorate is bonded through one of its oxygen atoms with a distance of 2.42(3) Å. A variable-temperature NMR study of both complexes revealed that the methylene carbon of **22** is chiral at low temperatures. Carbon monoxide formed a terminal adduct with **21**.



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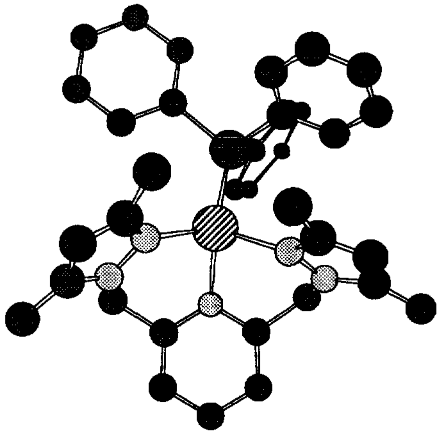

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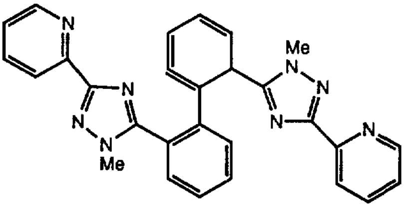
The synthesis of a new wrapping ligand, 2,2′-bis(2-pyridyl)-1-methyl-1,2,4-triazol-5-yl)biphenyl (**23**) is described [21]. This ligand induces similar, about 45°-crossed (skew), coordination geometries at both the Cu(I) and the Cu(II) ions. Both $[Cu^{I}(\mathbf{23})]ClO_4$ and $[Cu^{II}(\mathbf{23})](ClO_4)_2$ were characterized by X-ray structural determinations, UV–VIS spectroscopy, and electrochemical measurements. The electronic spectrum of the orange Cu(I) complex shows two MLCT bands at 442 nm and 340 nm, with $\epsilon = 1300\ M^{-1}\ cm^{-1}$ and $1600\ M^{-1}\ cm^{-1}$ respectively, corresponding to excitations into the lowest and the second lowest unoccupied ligand MO. The turquoise Cu(II) compound shows a broad d–d transition with a maximum at 799 nm ($\epsilon = 73.4\ M^{-1}\ cm^{-1}$) with a shoulder at 690 nm, as well as a ligand-to-metal charge transfer transition at 344 nm ($\epsilon = 55\ M^{-1}\ cm^{-1}$). The Cu(II)/Cu(I) potential (in acetonitrile) is 0.53 V (NHE).



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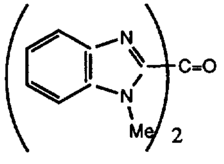
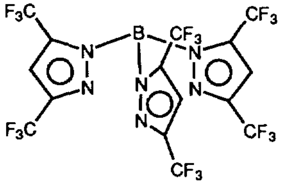


(24)

New bifunctional tri- and di-dentate nitrogen ligands have been prepared [22]. The coordination properties of BBIK (**24**) have been elucidated via the preparation and spectroscopic and structural characterization of its first metal complexes. The Cu(I) complex $[Cu(\mathbf{24})_2][BF_4]\cdot$solvent was prepared by mixing aerobically **24** and $CuBF_4\cdot 4MeCN$. The X-ray structure of the complex was determined. The ligand bite angle of 90° is ~14° smaller than the ideal value required for a regular tetrahedral geometry, resulting in the geometry around the Cu centre being pseudo-tetrahedral. The complex is air stable and only slowly oxidises to Cu(II) over a period of a few days. The Cu(II) complex $[Cu(\mathbf{24})_2(NO_3)][NO_3]$ was prepared as green crystals from the reaction of **24** with $Cu(NO_3)_2\cdot 3H_2O$. The coordination sphere incorporates four N imidazoles and at least one oxygen atom from a coordinated nitrate. The two **24** ligands bind Cu(II) in an axial-equatorial mode with a bite angle of 88°. The rings of the ligand are non-coplanar (24 and 31°) leading to a reduction in the exocyclic conjugation of the aromatic rings with the ketone carbonyl.

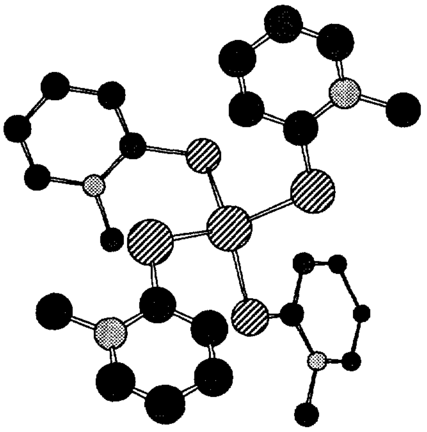
The synthesis and first structural characterization of the isocyanide adducts involving poly(pyrazolyl)borate complexes of Cu^I and the use of two highly fluorinated ligands in copper chemistry have been reported [23].

The fluorinated tris(pyrazolyl)borate ligands $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**25**) and $[HB(3\text{-}(CF_3)Pz)_3]^-$ (Pz = pyrazolyl) have been synthesized as their sodium salts from the corresponding pyrazoles and $NaBH_4$ in high yield [24]. These sodium complexes and the related [**25**]K(DMAC) were used as ligand transfer agents in the preparation of the copper and silver complexes [**25**]Cu(DMAC), [**25**]$CuPPh_3$, [**25**]$AgPPh_3$ and $[HB(3\text{-}(CF_3)Pz)_3]AgPPh_3$. Metal complexes of the fluorinated $[\mathbf{25}]^-$ ligand have highly electrophilic metal sites relative to their hydrocarbon analogues. This is evident from the formation of stable adducts with neutral oxygen donors such as H_2O, dimethylacetamide or thf. The metal compounds derived from the fluorinated ligands show fairly long-range coupling between the fluorine atoms of the trifluoromethyl groups and the hydrogen, silver, or phosphorus atoms. The solid state structures show that the fluorine atoms are in close proximity to these nuclei, thus suggesting a possible through-space coupling mechanism. Crystal structures of the sodium adducts exhibit significant metal–fluorine interactions.



(**25**)

The thione compounds tetrakis [1-methyl-2(1*H*)-pyridinethione-*S*]-copper(I) tetrafluoroborate and tetrakis-[1-methyl-2(1*H*)-pyridinethione-*S*]silver(I) tetrafluoroborate compounds, $[Cu(C_6H_7NS)_4]BF_4$ (**26**) and $[Ag(C_6H_7NS)_4BF_4$ have been characterized by X-ray crystallographic analysis [25]. Both are mononuclear complexes in which the central metal(I) cation (M^I) is surrounded by the four donor S atoms of the ligands with the M^IS_4 unit adopting a distorted tetrahedral geometry.



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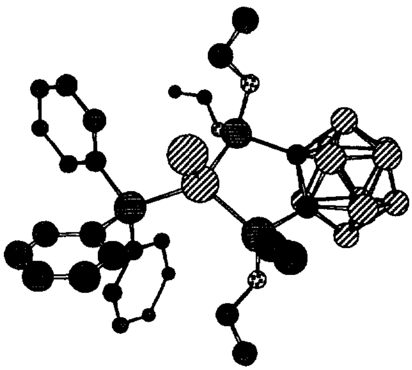
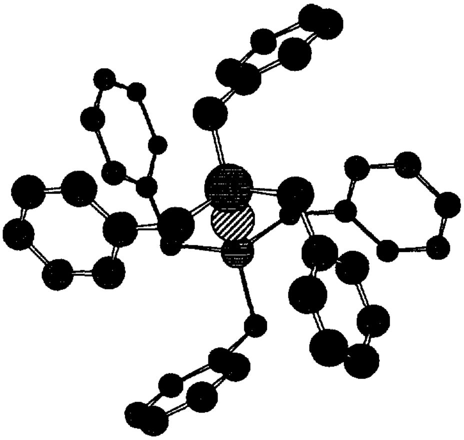


(27)

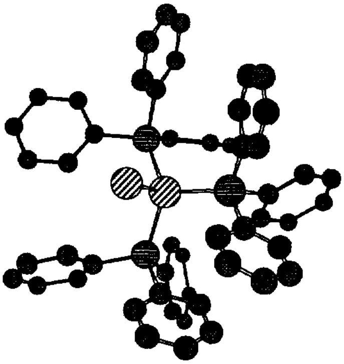
Three copper(I) chloride complexes of 1,2-bis(disubstituted phosphino)-1,2-dicarba-*closo*-dodecaboranes, $[CuCl\{1,2\text{-}[P(OEt)_2]_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}(PPh_3)]$, (**27**), $[CuCl\{1,2\text{-}[P(Et)_2]_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}(PPh_3)]$ and $[CuCl\{1,2\text{-}[P(^iPr)_2]_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}]$, were synthesized and the crystal structure of (**27**) determined [26]. The copper(I) atom is coordinated in distorted tetrahedral arrangement to two phosphorus atoms attached to the carborane cage, the phosphorus atom of PPh_3 and one chloride ion.

Copper(I) bromide has been shown to react under atmospheric conditions with tribenzylphosphine, PBz_3, in acetonitrile to give $[Cu(PBZ_3)_2][CuBr_2]$ [27]. The product, identified by spectroscopic techniques and X-ray diffraction, is claimed to be the first known example of an ionic copper(I) compound with a tertiary phosphine which possesses a linear CuP_2 coordination environment (**28**).



(28)

The phosphane complexes $[(Ph_3P)_2CuCl_2Li(THF)_2]\cdot1.5THF$, $[(Ph_3P)_2CuCl]\cdot0.5THF$, $[(Ph_3P)_3CuCl]\cdot MeCN$, $[(Ph_3P)_3CuCl]\cdot THF$ and $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ have been prepared and characterized on the basis of analytical, IR, mass and NMR spectral techniques [28]. The crystal structures of the complexes underline the ability of the copper(I) centre to exist in a distorted trigonal planar as well as in a distorted tetrahedral environment. The structure of $[CuCl\{P(C_6H_5)_3\}_3]\cdot C_4H_8O$ has been determined [29]. The structure consists of discrete $[CuCl\{P(C_6H_5)_3\}_3]$ (**29**) molecules containing pseudo-tetrahedrally coordinated copper, together with one disordered tetrahydrofuran solvent molecule per molecule of complex.



(29)

The effects of restricted rotation of phosphine ligands about the M–L bond and substituents on phosphine about the P–C bond have been studied in two-coordinate mononuclear complexes containing two equivalent phosphine ligands [30]. Trimesitylphosphine (Mes_3P) was used to prepare complexes of the form $[(Mes_3P)M]BF_4$, where $M=Cu^I$, Ag and Au. The room temperature NMR spectrum of the copper complex contained two resonances at δ -29.7 and -30.7 and two sets of ^1H signals and indicates that the small covalent radius of the copper ion results in the internal motions being severely hindered and in propeller isomerism being observed. Comparison is made with the complexes formed with the other metal ions.

Copper(I) bis(diphosphine) complexes have been shown to provide an excellent basis for development of short/medium-lived positron emission tomography imaging and therapy agents containing copper radioisotopes because of their extreme facility of synthesis and scope for derivatization and bioconjugate formation [31].

A series of primary phosphine homoleptic complexes $[ML_4]^{n+}X_n$ (including $M=Cu$, $n=1$, $X=PF_6$, $L=PH_2Mes$, $Mes=2,4,6\text{-}Me_3C_6H_2$) have been prepared. The copper complex was prepared from the reaction of mesitylphosphine and $[Cu(NCMe)_4]F_6$ [32]. These complexes were reacted with $MeC(CH_2PPh_2)_3$ (triphos) or $[P(CH_2CH_2PPh_2)_3]$ (tetraphos) and the complexes $[Cu(Ph_2Mes)_4][BF_4]$ and $[Cu(triphos)(Ph_2Mes)][BF_4]$ characterized crystallographically. The structural and spectroscopic studies suggest that the coordination properties of L are dominated by its relatively small cone angle and that the basicity of L is comparable with that of more commonly used tertiary phosphines. The solution structure and dynamics of all the complexes were studied by ^{31}P NMR spectroscopy (including the first reported analyses of a 12-spin system).

As part of a study to synthesize models for metal ion binding sites in blue copper proteins, attempts having been made to form copper complexes of new N_2S_2 compounds, in which one sulfur donor is thiolate and the other a thioether, by protecting the potential thiolate through *tert*-butylation and benzylating the other [33]. Whereas earlier work with symmetrical bis(*tert*-butylated thioethers) had shown that de-*tert*-butylation occurs upon coordination to copper, to yield the bis(thiolate) complex, this proves not to be the case with these asymmetric compounds.

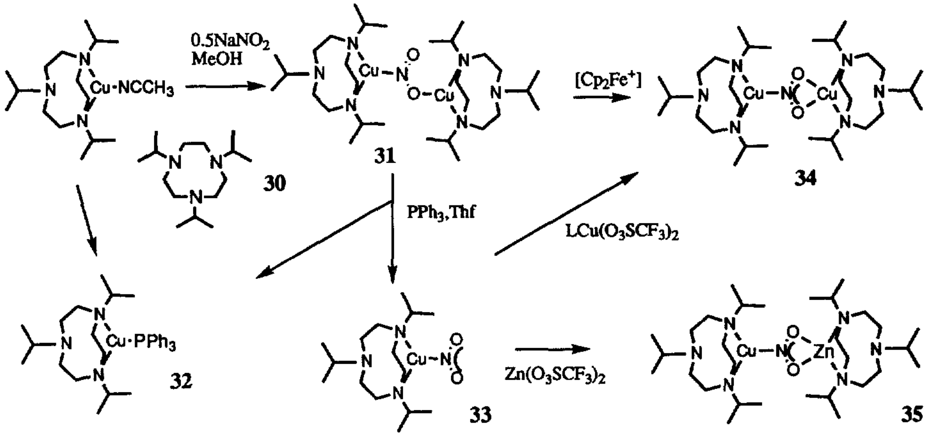
A study of the reaction of $(PPh_3)_4CuClO_4$, $(PPh_3)_2CuCl$, $(Cy_3P)_2CuNO_3$ and $(Cy_3P)_2CuClO_4$ with a range of monodentate and didentate heterocyclic *N*-donor ligands (imidazole, pyrazole and triazol derivatives) has been carried out [34]. The binding abilities of several polypyrazolylborato ligands towards bis(cyclohexylphosphine)Cu(I) nitrate have been investigated [35].

The interaction of optically pure 1*R*,2*R*-diammoniumcyclohexane mono-(+)-tartrate and 1*S*,2*S*-diammoniumcyclohexane mono-(−)-tartrate with 2 equiv. of *o*-(diphenylphosphino)benzaldehyde in the presence of 2 equiv. of potassium carbonate in a refluxing ethanol–water mixture gave the optically pure condensation products *N*, *N* '- bis [*o* - (diphenylphosphino) benzylidene] - 1*R*, 2*R* - diiminocyclohexane [1*R*,2*R*-cyclohexyl–P_2N_2] and *N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]-1*S*,2*S*-diiminocyclohexane [1*S*,2*S*-cyclohexyl–P_2N_2] respectively in good yield [36]. The coordination behaviour of the optically pure products with $[Cu(CH_3CN)_4][X]$ ($X = ClO_4^-$, PF_6^-) has been investigated and has shown the formation of optically pure complexes. Reduction of optically pure products with $NaBH_4$ in ethanol gave the optically pure reduced products in good yield.

The crystal structure of bromo(*N*,*N*-dibutyl-*N*′-phenylthiourea-*S*)bis(triphenylphosphine-*P*)copper(I) has been determined [37]. The coordination around the Cu-metal centre is distorted tetrahedral with bond lengths Cu–S 2.367(1), Cu–Br 2.469(1), CuP(1) 2.279(2) and Cu–P(2) 2.284(2) Å, and bond angles S–Cu–Br 111.86(5), S–Cu–P(1) 111.28(6), S–Cu–P(2) 98.01(6), Br–Cu–P(1) 103.08(5), Br–Cu–P(2) 108.60(5) and P(1)–Cu–P(2) 124.11(6)°. The H atom of the NH group is intramolecularly hydrogen bonded to the Br atom, with an NH···Br distance of 2.411 Å.

2.3. Dinuclear complexes with macrocyclic ligands

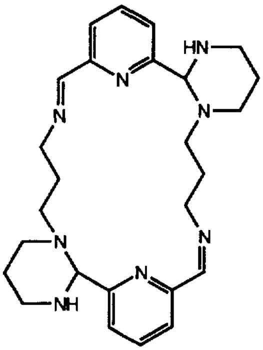
In an effort to provide precedence for postulated intermediates in copper–protein-mediated nitrite reduction, a series of novel complexes containing the $Cu^I–NO_2^-$ unit, including monocopper(I), dicopper(I,I), and mixed valence dicopper(I,II) and copper(I)–zinc(II) species were prepared (Scheme 3), fully characterized, and subjected to reactivity studies designed to probe their ability to produce nitric oxide [38]. Treatment of solutions of the copper(I) complex of 1,4,7-triisopropyl-1,4,7-triazacyclononane (**30**), or its benzyl analogue in MeOH with an excess of



Scheme 3.

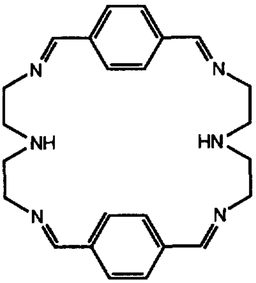
$NaNO_2$ yielded the novel dicopper(I,I) complexes $[(\mathbf{30}Cu)_2(\mu\text{-}NO_2)]PF_6$ (**31**) (Scheme 3). This complex was cleaved by PPh_3 to afford $[\mathbf{30}Cu(PPh_3)]PF_6$ (**32**) and $[\mathbf{30}Cu(NO_2)]$ (**33**), a structural model for the substrate adduct of copper nitrite reductase. Oxidation of the dicopper(I,I) compound **31** with $(Cp_2Fe)(PF_6)$ in CH_2Cl_2 yielded the deep red, mixed valent, dicopper(I,II) species $[(\mathbf{30}Cu)_2(\mu\text{-}NO_2)](PF_6)_2$ (**34**) which was structurally characterized as its $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ salt. A diamagnetic heterodinuclear (CuZn(II))–Zn(I) analogue, $[\mathbf{30}Cu(\mu\text{-}NO_2)Zn\mathbf{30}](O_3SCF_3)_2$ (**35**), was assembled by mixing $[\mathbf{30}Cu(NO_2)]$, $[Zn(O_3\text{–}SCF_3)_2]$ and **30** and was shown to adopt a structure similar to that of its (CuCu(II))–Cu^I relative. Both compounds exhibit an intense electronic absorption feature that was assigned as a Cu(I)→NO_2^- MLCT transition on the basis of resonance Raman spectroscopic results. Functional modelling of copper nitrite reductase was accomplished by treating solutions of $\mathbf{30}Cu(NO_2)$ with protonic acids or $Me_3SiO_3SCF_3$. Nitric oxide evolution was accompanied by the formation of $\mathbf{30}Cu(O_2CCH_3)_2$ and $\mathbf{30}Cu(O_3SCF_3)_2$ when acetic acid or $Me_3SiO_3SCF_3$ was used. The latter crystallized as a water adduct $[\mathbf{30}Cu(H_2O)(O_3SCF_3)](O_3SCF_3)$. The involvement of the (CuCu(II))–Cu(I) species as an intermediate in the reaction of $\mathbf{30}Cu(NO_2)$ with $Me_3SiO_3SCF_3$ at low temperature and a mechanism for NO generation involving both $\mathbf{30}Cu(NO_2)$ and $[(\mathbf{30}Cu)_2(\mu\text{-}NO_2)]^{2+}$ are discussed.

A Schiff-base macrocycle (**36**) was prepared by the 2:2 condensation of pyridine-2,6-dicarbaldehyde and 4-azaheptane-1,7-diamine and the X-ray structure determined [39]. This 20-membered ring-contracted form, with two Schiff-base double bonds, forms a deep red dinuclear copper(I) complex having two charge-transfer absorptions at 415 and 550 nm in a methanol–acetonitrile (4:1) solution. The complex forms a deep purple dicopper–dioxygen complex having absorption bands at 390 and 530 nm, with a rate constant at 25.0 °C of $5.6 \times 10^5\ s^{-1}$. This is spontaneously converted into a copper(II) complex with a half-life of 240 min. The dinuclear copper(I) dioxygen complex oxidizes 3,5-di-*tert*-butylcatechol catalytically to 3,5-di-*tert*-butyl-1,2-benzoquinone. The dinuclear copper(I) complex of the macrocycle was also found to oxidize this substrate to the same product at a much faster rate.



(36)

The dinuclear dicopper(I) complex of a 26-membered macrocycle, **37**, obtained from the 2+2 condensation of terephthalaldehyde and 3-azapentane-1,5-diamine, has been isolated as an air-stable red–orange complex in good yield [40]. The crystal structure of $[Cu_2(NCMe)_2\mathbf{37}][ClO_4]_2$ showed two distorted tetrahedrally coordinated copper(I) centres with a Cu–Cu separation of 7.04 Å. The air stability of $[Cu_2(NCMe)_2\mathbf{37})^{2+}$ contrasts with the oxygen sensitivity of the dicopper(I) complex of the 24-membered macrocycle **38** (formed from the 2+2 condensation of isophthalaldehyde and 3-azapentane-1,5-diamine) which leads to oxygenation of one of the aromatic rings. The marked difference in reactivity is discussed on the basis of the structural differences between the two isomeric compounds, analysed with molecular mechanics calculations. The dinuclear dicopper(II) complexes of the 24- and 26-membered macrocyclic hexaamines, derived by reduction of **37** and **38** respectively, exhibit dipole–dipole coupling in their EPR spectra. The solution structures of the two dicopper(II) complexes have been determined by a combination of molecular mechanics calculations and the simulation of their EPR spectra.



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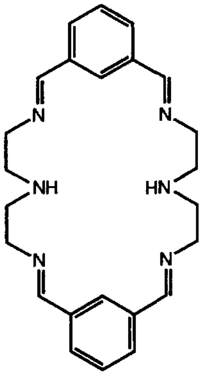
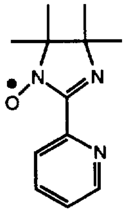


(38)

2.4. Dinuclear complexes with acyclic ligands

Reaction of CuI or CuBr with some imino nitroxides in methanol gave the halogen-bridged dinuclear Cu(I) complexes $[Cu(\mu\text{-}I)(\mathbf{39})]_2$, $[Cu(\mu\text{-}I)(\mathbf{40})]_2$, $[Cu(\mu\text{-}Br)(\mathbf{40})]_2$, and $[Cu(\mu\text{-}Br)(\mathbf{41})]_2$, where **39** = 2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl, **40** = 2-(6′-methyl-2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl, **41** = 2-(4′nitrophenyl)-4,4,5,5-tetramethyl-4,6-dihydro-1*H*-imidazolyl-1-oxyl) [41]. The crystal structures and magnetic properties of all the complexes have been studied. The complexes have dimeric structures where two copper ions are doubly bridged by halide ions in a μ_2 fashion. In $[Cu(\mu\text{-}I)(\mathbf{39})]_2$, $[Cu(\mu\text{-}I)(\mathbf{40})]_2$ and $[Cu(\mu\text{-}Br)(\mathbf{40})]_2$, each copper ion is tetrahedral with a didentate imino nitroxide and two halide ions; the two copper ions are separated by 2.592(2) Å, 2.6869(8) Å and 2.7357(6) Å respectively. In $[Cu(\mu\text{-}Br)(\mathbf{41})]_2$, triangular coordination sites of the copper ions are completed with a nitrogen atom from the imino nitroxide and two bromide ions bridging the two copper ions with a separation of 3.074(2) Å. Ligand imino nitroxides in all the complexes form one-dimensional radical chains, and the chains are linked with halocuprate dimer units. Structural and magnetic susceptibility data suggest that the radicals in the $[Cu(\mu\text{-}I)(\mathbf{39})]_2$ and $[Cu(\mu\text{-}Br)(\mathbf{41})]_2$ are ferromagnetically stacked, whereas the radicals in $[Cu(\mu\text{-}I)(\mathbf{40})]_2$ and $[Cu(\mu\text{-}Br)(\mathbf{40})]_2$ form an antiferromagnetic chain.



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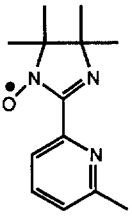

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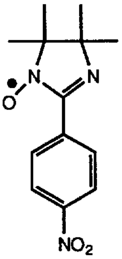
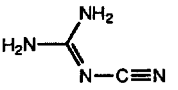


(41)

As part of a study to probe the redox chemistry of inorganic analogues of the active centre of copper containing nitrite reductase *Achromobacteur cycloclastes*, a series of cationic complexes containing two coordinatively unsaturated Cu(I) centres bridged by planar diimines has been synthesized [42]. Treatment of an acetonitrile solution of copper(I) tetrafluoroborate and 4,4′-bipyridine (4,4′-bpy) with 2-cyanoguanidine (**42**) yielded $[\{Cu(\mathbf{42})_2\}_2(\mu\text{-}4,4'\text{-bpy})][BF_4]_2 \cdot MeCN$. Structural analysis revealed a planar dinuclear cation containing two, three-coordinate T-shaped copper centres bridged by 4,4′-bpy and terminally coordinated by two cyanoguanidine molecules. In the absence of cyanoguanidine, but with an excess of copper(I), the product was $[Cu(4,4'\text{-bpy})(MeCN)_2]BF_4$; the structural analysis of this revealed a one-dimensional polymeric cationic zigzag chain, based on tetrahedral copper(I) atoms bridged by 4,4′-bpy and terminally coordinated by two MeCN molecules. The same reaction mixture but with an excess of 4,4′-bpy gave [Cu(4,4′-bpy)$_2$]BF$_4$·MeCN. The corresponding *trans*-1,2-bis(4-pyridyl)ethene (**43**) systems yielded the analogous [{Cu(**42**)$_2$}$_2$(μ-**43**)][BF$_4$]$_2$·6MeCN, [Cu(**43**)(MeCN)$_2$]BF$_4$ and [Cu(**43**)$_2$]BF$_4$ respectively. Only one product has been isolated from the corresponding bis(4-pyridyl) disulfide (**44**) systems: [Cu(**44**)(MeCN)$_2$]BF$_4$. Attempts to produce copper(I) derivatives of 3,6-bis(imidazolyl)pyridazine (**45**) were unsuccessful, with the copper(II) product, Cu(**45**)(MeCN)$_2$(BF$_4$)$_2$, invariably being formed. Whereas the [{Cu(**42**)$_2$}$_2$(diimine)]$^{2+}$ and [Cu(diimine)(MeCN)$_2$]$^+$ cations reacted with NOBF$_4$ and N^{t}Bu$_4$NO$_2$ forming copper(II) oxidation products, the [Cu(diimine)2]$^+$ cations were unreactive.



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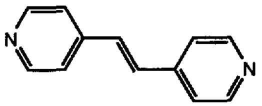

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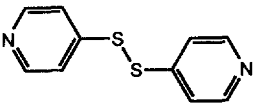

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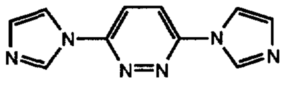
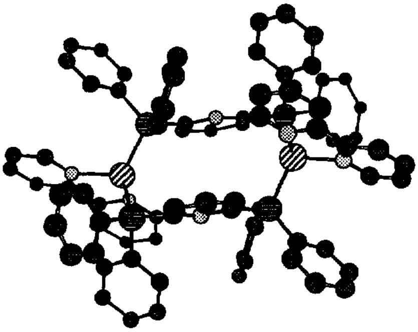


(45)

Treatment of [Cu(MeCN)$_4$]PF$_6$ in acetonitrile with 2,6-bis(diphenylphosphino)pyridine [(Ph$_2$P)$_2$py] afforded a colourless crystalline material characterized as [Cu$_2${μ-(Ph$_2$P)$_2$py}$_3$][PF$_6$]$_2$ [43]. An X-ray diffraction study confirmed that the three ligands bridge the two copper atoms bonding solely through the phosphorus atoms, with each copper being trigonally coordinated to produce a cavity in the centre of the dinuclear dication bounded by the nitrogen donor atoms, the Cu···Cu distance and the diameter of the cavity being 4.744(2) Å and *ca* 4.9 Å respectively (46). Measurements of the solution emission spectra of [Cu$_2${μ-(Ph$_2$P)$_2$py}$_3$][PF$_6$]$_2$, in the presence and absence of Cu$^+$ and Ag$^+$ ions, suggest that these metal ions are trapped in the cavity on their addition to an acetonitrile solution of the complex. Addition of (Ph$_2$P)$_2$py to [Cu(η^2-bpy)(MeCN)$_2$]PF$_6$ in acetone afforded a yellow crystalline solid characterized as [Cu$_2${μ-(Ph$_2$P)}$_2$(η^2-bpy)$_2$][PF$_6$]$_2$. A crystal structure determination revealed that the two copper atoms are bridged by the two (Ph$_2$P)$_2$py ligands bonding solely through the phosphorus atoms, with the irregular tetrahedral coordination at each copper being completed by the nitrogen atoms of the chelating bipyridyl ligands. The Cu···Cu distance is 6.806(2) Å.



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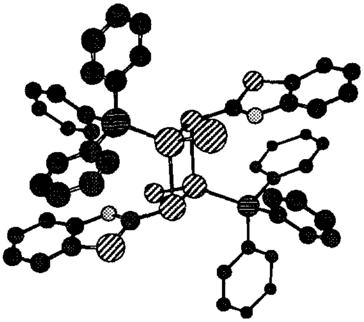
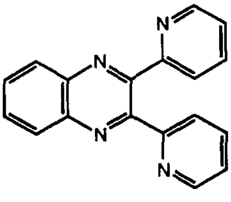


(47)

The synthesis and crystal structure of a dinuclear copper(I) bromide complex formed from the solid state reaction of benz-1,3-thiazolidine-2-thione (bztzdtH) and triphenylphosphine (**47**) has been reported [44]. The solid state structure shows that the complex [Cu(bztzdtH)(PPh$_3$)Br]$_2$ has two crystallographically equivalent copper atoms with a pseudo-tetrahedral geometry which are linked by the sulfur atoms of two bztzdtH ligands, forming a planar Cu$_2$S$_2$ moiety with Cu–S(1) = 2.514(1), Cu–S(1a) = 2.335(1) and Cu–Cu(a) = 2.928(1) Å.

μ- [1,2-Bis (diphenylphosphino) ethane] bis (3-trimethylsilyl-pyridine-2-thiolate-*S*)[1,2-bis(diphenyl-phosphino)ethane]dicopper(I), [Cu$_2$(3-Me$_3$Sipyt)$_2$(dppe)$_3$], was obtained by reaction of [Cu(3-Me$_3$Sipyt)] with 1,2-bis(diphenylphosphino)ethane (dppe) in acetone [45]. The compound is dimeric, with the dppe molecules acting as both bridging and chelating ligands and with the thione coordinating in the monoanionic form through the sulfur atom. The geometry around the copper centres is distorted tetrahedral.

Raman spectroelectrochemical and X-ray crystallographic studies have been made for the dinuclear copper(I) complex, [(Ph$_3$P)$_2$Cu(**48**)Cu(PPh$_3$)$_2$][BF$_4$]$_2$, where **48** is the bridging ligand 2,3-di(2-pyridyl)quinoxaline [46]. The X-ray data show that the pyridine rings are twisted out of the plane with respect to the quinoxaline ring, which is itself non-planar. The UV–VIS spectra of the MLCT excited state and those of the electrochemically reduced complex are similar. The resonance-Raman spectrum of the latter species exhibits little change in the frequency of the pyridinylquinoxaline inter-ring C–C bond stretching mode, compared with the ground electronic state. This suggests minimum change in the inter-ring C–C bond order in the electrochemically or charge-transfer generated radical anion.



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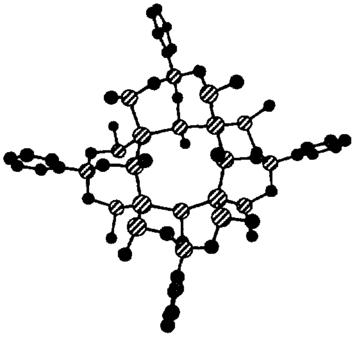
Dicarboxylate complexes of copper(I) with triphenylphosphine have been prepared in high yield from copper(I) butyrate and 0.5 equiv. of the corresponding dicarboxylic acid [47]. The bis-triphenylphosphine copper(I) glutarate, adipate and terephthalate salts synthesized have been structurally characterized by single-crystal X-ray diffraction studies. The structures consist of two copper(I) centres each bound to two triphenylphosphine ligands with the metal centres bridged by the dicarboxylate group. In each of these derivatives the geometry about copper(I) is that of a distorted tetrahedron with a varying degree of asymmetry in the chelating carboxylate ligand. For example, in the $(Ph_3P)_2Cu(O_2C(CH_2)_4CO_2)Cu(Ph_3P)_2$ complex the Cu–O bond distances at a single copper centre vary by 0.125 Å. Even more dramatic Cu–O bond length differences were noted in the glutarate analogue. Nevertheless, in this instance the asymmetry in Cu–O bond lengths was found to be influenced by the presence of solvent molecules in the crystal lattice; hence some of the asymmetry seen in the solid-state may be due to crystal packing forces.

The solid state structure of μ-trithiooxalato-bis[bis(triphenylphosphane) copper(I)] complex has been determined [48]. The trithiooxalat (trto), a multidentate, chalcogen-rich, ligand is found to be exclusively side-on (S,S′ and S″,O) coordinated involving the oxygen donor atom. This is in contrast to the corresponding dinuclear silver complex $[(Ph_3P)_2Ag]_2(trto)$, which is side-on(S,S′)/end-on(S,S″) coordinated. In the structure of $[(Ph_3P)_2Cu]_2(trto)$ the bridging ligand with its non-symmetrical donor atom set is disordered around the centre of symmetry (inversion centre).

2.5. Tetranuclear complexes

A homoleptic copper(I) tetramer, $[Cu(PhTt)]_4$ **49**, has been synthesized from the reaction of $[NBu_4][PhTt]$ with $[Cu(MeCN)_4][BF_4]$ (1:1), where $PhTt^-$ is phenyltris[(methylthio)methyl)]borate [49]. The ^1H NMR spectrum of the product showed three aliphatic resonances consistent with the presence of two magnetic environments for the (methylthio)methyl chelates. The X-ray structure of **49** was obtained and shows a similar approximately tetrahedral, coordination sphere about each Cu^I ion with an average S–Cu–S angle of 109.5°. Each borate ligand is oriented such that one sulfur is in a μ_2 position and the remaining two sulfur atoms are terminally ligated to adjacent metal ions. This results in the Cu^I ions and bridging S atoms forming an eight-membered ring in which the four Cu^I ions are essentially planar with the bridging sulfur atom displaced alternately above and below the plane. The complex is inert to CO, O_2 and H_2O over several hours in solution, but it does react with py, PPh_3 or $[NEt_4]SPh$ to give the corresponding monomer [Cu(PhTt)L]. The complex shows two irreversible one-electron oxidations at 0.720 and 0.910 V *vs* Fc/Fc^+. The X-ray structure of $[Cu(PhTt)PPh_3]$ is also reported.

The S_4-symmetric copper(I) tetramer $Cu_4(MEPA)_4$, MEPH = *N*-(2-mercaptoethyl)picolylamine has been synthesized by the anodic oxidation of copper in CH_3CN–2 mmol Bu_4NClO_4 and in the presence of MePAH [50]. The yellow tetrameric compound exhibits a tetragonal bisphenoidal (D_{2d}) arrangement of the metal centres. The $MEPA^-$ ligands use μ-thiolate and the amine nitrogen centres for



(49)

coordination, whereas the 2-pyridyl groups are not involved in Cu(I) coordination but in an intramolecular hydrogen-bonding network with the metal-bound, and thus cooperatively activated, secondary amine functions.

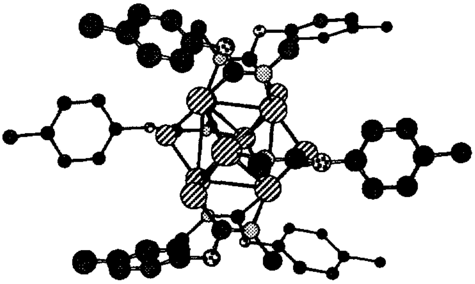
2.6. Cluster complexes

The $[Cu_3(dppm)_3OH](BF_4)_2$ (dppm = bis(diphenylphosphino)methane) cyclic cluster host has been demonstrated to be luminescent at 298 K in degassed ethanol solutions and at 77 K also in ethanol [51]. The nature of the lowest energy excited states has been addressed theoretically using density functional theory and experimentally using UV–VIS luminescence and polarized luminescence spectroscopy.

Anodic oxidation of copper in acetonitrile–2 mM tetrabutylammonium perchlorate and in the presence of bis(2-methyl-imidazol-2-yl)ketone (BIK) and an excess of *o*-thiocresol RSH yields $\{[Cu(BIK)_2]^+\}_2\{[Cu_4(SR)_6]^{2-}\}\cdot 3(CH_3OH)\cdot(RSH)$, where R = *o*-tolyl compound, as the main product [52]. Whereas the dianionic cluster $[Cu_4(SR)_6]^{2-}$ is similar to previously reported species with R = phenyl or methyl, the purple cations $[Cu(BIK)_2]^+$ exhibit spectroscopic and structural effects consistent with occurrence of the back bonding between electron-rich Cu^I and the π acceptor ligand BIK. In contrast to the formally related $[Zn(BIK)_2]^{2-}$, the copper(I) complex cations exhibit distorted tetrahedral structures with almost coplanar BIK chelate arrangements, ensuring maximum metal–ligand π interaction.

Four complexes of the type $[Cu_4I_4(CH_3CN)_2(L)_2]$, L = aniline derivative have been examined by single crystal X-ray diffraction [53]. *Ab initio* calculations based on the atomic positional parameters of complexes containing the three types of symmetry element reveal HOMO orbitals to be dominated by the p orbitals of the iodine atoms, whereas the LUMO orbitals contain major contributions from copper-based p orbitals.

A study has shown that MeNCS undergoes insertion into a copper(I)–aryloxide bond in the absence of ancillary ligands to form [*N*-methylimino(aryloxy)-methanethiolato]–copper(I) complexes [54]. This insertion occurs unlike the analogous insertion of PhNCS. In the case of the reaction with 4-methylphenoxide, hexakis[[*N*-methylimino(4-methylphenoxy)methanethiolato[copper(I)] (**50**) is formed. The solid state structure has been determined and shows a cluster with paddle wheel geometry. Six copper atoms are in octahedral arrangement with each copper atom coordinated to two sulfur atoms and one nitrogen atom, each belonging to three different ligands. Addition of stoichiometric amounts of PPh_3 to the oligomeric complexes typically results in the extrusion of MeNCS, with the ease of extrusion being dependent on the substituents on the aryloxide, and is accelerated by water.



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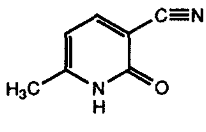
2.7. Polymeric complexes

Reaction of the appropriate copper(I) salt with 3-cyano-6-methylpyridin-2(1*H*)-one (Hcmp) (**51**) gave three polymeric coordination compounds, [Cu(**51**–H)(Hcmp)$_3$]·C_5H_{12}, [Cu_2(**51**)$_4$(Me_2CO)$_2$][BF_4]$_2$ and [Cu_5(**51**–H)$_4$]ClO_4, the structures of which have been determined by X-ray crystallography [55]. The solid state structure of [Cu(**51**–H)(**51**)$_3$]·C_5H_{12} contains a three-dimensional supramolecular framework of tetrahedral CuN_4 centres linked by intermolecular hydrogen bonds through the pyridone N and O atoms. The open square microchannels created enclathrate *n*-pentane as the guest molecule. [Cu_2(**51**)$_4$(Me_2CO)$_2$][BF_4]$_2$ contains a dimeric unit weakly bound by the bridging acetone oxygen atoms. Each Hcmp moiety in the dimer is hydrogen-bonded pairwise to one adjacent Hcmp molecule belonging to the other dimer, giving a one-dimensional array of copper atoms. [Cu_5(**51**–H)$_4$]ClO_4 does not involve hydrogen bonding as in the other two complexes, but instead each cmp monoanion employs all its three functional groups bridging three copper atoms forming a supramolecular channel architecture containing a Cu_4 cluster.



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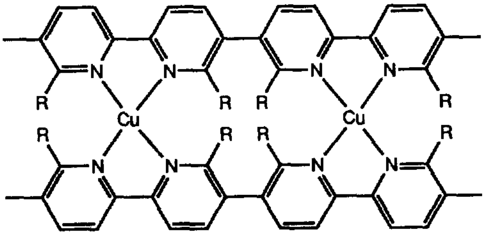
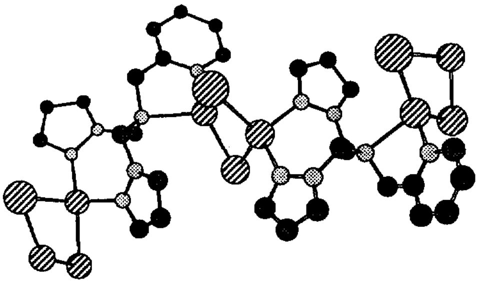
π-Conjugated electrically conducting polymer chelate ligands, poly(6,6′-dimethyl-2,2′-bipyridine-5,5′-diyl) (P6MeBpy) and poly(6,6′-dihexyl-2,2′-bipyridine-5,5′-diyl) (P6HexBpy), react with $[Cu(CH_3CN)_4]X$ ($X = BF_4$, ClO_4) to give the corresponding semiconductive copper(I) complexes **52**,**53** [56]. The P6HexBpy–$CuBF_4$ complex (**53**–BF_4) exhibits an MLCT absorption at 469 nm ($\epsilon = 3300\ M^{-1}\ cm^{-1}$). The cyclic voltammogram of a film of the **53**–BF_4 complex laid on a Pt electrode shows reversible redox peaks with an $E°$, value of 0.59 V *vs* Ag^+/Ag due to a Cu^{II}/Cu^{I} couple, whereas, in the reduction region, the film of the complex exhibits an electrochemically active cycle at $E°$ of −1.84 V attributable to a Cu^{I}/Cu^{0} couple. The redox process at −1.84 V is accompanied by a colour change of the film from orange to dark red.



R = Me (**52**) C_6H_{13} (**53**)

Diffusion of a solution of $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN into a solution of 2,4,6-tri(4-pyridyl)-1,3,5-triazine, tpt, in $CHCl_3$/1,1,2,2-tetrachloroethane gave very dark red, almost black, crystals of solvated $[Cu_3(tpt)_4](ClO_4)_3$ whose structure was determined by X-ray crystallography [57]. All the tpt units are attached to three copper centres at the corners of an equilateral triangle with edge length 12.898(3) Å. All the copper centres are equivalent and are coordinated by four tpt-derived pyridine donors in a distorted tetrahedral arrangement resulting in an infinite network. A repeated structural unit apparent in the network comprises six copper centres at the corners of a regular octahedron with tpt units occupying alternate triangular faces of the octahedron. These octahedral chambers are large, with the diametrically opposed copper atoms separated by 18.241(4) Å. Each copper atom is shared by two such units. The tpt units are significantly bowed away from the centre of the chamber, which allows the coordination geometry of the copper atoms to approach more closely to tetrahedral. Each chamber is connected by its six copper vertices to six others whose centres are arranged octahedrally around the first, producing an infinite cubic collection of chambers. At the centre of each collection of eight chambers is a cavity of the appropriate size, shape and chemical character to accommodate a chamber belonging to a second completely independent, but identical, infinite framework.

The synthesis and structure of *catena*-poly[copper-di-μ-iodo-copper-μ-{bis(1-pyrazolylmethyl)(2-pyridylmethyl)amine}-*N*,*N*′:*N*^{2},*N*$^{2\prime}$, $[Cu_2I_2(C_{14}H_{16}N_6)]$ (**54**), formed by the reaction of bis(1-pyrazolylmethyl)(2-pyridylmethyl)-amine with copper(I) iodide in acetonitrile, have been reported [58]. The structure shows the ligand binding in a bis-didentate manner and with one Cu^I atom ligated by two pyrazole groups from one ligand and the other Cu^I atom ligated by one pyridine group and an amine from another ligand. The Cu^+ ions are separated by a distance of 2.587(1) Å.



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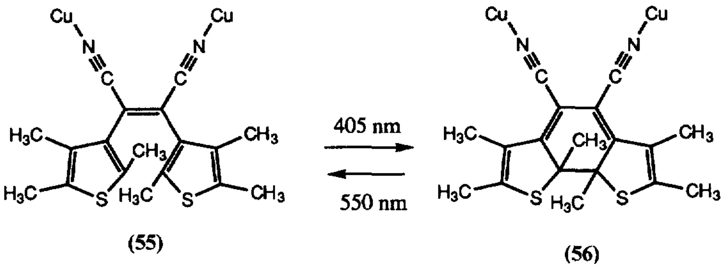
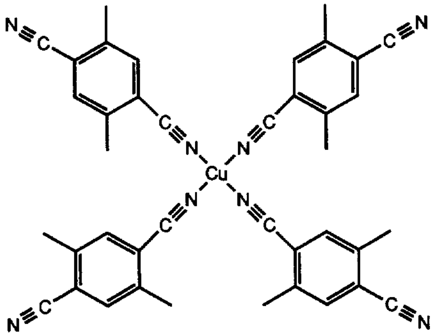
Reduction of $Cu(ClO_4)\cdot 6H_2O$ by a copper sheet under an ethylene atmosphere has been shown to afford a colourless Cu(I) solution; this reacts with *cis*- and *trans*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (L), in thf and acetone respectively, at ambient temperature to yield orange crystals in both cases [59]. The crystal structure with the *trans*-(L) shows it contains [Cu(*trans*-(L))(thf)ClO_4)] units bridged sequentially by the two trans CN groups of each dithienylethene to form zigzag chains. The coordination environment around each copper centre is best described as a distorted tetrahedron. The structure of the complex formed with *cis*-(L) is composed of non-interacting ClO_4^- anions and cations $[Cu(cis\text{-}(L))_2]^+$ (**55**) with the two thiophene rings significantly twisted with an average dihedral angle of 48.3°. Each copper centre is coordinated to one CN group of the four dithienylethene molecules and each ligand in turn bridges two copper(I) ions with cyano groups leading to an infinite network of cations. The two complexes show a rather different photoresponsive behaviour toward irradiation with light: the *trans*-(L) complex shows no visible colour change, whereas *cis*-(L) shows normal photochroism in the single crystalline state. On irradiation with 405 nm light for 1 h at room temperature, the orange crystals gradually turned red. This is attributed to the formation of the ring-closed form of the free ligand. This photogenerated ring-closed form **56** is stable, and the red colour hardly fades over 2 days, but it can be reverted to the orange ring-opened form by irradiating at 550 nm. This cycle can be repeated several times.

Two novel coordination polymer compounds, $[Cu(DMTPN)_2]X(DMTPN)(thf)$ (DMTPN = 2,5-dimethylterephthalonitrile, $X = BF_4$ and ClO_4) have been prepared and characterized by single-crystal X-ray analysis [60]. Both complexes are isostructural and have threefold interpenetrated diamondoid structure with a π–π stacking column of alternate coordinated and uncoordinated DMTPN. The Cu(I) is tetrahedrally coordinated to four nitrogen atoms of four cyano groups of different DMTPN



molecules (**57**). The N–Cu–N′ angle of 109.4° is very close to the internal angle of diamond (109.5°) indicating that the CuN_4 chromophores are an almost regular tetrahedron. The cyano group at the other end of each ligand also coordinates to another Cu atom giving a 3D diamondoid framework. The solid state structure shows that three independent frameworks interpenetrate each other. Metal-free DMTPN molecules are incorporated in the $Cu(DMTPN)_2$ lattice and participate in the formation of π–π stacking columns.



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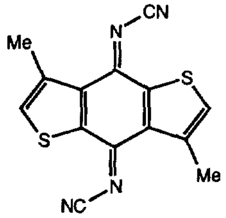
Thiophene-fused *N,N*-dicyanoquinonediimine (DCNQI) compounds have been shown to yield conducting CuI complexes built up of a unique three-dimensional supramolecular coordination structure in which the zigzag ladder Cu^I polymers are bridged by the π-stacked acceptors acting as a didentate ligand [61]. Single crystals of (**58**)·2CuI were obtained: the electrical conductivity measured at room temperature was 7.6×10^{-3} S cm^{-1} and the temperature-dependent conductivities down to 200 K revealed that this complex is a semiconductor with an activation energy of 0.18 eV. The X-ray structure of (**58**)·2CuI was reported and showed the copper atoms to be in nearly regular tetrahedral geometries, coordinating to three iodine atoms and the nitrogen atom of the CN groups to the copper centre. The π-acceptor molecules of (**58**) are almost planar and stacked in a face-to face arrangement with overlapping π-planes with an interplanar distance of 3.56 Å. The Cu···Cu distance in the ladder is 2.89 Å, close to that of 2.56 Å in metallic copper.



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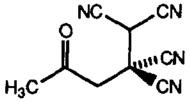
In a study to obtain novel extended frameworks bridged by the neutral tetracyanoethylene (TCNE) ligand, the high reactivity of TCNE led to the unexpected formation of **59** which exhibits a pronounced tendency to form networks with metal ions [62]. The reaction of $[Cu(MeCN)_4](PF_6)$ with the preformed conjugated acid of **59** gave colourless crystals of $[Cu(AcTCNE)] \cdot Me_2CO$ **60** which exhibits a 3D open zeolite-like framework. The framework consists of a 3D neutral network of four-coordinate Cu(I) ions linked by anions of **59** which act as tetradentate ligands. The framework resembles a honeycomb with large channels, with average radius 4.7 Å, which contain guest acetone molecules. The copper centres reside in distorted tetrahedral environments with the Cu–N bonds and N–Cu–N angles lying in the ranges 1.938(5)–2.034(5) Å and 103.6(2)–114.3(2)° respectively. A similar reaction with $Ag(CF_3OSO_3)$ formed a 2D network.



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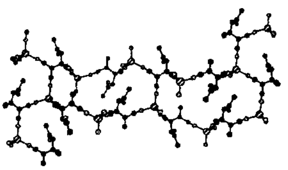

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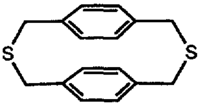
The compound $[\{CuLCl\}_\infty]$ (L = (1,3-bis(ethylthio)methyl)benzene) has been synthesized and its structure determined by X-ray crystallography [63]. The complex has a three-dimensional polymeric structure with each Cu^I cation having a distorted tetrahedral environment defined by two sulfur atoms of different ligands and two bridging chlorine atoms.

The compounds $Cu(SCN) \cdot CH_3CN$ and $[(CH_3)_3NH]^+[Cu_2(SCN)_3]^-$ have been synthesized using a direct method of interaction and characterized by X-ray crystallography [64]. The planar Cu_2S_2 units, with copper–copper distances 3.095 and 2.972 Å, form the basis of both structures. $Cu(SCN) \cdot CH_3CN$ consists of infinite puckered layers with an interlayer distance of 6.657 Å. The three-dimensional polymeric anion $[Cu_2(SCN)_3]^-$ in $[(CH_3)_3NH]^+[Cu_2(SCN)_3]^-$ comprises two crystallographically independent copper(I) atoms and two bridging thiocyanate groups with different coordinations.

A copper(I) complex with triphenylphosphine and 4,4′-bipyridine results in a one-dimensional polymer, $\{[Cu_2(NO_3)_2(C_{18}H_{15}P)_2(C_{10}H_8N_2)] \cdot 2C_4H_8O\}_n$ [65]. The Cu centres are alternately bridged by nitrate counterions and bipyridine ligands. The four-membered Cu_2O_2 ring lies on an inversion centre and the bipyridyl ligand lies on another inversion centre. The triphenylphosphine ligand coordinates to copper, providing a distorted tetrahedral coordination environment with bond lengths Cu1–P = 2.168(1), Cu–N = 2.013(3) and Cu–O = 2.177(2) and 2.147(2) Å. The cavities between the chains contain tetrahydrofuran solvent molecules.

The salts (paraquat) Cu_2X_4 (X = Cl, Br, I) have been synthesized and their crystal structures determined [66]. Infinite chains of distorted, edge sharing, $Cu^IX_4^{3-}$ tetrahedra are common to all three structures. The bond distances and angles about the copper centres are consistent with known $Cu^IX_4^{3-}$ species. The paraquat cations form stacks parallel to the chain axis, and all three structures show weak N···X and C···X contacts. The chloride and iodide salts are nearly isostructural, and differential scanning calorimetry shows a phase transition in the chloride salt at 188 °C. The iodide salt is a pure copper(I) system. A temperature-dependent magnetic susceptibility experiment shows the bromide salt to contain a 2% $Cu_2Br_6^{2-}$ impurity. Two chloride compounds showing the same structure have been synthesized. One of these salts has 1% copper(II) character, whereas the other has 10% copper(II) character. EPR shows the 1% character to be a $CuCl_2 \cdot 2H_2O$ impurity. Magnetic susceptibility, EPR, powder diffraction and electrical conductivity results show that the 10% copper(II) character is incorporated into the $[CuC_2]$(infinity) chain structure, with an accompanying vacancy. Preliminary conductivity measurements show that the Cl and I salts are insulators, but hint at enhanced conductivity for the bromide analogue.

Two copper(I) and one silver(I) complex of 2,11-dithia[3.3]paracyclophane (**61**), $[Cu_2Br_2(\mathbf{61})(MeCN)_2]$ **62**, $[Cu_2I_2(\mathbf{61})_2] \cdot$ thf **63** and $[Ag(\mathbf{61})(NO_3)]$, have been synthesized and their molecular structures determined by X-ray crystallography [67]. All three structures contain an infinite network comprising metal cations linked via dithia-bridged paracyclophane and the counter anions. Complexes **62** and **63** are not isostructural. The repeating dinuclear units $[Cu_2Br_2(\mathbf{61})MeCN)_2]$ joined by **61** and **62** generate a one-dimensional polymeric chain. Complex **63** is a two-dimensional sheet structure in which a large ring containing six copper atoms includes a tetrahydrofuran molecule as guest inside the open cavity. The one-nitrate oxygen bridging two metal centres in the silver complex yields a unique three-dimensional channel framework of silver(I) ions. The iodine-doped black products of the complexes **61**–**63** at room temperature exhibited conductivities of $10^{-5.9}$, $10^{-5.1}$ and $10^{-4.7}$ S cm^{-1} respectively.



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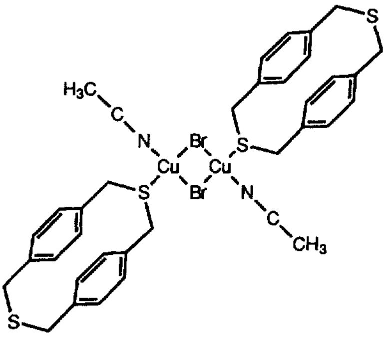

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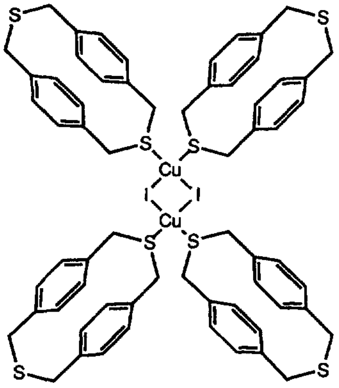
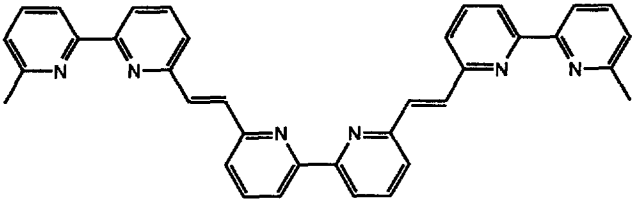


(63)

2.8. Supramolecular complexes

The unsaturated and saturated trimeric ligands **64** and **65** were synthesized and the formation of complexes with copper(I) studied as well as the self-recognition properties of (tris)bipyridyl ligands [68]. The ^1H NMR results indicate that a double-stranded trihelicate $[(\mathbf{65})_2Cu_3]^{3+}$ is formed from two ligand (**65**) molecules and three copper(I) cations. However, with **64** the presence of the CH=CH bridge results in more complicated binding features. Competitive binding of Cu(I) in a mixture of **65** and its oxygen-bridged analogue shows that moderate self-recognition takes place with formation of both the two homostranded double helicates and its heterostrand double helix analogue.



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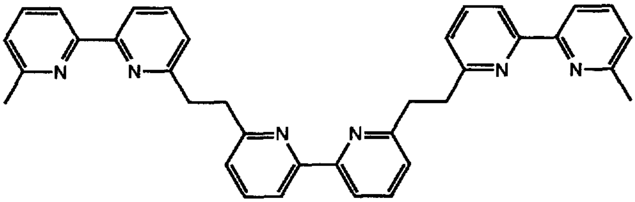

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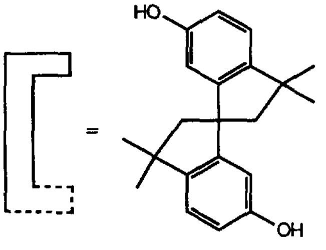
An investigation into the synthesis and metal complexing behaviour of a series of oligobipyridines hybridized to chiral organic templates has been performed [69]. A chiral template has been shown to provide the necessary symmetry condition for distinguishing right-hand from left-hand helicates and the template (**66**,**67**) can set the pitch and direction of the helix (**68**) by restricting the conformational freedom of the bpy strands as the metal binds to the ligand. Adding Cu(I) to the ligand strands results in the formation of a single enantiomer of the head-to-head isomer. The complexes show $[\alpha]_D$ values of approximately +500°.



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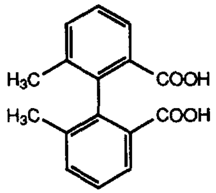

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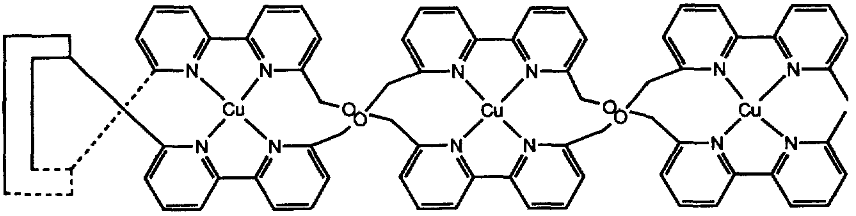
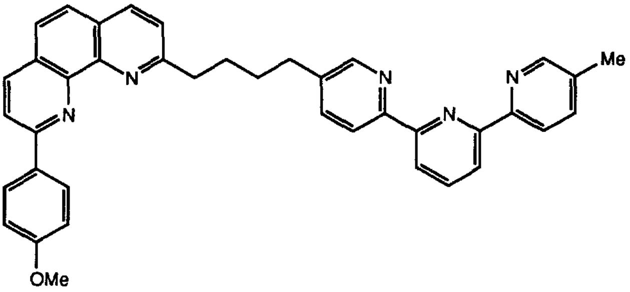


(68)

As part of a study to increase the lifetime of the charge separated state by increasing the distance between donor and acceptor units, but at the same time keeping a strong coupling between both components, a [3]rotaxane and [5]rotaxane have been reported [70]. Preliminary studies show that relatively efficient quenching of the free base of Zn porphyrin fluorescence by the Cu^I complex components takes place.

A pseudorotaxane consisting of a coordinating ring, a molecular thread bearing two different coordination sites and a copper(I) ion displays electrochemically induced motions of the ring from one site to the other [71]. Mixing stoichiometric amounts of **69** and **70** and $[Cu(MeCN)_4]BF_4$ under argon gave the pseudorotaxane as a red–brown solid in 75% yield. The ^1H NMR spectrum showed the typical chemical shifts to higher field of the hydrogen atoms of the phenoxy moieties of the 1,10-phenanthroline unit, consistent with two phen units entwined around a Cu centre. Cyclic voltammetry of a red solution of the complex showed a reversible wave at +0.84 V *vs* SCE, characteristic of a tetrahedral Cu^I species. Controlled potential electrolysis ($E_{applied} = +1.1$ V) resulted in the solution becoming light green and the display of a reversible couple at 0.1 V attributed to a five-coordinate Cu^{II} centre. A second electrolysis at −0.6 V restored the initial colour and redox couple.



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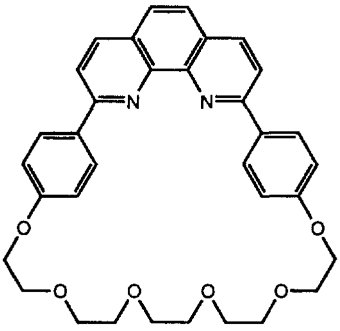
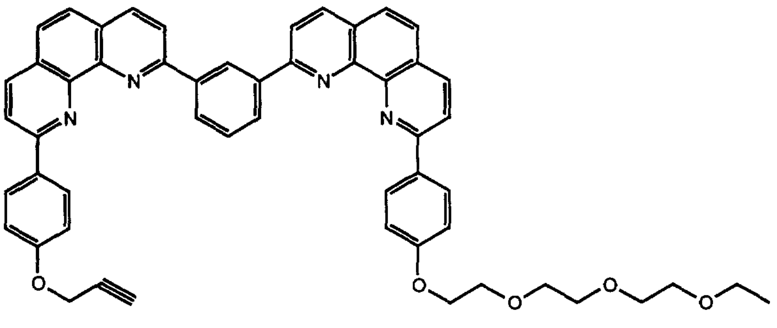


(70)

Molecular composite knots have been prepared from transition-metal-assembled precursors via a Glaser acetylenic coupling reaction [72]. The templating metal is copper(I), and the coordinating fragments incorporated into the final structure are 1,10-phenanthroline-type chelates. By combining two tied open-chain fragments (**71**) in a cyclodimerization reaction, the simplest composite knots are obtained as a mixture of two topological diastereomers. The minimum number of crossing points used to represent the molecules in a plane is six. Owing to the complexity of the entangled precursors and to the several cyclization possibilities, the formation yield of composite knots is only modest (*ca* 3%) but they have been fully characterized by ES-MS and by ^{1}H NMR spectroscopy.

The first synthesis of a 4-crossing [2]-catenane via a copper(I) template approach has been described [73]. Its topological isomer, the singly interlocked [2]-catenane, was also prepared. Unambiguous assignment of their topology was made by comparison of their NMR and mass spectra.

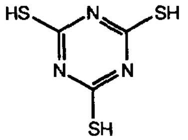
Four novel hydrogen-bonded copper(I) supramolecules with channel structures have been reported [74]. The reactions of copper(I) salt with 3-cyano-6-methyl-2(1*H*)-pyridinone (Hcmp) in acetone have enabled four polymeric coordination products $[Cu(Hcmp)_4]X$, where $X = ClO_4^-$, BF_4^-, PF_6^- and $CF_3SO_3^-$ to be



(71)

isolated. All four compounds crystallized in the tetragonal system. Each structure contains a three-dimensional framework of tetrahedral CuN_4 centres linked by intermolecular hydrogen bonds through pyridone N and O atoms in a head-to-tail mode. The very special structural features of the four compounds are related to the two types of hydrogen-bonding. Complexes with the smaller counteranions ClO_4^- and BF_4^- involve each Hcmp group hydrogen-bonded to two adjacent others, which generates an open square channel filled with aligned ClO_4^- or BF_4^- ions. The complexes with the larger counterions involve 1:1 pairwise hydrogen-bonding of Hcmp, which results in four independent interpenetrating diamond-like frameworks with big cavities to accommodate the larger anions of PF_6^- and $CF_3SO_3^-$.

A novel luminescent inorganic cyclophane showing a weak π–π stacking interaction obtained by the self-assembly of Cu^I and trithiocyanuric acid (**72**) has been reported [75]. In CH_2Cl_2 $[(CuPPh_3)_6(\mathbf{72})_2]$ shows an irreversible oxidation wave at $E=0.99$ V *vs* SCE. The X-ray structure of the complex shows it can be considered as "cyclophane-like" with six Cu–S bridges with C–S–Cu angles of ~99°. The Cu^I centres are far apart, ranging from 3.461(1) to 5.684(1) Å. The two triazine rings are virtually parallel, being held in a close proximity of 3.07 Å by the six Cu–S bridges. The complex shows room temperature photoluminescence in both the solid state and in solution, with emissions at 562 nm (lifetime 0.59 μs at 298 K) and at 580 nm in CH_2Cl_2 (lifetime 0.82 μs at 298 K). These are higher in energy than other Cu(I) complexes with sulfur donor ligands.



(72)

The self-assembly reaction between bischelating 2,2′-bipyrimidine, metallic copper, Cu^{2+}, and two equivalents of didentate $Ph_2P(CH_2)_nPPh_2$ has produced crystallographically characterized dinuclear complexes with a $[Cu^I(\mu\text{-bpym})\text{–}Cu^I]^{2+}$

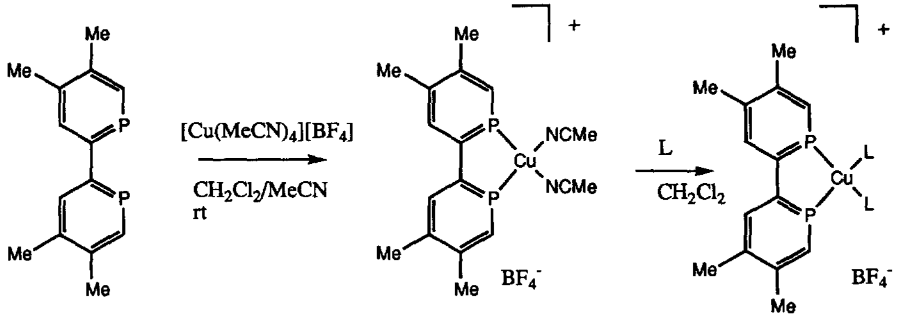
core and chelating ($n=5$) or bridging diphosphine ligands ($n=6,8$) [76]. The structural data of the solids and the spectroscopic results for the dissolved species indicate a strained configuration in the case of complex $[(\mu\text{-bpym})Cu_2\{\mu\text{-}Ph_2P\text{–}(CH_2)_nPPh_2\}_2]^{2+}$ with $n=6$. Once the polymethylene chain length is reduced to $n=5$, the diphosphines can no longer bridge but help to form eight-membered chelate rings. In this complex there is a distortion towards a trigonal-pyramidal coordination geometry at the coper(I) centres, which is supported by the formation of an organic sandwich arrangement between the central bpym acceptor and two phosphino phenyl rings.

Upon reaction with $[Cu(MeCN)_4]^+$, 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (**73**) gives a $[Cu(tmbp)(MeCN)_2]^+$ (**74**) cationic chelate which is a convenient source for a variety of [Cu(**73**)$L_2]^+$ (**75**) complexes with L = Et_2S, Ph_3As, Ph_3P, dppe and pyridine [77]. The X-ray crystal structure analysis of the complex with L = Ph_3P shows a chelate structure weakened by the non-coplanarity of the two phosphinine rings and by the absence of electronic delocalization. It has been shown that **73** can indifferently adopt a chelating or a bis (η^1-P) complexing mode towards the copper(I) centre, as shown by the reaction of a 1:1 mixture of 2,2′-bipyridine (bpy) and **73** with $[Cu(MeCN)_4]^+$. A polymeric helix (**76**) is thus produced, where [Cu(bpy)] subunits are bridged by tmbp acting as two separate P-donors. The two phosphinine rings are non-coplanar so as to partly reduce the strain within the chelate ring by expanding the P–Cu–P angle to 83.22(5)°. As a result of the distortion, the Cu atom lies outside of the two phosphinine planes (~1.22 Å); hence, overlap between the lone pair orbitals of the phosphinines and the copper d orbitals is reduced and the Cu–P bonds are weakened (Cu–P = 2.33 Å *vs* 2.28 Å for Cu–PPh_3). The X-ray structure of **76** shows a helical polymeric structure where [Cu(bpy)] planar units are connected together by the diphosphinine acting as two independent P donors. The structure suggests that the [Cu(**73**)] unit is apparently less stable than the [Cu(bpy)] unit. The Cu–P bonds are shorter than in **1** (2.252(6) and 2.2090(6) *vs* 2.3273(9) and 2.3286(9) Å). The geometry of the biphosphinine is transoid and the C_6–C_7 bridge has the same length as in the free ligand (1.48 Å).

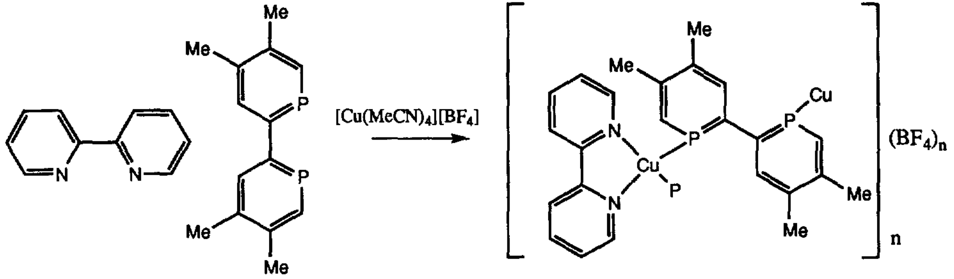
3. Copper(II)

3.1. Mononuclear complexes with macrocyclic ligands

In order to explore the role of labile metal complexes in promoting phosphodiester hydrolysis, detailed kinetic and mechanistic studies with Cu[9]aneN_3Cl_2 have been performed [78,79]. The hydrolysis of bis(4-nitrophenyl)phosphate by Cu[9]aneN_3Cl_2 has been shown to be catalytic, as determined by the observation of both rate enhancement and turnover. This reaction showed a half-order dependence on the catalyst, implicating a monomer–dimer equilibrium with the monomer as the catalyst with an equilibrium constant of 1220 M^{-1}. The catalyst is selective for phosphodiesters; the rate of hydrolysis for 4-nitrophenylphosphate is 50 times slower than the hydrolysis rate of bis(4-nitrophenyl)phosphate. A rate enhancement



(73) (74) (75)



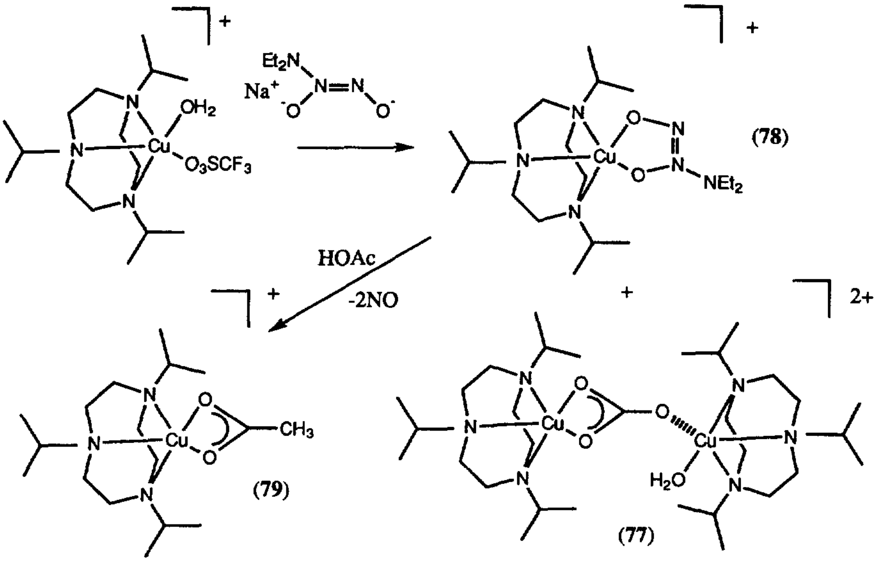
(73) (76)

of 2000 is observed relative to hydroxide-ion-mediated hydrolysis, and the rates reported are comparable with the rates reported for phosphodiester hydrolysis by other labile metal complexes.

The compound, (tris(2-aminoethyl)amine)(4,5-diazafluoren-9-one) copper(II) perchlorate, $[Cu(C_6H_{18}N_4)(C_{11}H_6N_{20})(ClO_4]$, has been synthesized [80]. The electronic and ESR spectra are very different from those of $[Cu(tren)L)^{2+}$ complexes where L is a monodentate ligand. The X-ray analysis revealed that the copper(II) ion is coordinated by four nitrogen atoms from tris(2-aminoethyl)amine (tren) and two nitrogen atoms from 4:5-diazafluoren-9-one (dzf) to form an unusual six-coordinate $(4+1+1')$ geometry. The structure is reported to be the first example of an asymmetric didentate phenanthroline derivative metal complex. The structure could be used as a model of the associative complex in the ligand-exchange and ligand-substitution reactions of $[Cu(tren)L]^{2+}$ and the catalytic mechanisms of enzymes involving copper sites. As a comparison, the complex $[Cu(tren)(ImH)(ClO_4)_2]$ was also synthesized and characterized, where ImH is imidazole.

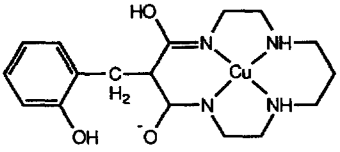
As part of a study to make copper complexes of NONOates with increased stability and hence have greater potential as prodrugs for the controlled and selective release of NO (NONOates $= [R_2N(N_2O_2)]$ ions), a novel mononuclear copper complex of the "NONOate" $[Et_2N(N_2O_2)]^-$ has been prepared and its X-ray crystal structure determined [81]. Comparison of rate constants for NO evolution from the complex and from $Na[Et_2N(N_2O_2)]$ revealed that the complex decomposes approximately half as fast as the sodium salt in aqueous solution (pH 7.4, PBS buffer, 37 °C), implicating a decomposition mechanism for the complex different from that postulated for other reported polynuclear copper complexes of this NONOate. Admixture of solutions of $[L(ipr_3)Cu(H_2O)(O_3SCF_3)]O_3SCF_3$ and $Na[Et_2N(N_2O_2)]$ in MeOH at -35 °C gave a deep blue–green solution and a green precipitate after 30 min. The precipitate, formed in low and variable yield, was identified as the carbonate complex (**77**) $\{(L(ipr_3)Cu)_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-}CO_3)(H_2O)](O_3SCF_3)_2\}$ (Scheme 4). Removal of the solvent from the blue–green solution and recrystallization from acetone–Et_2O at -20 °C gave (**78**), $\{L(ipr_3)Cu[Et_2N(N_2O_2)]\}O_3SCF_3$, in 49% yield. This product consisted of a mixture of blue and blue–green crystals which X-ray structural analysis showed were almost identical: there were only slight differences apparent in their metal ion geometry, with both best described as distorted square-planar, and minor differences in interligand and bond angles. **78** is stable at ambient temperature for long periods of time as a solid or in deionized aqueous solution at pH > 7, but rapid evolution of NO (~80%) occurs on addition of protonic acids (HCl, HOAc) or thiols (EtSH). Addition of HOAc enabled the copper-containing product to be isolated as $[L(ipr_3)Cu(OAc)]O_3SCF_3$ (**79**). The X-ray structure of **79** showed μ^2-binding of the acetate anion to a square-planar Cu(II) centre.

The synthesis and aqueous complexation behaviour of C- and N-linked *o*-hydroxyaryl-substituted derivatives of 1,5,9-triazacyclododecane have been reported [82]. The N-linked ligand forms strong 1:1 complexes with copper and zinc ($\log K_{ML} = 18.7$ and 14.1 respectively) in which the phenolate acts as an effective donor ligand in the expected tetrahedral complex. The ligand substituted at carbon at the 3-position is less basic and forms much weaker complexes with Cu^{2+}



Scheme 4.

(log $K_{CuL}=10.2$) in which phenolate participation is absent. A similar trend is seen for Ni^{2+} and Zn^{2+}.



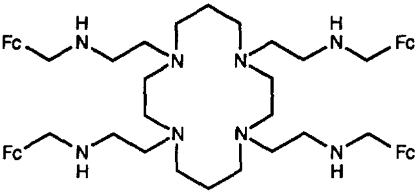
(80)

A singly deprotonated macrocyclic dioxotetraamine copper(II) complex (**80**) and two double deprotonated copper(II) complexes have been prepared and characterized [83]. In **80**, both amido (peptide) nitrogen atoms are coordinated to the Cu(II) centre. One amido group is deprotonated, with the other amido hydrogen atom having migrated to an amido oxygen atom forming a C-hydroxy Schiff base (enolic tautomer) instead of deprotonation, thereby establishing an enolic tautomer of an amide coordinated to a metal centre. In the complex there is an approximately square-planar geometry around the metal centre, comprising two secondary amino nitrogen atoms and two peptide nitrogen atoms. The phenolic oxygen atom remains uncoordinated. This singly deprotonated dioxotetraamine Cu(II) complex exists both in the solid state and in solution. The complex has been shown to deprotonate in a stepwise manner. The study has been extended with the synthesis of a series of new dioxocyclams with pendant phenol groups derived from the reaction of coumarin 3-carboxylic ester with linear polyamines [84]. The corresponding saturated cyclam derivatives were obtained by $B_2H_6 \cdot THF$ reduction. When coordinated to a copper(II) centre, the amido group deprotonates with $pK_a = 4.3$. Potentiometric, electrochemical and EPR spectral data of the complexes were studied. In the region pH 3–9 the phenol substituent does not coordinate to the copper(II) ion, but substituents were found to have some effect on the Cu^{II}/Cu^{III} potential and complex stability. This study shows that singly deprotonated dioxotetraamine complexes, as well as doubly deprotonated copper(II) complexes, exist both in aqueous solution and in the solid state with considerable stability. The existence of the singly deprotonated dioxotetraamine copper(II) complex indicates that the complex deprotonates in a stepwise and not in a simultaneous manner.

The spectral characteristics of 13- and 14-membered C-functionalized macrocyclic dioxotetraamine and the corresponding saturated polyamine copper(II), copper(III) and nickel(III) complexes have been studied [85]. It was shown that C-functionalized substituents, although not coordinating to the metal ion, have significant effects on the spectral properties of their M(III) complexes. In the case of the copper(II) complexes, substituents are found to increase the in-plane ligand field and decrease the wavelength of the d–d absorption of their complexes.

As part of a study in developing electrochemically active ligands containing redox-active groups in close proximity to metal binding sites, the redox-active receptor *N*,*N*′,*N*″,*N*‴-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (**81**) has been synthesized from the reaction of *N*,*N*′,*N*″,*N*‴-

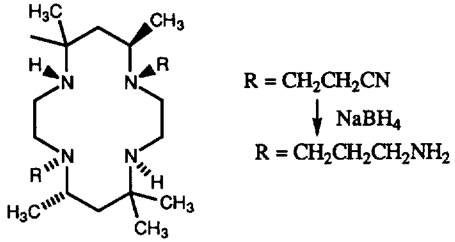
tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane with ferrocenecarbaldehyde followed by reduction with $LiAlH_4$ [86]. The protonation behaviour of (**81**) and its complex formation with Cu^{II}, Zn^{II} and Cd^{II} have been studied in tetrahydrofuran–water (70:30 v/v) (0.1 mol dm^{-3} $N^tBu_4ClO_4$, 25 °C). The potentiometric and electrochemical data indicate the formation of 1:1 and 1:2 ((**81**):M^{2+}) stoichiometries. The $E_{1/2}$ values for (**81**) shift as a function of the pH from 389 mV at pH 10 to 482 mV at pH 2.5 and $E_{1/2}$ *vs* pH curves for the tfabc–H^+–M^{2+} systems (M = Cu, Zn or Cd) show that tfabc electrochemically recognises the presence of copper(II) selectively at pH < 5. The shift of $E_{1/2}$ appears to be caused by electrostatic forces and the $E_{1/2}$ *vs* pH curves can be predicted in terms of the distribution diagrams of the tfabc–H^+–M^{2+} systems.



(81)

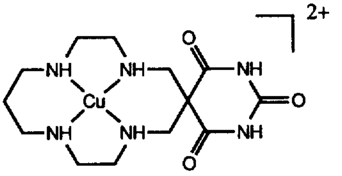
In the reaction of $[Cu^{II}(en)]^{2+}$ (en = 1,2-diaminoethane) with 3 equiv. of diethylmalonate in the presence of formaldehyde and triethylamine the 1,4,8,11-tetraazacyclotetradecane-6,6,13,13-tetracarboxylic acid tetraethyl ester copper(II) diperchlorate complex salt is formed [87]. It was demonstrated that the formaldehyde building block can be replaced by benzaldehyde in the same type of template procedure if the two en fragments are replaced by the tetraamine *N*,*N*′-bis(2-aminoethyl)-propane-1,3-diamine and if the synthesis was carried out under strictly anhydrous conditions. The 5,7-diphenyl-1,4,8,11-tetraazacyclotetradecane-6,6-dicarboxylic acid diethyl ester copper(II) diperchlorate complex was obtained in good yield and exhibits a regular square coordination which is not disturbed by the bulky phenyl substituents.

The preparation of the ligand bis(*N*-2-cyanoethyl)-C-*meso*-5,7,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**82**) has been reported [88]. The ligand can be reduced with H_2/Raney nickel in the presence of $NaBH_4$ to give the bis(*N*-3-aminopropyl) derivative. The red copper(II) complex $[Cu(\mathbf{82})](ClO_4)\cdot 0.5MeOH$ has been characterized by X-ray crystallography. The complex has a $\nu_{C{\equiv}N}$ at 2225 cm^{-1} identical to that found in the free ligand, indicating that there is no interaction between the central metal ion and the pendant cyanoethyl groups. The crystal structure confirms that the copper(II) centre is four-coordinate and planar with the four ring nitrogen atoms acting as donors with Cu–N bond lengths of 2.068(6) and 1.980(5) Å. The macrocyclic ligand has the centrosymmetric trans-III configuration with the six-membered chelate rings in chair conformations and the five-membered rings in gauche conformations. The methyl groups on C(3) and C(5) are equatorial.



(82)

The reaction of $[Cu(danda)]^{2+}$ (danda = 3,7-diazanoqane-1,9-diamine) with formaldehyde and barbituric acid resulted in a new macrocyclic compound (**83**), containing barbituric acid as a spiro substituent, which was characterized by spectral and potentiometric methods, cyclic voltammetry and single-crystal X-ray diffraction [89]. The mutual influence of the substituent and the metal centre is evident from electrochemical data with $E_{1/2}$ Cu^{III}/Cu^{II} in 10 mol dm^{-3} $HClO_4$ being ~1.1 V *vs* SCE. This is 0.1 V higher than for the same redox couple in cyclam under the same conditions. This is indicative of the barbituric acid fragment exhibiting a substantial electron-withdrawing effect. The X-ray structure of the complex shows both six-membered rings of the macrocycle to have a chair conformation and with the barbituric acid fragment disposed nearly perpendicular (85°) to the macrocycle plane.



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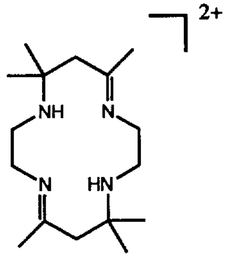

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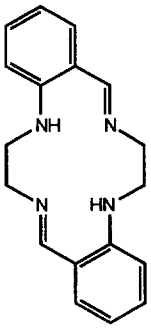
The copper(II) complex of the β-aminoketone 14-amino-4,4,9,11,11-pentamethyl-5,8,12-triazatetradec-8-en-2-one (**84**), $[Cu(\mathbf{84})\}](ClO_4)_2 \cdot MeCN$ has been prepared and its structure established by X-ray crystallography [90]. In basic solution the complex undergoes base-catalysed ring closure to give the copper(II) complex of the macrocycle *trans*(**84**). The kinetics of the ring closure reaction have been studied in detail and show ring closure occurs by an intramolecular reaction involving the hydroxo complex $[Cu(\mathbf{84})OH]^+$.

The synthesis and structural characterization of complexes of the 14-membered macrocyclic *trans*-N_4 dibenzo ligand 7,8,9,16,17,18-hexahydrodibenzo[e,1][1,4,8,11]-tetraazacyclotetradecine (**85**) have been described [91]. The crystal structures of six compounds were determined by single-crystal X-ray diffraction, including $[Cu(\mathbf{85})]^{2+}$ in which the metal atom is tightly bound within the macrocyclic cavity. The Cu–N bonds (2.012(3) and 1.918(3) Å) are rather short.



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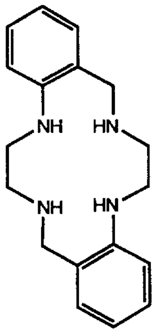

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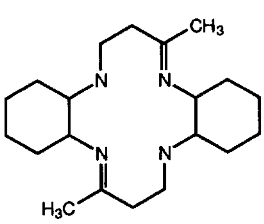
The synthesis and structural characterization of complexes of the 14-membered macrocyclic *trans*-N_4 dibenzo ligand 5,6,7,5,9,14,15,16,17,18-decahydrodibenzo-[e.1][1,4,8,11]-tetraazacyclotetradecine (**86**) have been reported [92]. The crystal structures of six compounds were determined by single-crystal X-ray diffraction. Both the free ligand **86** and the Cu(II) complex have been shown to have saddle-shaped structures with short intramolecular hydrogen bonds with a more or less planar arrangement of the four N donor atoms. A similar conformation is seen in the Zn^{II} and Pd^{II} complexes. In $[Cu(\mathbf{86})(CF_3SO_3)]^+$ the metal atom is incorporated within the macrocyclic cavity with rather short metal-to-nitrogen bond lengths. In all of the complexes, the metal-to-ligand distances originating at the nitrogen atoms in β-position (with respect to the aromatic ring) are significantly shorter than the donor bonds of the "anilinic" N atoms.

The square-planar copper(II) complex $[Cu(\mathbf{88})]^{2+}$ (**88** = 3,14-dimethyl-3-nitromethyl-2,6,13,17-tetraaztricyclo[16.4.0.0(7.12)]docosa-13-ene) containing one C-nitromethyl pendant arm was synthesized by the nucleophilic addition of deprotonated nitromethane to the diimine complex $[Cu(\mathbf{87}))]^{2+}$ (**87** = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0.(7.12)]docosa-2,13-diene) [93]. The copper(II) complex of **88** is relatively stable against the dissociation of the nitromethyl group even in basic acetonitrile solutions, in contrast to the corresponding nickel(II) complex. Reduction of the nitro group of $[M\mathbf{88}]^{2+}$ (M = Ni^{II} or Cu^{II}) produced the square-pyramidal complex $[Cu(\mathbf{89})]^{2+}$ (**89** = 3,14-dimethyl-3-aminomethyl-2,6,13,17-tetraaza-tricyclo[16.4.0.0(7.12)]docosa-13-ene) or the octahedral complex $[Ni(\mathbf{89})(H_2O)]^{2+}$ containing one C-aminomethyl group, which is coordinated to the metal ion.



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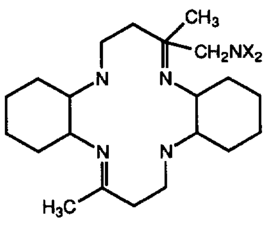
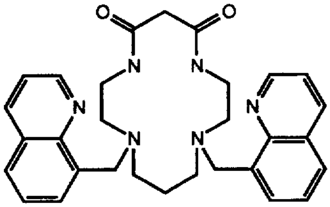


(88), X = O
(89), X = H

Several tetraazamacrocycle-bonded silica gels have been synthesized and characterized [94]. 1,4,7,10-tetraazacyclododecane, 1,4,8,11-tetraazacyclotetradecane and 1,5,9,13-tetraazacyclohexadecane have been covalently bound to silica gel and their respective copper(II) complexes characterized. Capacity determinations were determined by quantitative ESR measurements of copper(II) complexes, nitrogen, carbon and copper elemental analyses and UV–VIS measurements.

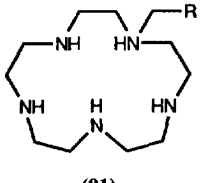
A macrocyclic dioxotetraamine ligand 1,11-bis(quinolin-8-ylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (**90**) has been synthesized and characterized [95]. The resulting dioxocyclam readily coordinates Cu(II) with concomitant double deprotonation of the ligand. The Cu(II) complex of H_2(**90**) (Cu(**90**)·CH_3COOH) has been isolated as a single crystal and the structure determined by X-ray diffraction analysis. The Cu^{II} centre is five coordinate and forms a distorted square-pyramidal configuration with one of the quinoline pendants coordinated. The solution behaviour of Cu(**90**) has been further studied with ESR and UV–VIS techniques. A remarkable red-shift was observed for the maximum absorption band of the electronic spectra of Cu(**90**) in comparison with that of CuL (H_2L, dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione).



(90)

Single *p*-toluic acid pendant groups were attached to 1,4,7,10,13-pentaazacyclopentadecane ([15]aneN_5) and 1,4,8,11-tetraazacyclotetradecane (cyclam) to prepare bifunctional reagents for radio-labelling monoclonal antibodies with ^{64}Cu, ^{67}Cu [96]. The ligands used in the study were 1,4,7,10,13-pentaazacyclopentadecane-1-(α-1,4-toluic acid) (**91**) and 1,4,8,11-tetraazacyclotetradecane-1-(α-1,4-toluic acid) (**92**). For the parent macrocycles and their pendant arm derivatives, the 1:1 Cu^{2+} complexes dissociate only below pH 2. At pH 0.0 and 25 °C the (**91**)–Cu complex was found to have a half-life towards complete dissociation of 24 days. A new approach was developed for the estimation of the Cu^{2+} stability constant for the kinetically robust **91**. All other formation constants were determined at 25.0 °C with batch spectrophotometric techniques. Potentiometric titrations were used to determine the protonation constants of the macrocyclic ligands as well as of the metal chelates.

The copper(II) and nickel(II) complexes of hexacyclen (1,4,7,10,13,16-hexaazacyclooctadecane, [18]aneN_6) have been characterized as their perchlorate salts and their analytical, conductivity, spectral and magnetic measurements reported



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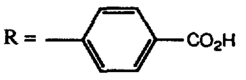
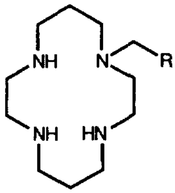


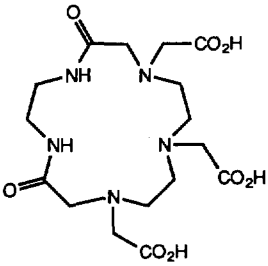


(92)

[97]. The kinetics of dissociation of the copper(II) and nickel(II) complexes in acidic solution have been studied in detail. For the copper complex the results demonstrate that cleavage of the first equatorial Cu–N bond is slow with all of the subsequent steps being rapid.

The macrocycle 1,5,9,13,17,21-hexaazacyclotetracosane ([24]aneN_6) was synthesized as both its HNO_3 and HCl salts [98]. The protonation and stability constants with Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} have been determined potentiometrically in 1.0 mol dm^{-3} KNO_3 aqueous solution at 25 °C. For all these metal ions only mononuclear complexes are formed. In the case of the HNO_3 salt $\log K_{ML} = 14.87 \pm 0.04$ was obtained for $[CuL]^{2+}$, whereas for the HCl salt $\log K_{ML} = 16.47 \pm 0.02$ for $[CuL]^{2+}$ in 1.0 mol dm^{-3} KCl aqueous solution at 25 °C. The smaller value of K_{CuL} in the nitrate system compared with that in the chloride system suggests an affinity of the macrocycle towards Cl^-.

Formation constants, UV–VIS spectra and EPR spectra have been obtained for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes formed in aqueous solutions with 15-, 16- and 17-membered macrocycles, which are 9,14-dioxo-1,4,7,10,13-pentaaza-1,4,7-cyclopentadecanetriacetic acid (**93**), 9,15-dioxo-1,4,7,10,14-pentaaza-1,4,7-cyclohexadecanetriaceticacid (**94**) and 9,16-dioxo-1,4,7,10,15-pentaaza-1,4,7-cycloheptadecanetriacetic acid (**95**) respectively [99]. The ligands **94** and **95** were characterized by single-crystal X-ray analyses. In **94**, the central carboxylate oxygen and two terminal amine nitrogen atoms are protonated; in **95** two terminal carboxylate oxygen atoms and the central amine nitrogen are protonated. The molecular conformation of **95**, is preorganized for complex formation, whereas **94** is not preorganized. These structural features of the ligands are reflected in the pH dependence of the electronic and EPR spectra of the metal chelates.



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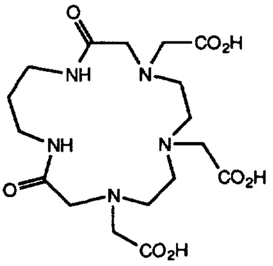

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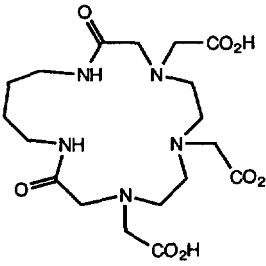

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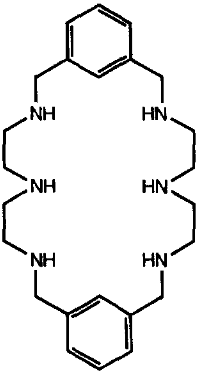
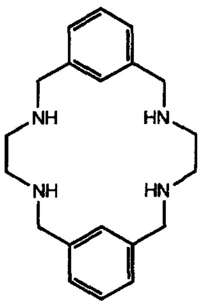
The kinetics of formation and decomposition of mono- and dinuclear copper(II) complexes of the macrocycle 3,6,9,17,20,23-hexaazatricyclo[23.3.1.1(11,15)]-triaconta-1(29),11(30),12,14,25(26),27-hexaene (**96**) have been studied at 25 °C and 1.0 M ionic strength under a variety of conditions [100]. All reactions occur in the stopped-flow time scale and results indicate that upon addition of a large excess of acid the dinuclear complexes convert rapidly into mononuclear species in which some nitrogen atoms of the ligand are uncoordinated. The kinetics of decomposition of the resulting mononuclear species are intermediate between those of complexes with linear polyamines and those with mononucleating macrocycles. However, the formation of Cu^{II} complexes at high concentrations of OH^- occurs essentially through the reaction of $Cu(OH)_3^-$ with the unprotonated form of the ligand, at a rate similar to that observed for reactions with simpler ligands. Coordination of the second Cu^{II} is very rapid under these conditions.



(96)

The protonation, as well as the metal-binding constants with M^{2+} for the macrocyclic hexadentate ligands **97** {3,6,14,17,23,24-hexaazatricyclo[17.3.1.1(8,12)]-tetracosa-1(23),8,10,12(24),19,21-hexaene} and **98** {3,7,15,19,25,26-hexaazatricyclo[19.3.1.1(9,13)]hexacosa-1(25),9,11,13(26),21,23-hexaene} have been determined at 25 °C in 0.1 mol dm^{-3} KNO_3 or KCl [101]. The heats of protonation and of complexation with Cu^{2+}, Cd^{2+} and Pb^{2+} were determined calorimetrically. The value for the fourth protonation step of **97** showed a medium dependency, being much higher in KNO_3(aq) than in KCl(aq). Mononuclear 1:1 metal- ion complexes were identified with **97** and **98**. Electronic spectral data indicate octahedral six-coordination for the complexes of Cu^{2+} and Ni^{2+} with **97** and **98**. Copper(*n*) was also been shown to form a monoprotonated mononuclear complex and a dinuclear complex with **98**. The larger stability determined for Cu^{2+} with **97** relative to that with the fully saturated 1,4,7,10,13,16-hexaazacyclooctadecane is explained as being entirely due to a more favourable entropy change, indicating that ligand preorganization is the main reason for the increased stability. The metal-ion affinity of **98** is lower than that of **97** owing to the less exothermic heats of complexation.



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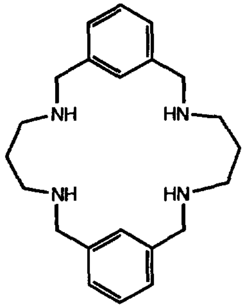
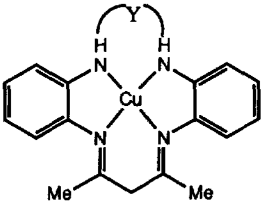


(98)

A new series of 13–14-membered tetraazamacrocyclic complexes [M(**99**)]X_2 (M = Ni^{II} and Cu^{II}, X = Cl or NO_3) have been synthesized by template condensation reaction of *o*-bromoaniline, 2,4-pentanedione and primary diamines in methanol solution and have been characterized through IR, ^1H NMR, EPR and electronic spectral studies, conductivity and magnetic susceptibility measurements [102]. A square-planar geometry is proposed for the nickel and copper complexes.



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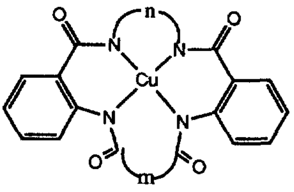


(100)

A new series of 16–18-membered tetraazamacrocyclic copper(II) complexes [Cu(**100**)]Cl_2 have been prepared via the template condensation reaction of *o*-aminobenzoic acid with phthalic or glutaric acid and 1,2-diaminoethane or 1,3-diaminopropane [103]. These complexes have been characterized by IR, ^1H NMR, EPR and electronic spectral studies, and conductivity and magnetic susceptibility measurements. A square-planar geometry has been assigned for the copper centre.

Metal phthalocyanines (M = Cu, Ni, Co) bearing four 16-membered diazadithia macrocycles at the peripheral positions have been prepared [104]. Detosylation with concentrated sulfuric acid afforded products containing both sulfonated groups on the aromatic rings of the macrocyclic substituents which had a high solubility in water and donor sites for binding four Cu^{II} ions to give a pentanuclear complex. When R′ = SO_3Na or SO_3H the complex is soluble in water. In extremely dilute solutions of CH_2Cl_2 ($\approx 10^{-6}$ mol dm^{-3}) the molecules are present as monomers, but an increase in concentration leads to aggregation.

The kinetic parameters for the formation of the sitting-atop (SAT) complex of the copper(II) ion with 5,10,15,20-tetraphenylporphyrin (H_2tpp) were directly determined in acetonitrile [105]. The large $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values imply that deformation of the porphyrin ring is required during the activation process. In the SAT complex, the protons bound to the pyrrole nitrogen atoms remain on the nitrogen atoms and, by the addition of a base such as pyridine, they are abstracted to form the Cu(tpp) complex, in which the copper(II) ion is incorporated into the porphyrin core. This is claimed as the first report indicating direct evidence for the existence of the SAT complex in solution. The kinetics for the formation of the SAT complex and the proton abstraction process from the SAT complex are very important in order to understand the general metallation mechanism of porphyrins.

The three regioisomers of β-cyclodextrin 6-difunctionalized with NH_2 groups have been synthesized and their binary and ternary copper(II) complexes with amino acids characterized by ESR and electronic spectroscopy [106]. The binary copper(II) complexes have been investigated in eluents for ligand exchange chromatography to resolve racemates of unmodified amino acids.

A thermodynamic and spectroscopic investigation has been carried out on the protonation and copper(II) complexation of the 6-diethylenetriamine derivative of β-cyclodextrins [107]. By ^{13}C NMR titration, the order of protonation of the three nitrogen atoms has been ascertained. The unusual entropy changes accompanying the different steps of protonation, as well as the copper(II) complexation, are discussed. The Cu^{II} centre in the complex $[Cu(CDdien)]^{+}$ is in a square-planar arrangement with the three nitrogen atoms from the pendant arm and with the fourth site occupied by an oxygen atom from a coordinated water molecule.

A pH titration study shows that 6(A)-((2-(bis(2-aminoethyl)amino)ethyl)-amino)-6(A)-(deoxy-β-cyclodextrin) (β CDtren) forms binary metallocyclodextrins, $[M(\beta\,CDtren)]^{2+}$, for which $\log(K/dm^3\,mol^{-1}) = 11.65 \pm 0.06$, 17.29 ± 0.05, and 12.25 ± 0.03 respectively, when $M^{2+} = Ni^{2+}$, Cu^{2+}, and Zn^{2+}, where K is the stability constant in aqueous solution at 298.2 K and $I = 0.10$ mol dm^{-3} ($NaClO_4$) [108]. The ternary metallocyclodextrins $[M(\beta\,CDtren)Trp]^{+}$, where Trp^{-} is the tryptophan anion, are characterized by $\log(K/dm^3\,mol^{-1} = 8.2 \pm 0.2$ and 8.1 ± 0.2, 9.5 ± 0.3 and 9.4 ± 0.2, and 8.1 ± 0.1 and 8.3 ± 0.1 respectively, where the first and second values represent the stepwise stability constants for the complexation of (R)- and (S)-Trp^{-} respectively, when $M^{2+} = Ni^{2+}$, Cu^{2+}, and Zn^{2+} respectively. From comparisons of stabilities and UV–VIS spectra, the binary and ternary metallocyclodextrins appear to be six-coordinate when $M^{2+} = Ni^{2+}$ and Zn^{2+} and five-coordinate when $M^{2+} = Cu^{2+}$. The factors affecting the stoichiometries and stabilities of the metallocyclodextrins, are discussed and comparisons are made with related systems.

3.2. *Mononuclear complexes with acyclic ligands*

3.2.1. *Nitrogen coordination*

The stability constants of the ternary complexes [MAL] (where M(II) refers to Cu^{II} and Ni^{II}, A refers to diethylenetriamine and dipropylenetriamine and L refers to catecholate, *o*-amino phenolate, *o*-phenylenediamine, oxalate, malonate, glycinate, beta-alaninate, ethylenediamine and 1,3-diaminopropane) have been determined potentiometrically [109]. The crystal structure of $[Cu(DET)en](ClO_4)_2$ has been determined by single-crystal X-ray diffraction.

Complexes with different structural features were formed from the reaction of $Cu_2(MeCOO)_4(H_2O)_2$ with various *N*-methyl derivatives of diethylenetriamine (dien) in the presence of ClO_4^- or PF_6^- [110]. The four compounds $[Cu(Me_5dien)(MeCOO)(H_2O)](ClO_4)$, $[Cu(1,4\text{-}Me_2dien)(MeCOO)](ClO_4)$, $[Cu(1,1\text{-}Me_2dien)(MeCOO)]_n(ClO_4)_n$ and $[Cu[1,2\text{-}Me_2dien)(MeCOO)]_n(PF_6)_n$ were obtained and studied by crystallographic methods. The differences between the three perchlorate compounds arise in the coordination modes exhibited by the acetato groups: monodentate terminal, asymmetric chelating and syn–anti bridging.

The structures of aqua-di(1,3-diaminopropane-*N*,*N*′)copper(II) dichloride $[Cu(tn)_2H_2O]Cl_2$ and chloro-di(1,3-diaminopropane-*N*,*N*′)copper(II) chloride methanol solvate $[Cu(tn)_2Cl]Cl \cdot MeOH$ (tn = 1,3-diaminopropane) were determined by single-crystal X-ray methods [111]. If the remote chloride is not taken into consideration, the coordination polyhedron in $[Cu(tn)_2H_2O]Cl_2$ is a square-pyramid around the copper(II) cation. The distances from the central copper(II) cation to the two nearest chloride ions are different in $[Cu(tn)_2Cl]Cl \cdot MeOH$, 2.736(2) and 3.322(2) Å. In both compounds the chelate rings display a chair conformation. In $[Cu(tn)_2H_2O]Cl_2$ the two tn ligands are coordinated to copper in a *syn*-like fashion, whereas in $[Cu(tn)_2Cl]Cl \cdot MeOH$ the rings are in a normal *anti*-like conformation. The optimized *syn*-like conformation is favoured by 16.38 kJ mol^{-1} over the optimized *anti*-like conformation of the $[Cu(tn)_2(H_2O]^{2+}$ cation.

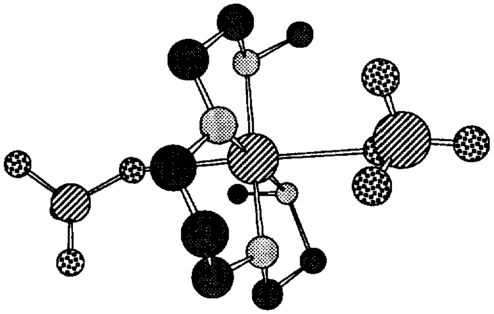
The structure of (acetonitrile)[tris(3-amino-propyl)amine-*N*,*N*′,*N*″,*N*‴]copper(II) diperchlorate has been determined [112]. The structure consists of (acetonitrile)[tris(3-amino-*n*-propyl)amine-*N*,*N*′,*N*″,*N*‴]copper(II) cations and perchlorate anions linked by an extensive network of weak N–H···O and C–H···O hydrogen bonds. The Cu^{II} atom has a coordination geometry intermediate between tetragonal-pyramidal (with one of the three primary amine N atoms occupying the apical coordination site) and trigonal-bipyramidal (with the tertiary amine and acetonitrile N atoms in the axial positions).

A study has been carried out to determine the effects of the C- and N-substituents of the amino acid ligands on the stabilities of the mixed-ligand copper(II) complexes $[Cu(pmdt)(Am)]^+$ containing *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdt) and ten different α-amino acid anions (Am^-) and their absorption, circular dichroism (CD) and ESR spectra [113]. The stability depression of the N-substituent is large, whereas that of the C-substituent is quite small without regard to its bulkiness. This distinguishable substituent effect is assigned to the ternary complexes being five-coordinate type with a trigonal-bipyramid-based geometry.

Copper(II) and H^+ complexes of 3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioxime, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime and 3,3,10,10-tetramethyl-4,9-diazadodecane-2,11-dione dioxime have been studied at 25 °C and ionic strength 0.15 mol dm^{-3} NaCl, using glass-electrode potentiometry [114]. Electronic spectra have been used to postulate structures for the different species in solution. In each case the metal binds to the four nitrogen atoms of the oxime. In the MLH_{-1} species, hydrogen bonding between the terminal oxime groups produces a pseudo-macrocycle. Computer simulation has been used to predict the effect of the ligands on the blood-plasma metal- ion distribution *in vivo*.

The syntheses of the aliphatic tripodal tetramine ligands $N(CH_2CH_2CH_2NH_2)_3$, $N[(CH_2CH_2CH_2NH_2)_2(CH_2CH_2NH_2)]$, and $N[(CH_2CH_2CH_2NH_2)(CH_2CH_2NH_2)_2]$ have been reported [115]. The tripodal N_4-ligands react with $Cu(OH)_2$ in water to give blue copper(II) complexes and addition of NH_4PF_6 to such solutions yields complexes of the type $[Cu(N_4)(NH_3)](PF_6)_2$ (N_4=1,2,3) depending on the ligand. The molecular structures of the complexes have been determined by X-ray diffraction, with all three complexes being crystallized from water. The complex dications exhibit a trigonal-bipyramidal geometry with the tertiary nitrogen of the tripodal ligand and the ammonia nitrogen in the axial positions. Complexes with the unsymmetric ligands possess both five- and six-membered chelate rings. Depending on the ligand, the size of the cavity for the ammonia ligand increases, which leads to a shortening of the Cu–NH_3 bond length.

The structure of diperchlorato[(2*RS*,5*SR*,9*RS*,12*RS*)-2,5,9,12-tetraazatridecane]copper(II), $[Cu(C_9H_{24}N_4)(ClO_4)_2$ (**101**), has been determined and shows the Cu^{II} ion is six-coordinate in a distorted square-bipyramidal environment with four tetraamine N atoms equatorial and two O atoms, one from each perchlorate ion, axial [116]. The tetradentate ligand is in its stable planar conformation with the central six-membered chelate ring in a chair form and both terminal five-membered rings in gauche forms. The four chiral N-atom centres have configurations 2*RS*, 5*SR*, 9*RS* and 12*RS*.



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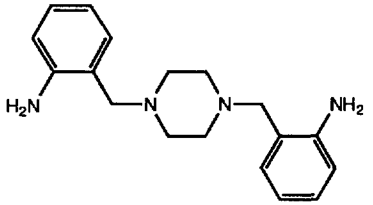
A series of copper(II) complexes with tripodal polypyridylmethylamine ligands, such as tris(2-pyridylmethyl)amine (tpa), ((6-methyl-2-pyridyl)methyl)bis(2-pyridylmethyl)amine (Metpa), bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine (Me_2tpa), and tris((6-methyl-2-pyridyl)methyl)amine (Me_3tpa), have been synthesized and characterized by X-ray crystallography [117]. The Cu atoms of the complexes $[Cu(H_2O)(tpa)](ClO_4)_2$, $[CuCl(Metpa)]ClO_4$, $[CuCl(Me_2tpa)]ClO_4$, $\{[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]ClO_4\}$ have pentacoordinate geometries with three pyridyl and one tertiary amino nitrogen atoms, and a chloride or aqua oxygen atom. A nitrite ion is coordinated to the Cu(II) centre of Metpa,

Me_2tpa and Me_3tpa complexes through only one oxygen atom forming nitrito adducts. The cyclic voltammograms of $[Cu(H_2O)(Me_n tpa)]^{2+}$ ($n=0,1,2,3$) in the presence of NO_2^- in H_2O (pH 7.0) revealed that the catalytic activity for the reduction of NO_2^- increases in the order $Me_3tpa \ll Me_2tpa \ll Metpa < tpa$ complexes.

1,4-Bis(*o*-aminobenzyl)-1,4-diazacyclohexane (**102**) has been synthesized and its coordination chemistry with copper(II), nickel(II) and palladium(II) investigated [118]. Reaction of **102** with $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ in $CHCl_3$–EtOH produced blue crystals of square-planar [Cu(**102**)]$[ClO_4]_2$ and five-coordinate [Cu(**102**)(H_2O)]$[NO_3]_2 \cdot H_2O$ respectively. The crystal structures of the complexes have been determined by X-ray crystallography. In the solid state the ligand is always equatorially coordinated in a transoid fashion where one of the two Cu–N-amine–C–C–C–N-aniline chelate rings adopts a boat and the other a twist-boat conformation. Recrystallization of [Cu(**102**)]$[ClO_4]_2$ from MeCN produced blue crystals of [Cu(**102**)]$[ClO_4]_2 \cdot$ 2MeCN.



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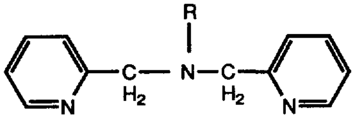
The solid state structures of dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate and dichlorobis[dimethyl 2,6-dimethyl-4-(2-nitrophenyl)pyridine-3,5-dicarboxylate-*N*]copper(II)}, two decomposition products of the calcium channel blocker nifedipine, have been determined and show approximately perpendicular orientations of the pyridine and phenyl rings [119]. Unlike in the parent compound, the ester groups are not coplanar with their pyridine ring, but the nitro and nitroso substituents are coplanar with their respective phenyl rings.

Re-examination of the X-ray data of the complex $[Cu(tppa)(O_2)]ClO_4$ (tppa = tris[6-(pivaloylamido-2-pyridyl)methyl]amine) suggests that it was incorrectly interpreted as having an η' "end-on" superoxide, but it is a monocopper hydroxide complex [120, 121]. The complex has been independently synthesized and structurally characterized.

The novel Cu,Zn, superoxide dismutase (Cu_2Zn_2SOD) mimic compound $[Cu(appn)](ClO_4)_2 \cdot H_2O$ (where appn = *N*,*N'*-propylenebis(2-actoylpyridineiminato)) has been prepared [122]. Single-crystal X-ray analysis revealed that the copper(II) ion has a distorted square-pyramidal environment very similar to that of Cu_2Zn_2SOD with the basal positions occupied by four nitrogen atoms from the Schiff base ligand and the apical position by an oxygen atom of a hydrate molecule. The Cu–N and Cu–O bond lengths are 1.972(2)···2.029(2) Å and 2.326(2) Å respectively.

A study of the relaxation of pBR322 form I DNA by copper(II) complexes and hydrogen peroxide systems found it to be highly dependent on the chelate structure of the copper(II) complex used [123]. The complexes used had the general formula Cu(**103**)Cl$^+$, where **103** is a tetradentate ligand, and the X-ray structures of two of the complexes have shown the copper(II) centre in a square-pyramidal environment. This study suggests that the active species for nicking the DNA may be a copper(II) hydroperoxide adduct.



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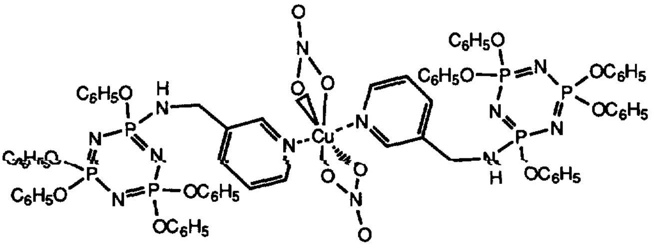


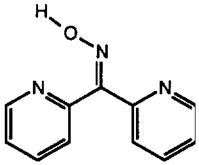
(104)

The solid state structure (**104**) of the product formed from the reaction of 3-(aminomethyl)pyridylpentaphenoxycyclotriphosphazene, an *N*-donor ligand with five nitrogen atoms as potential coordination centres, with copper(II) nitrate has been determined and shows that the copper ion is coordinated by two nitrogen atoms of the pyridine rings and four oxygen atoms of the unsymmetrical didentate nitrate groups in a Jahn–Teller distorted octahedral arrangement [124].

The structure of the complex dichloro(di-2-pyridylamine-*N*,*N*′)copper(II), [$CuCl_2(C_{10}H_9N_3)$], has been determined as being a monomer, with the Cu atom in a rather distorted tetrahedral environment provided by two Cl^- ions and two N atoms from the didentate bipyridine derivative [125]. The deformation of the coordination tetrahedron is due to the Cl^- ion taking part in intramolecular interactions.

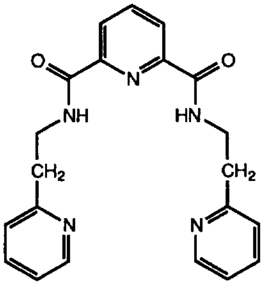
The solid state structure of the complex dibromo[*N*-(2-pyridylmethylidene)-2-pyridylmethylamine-*N*,*N*′,*N*″]copper(II) has also been shown to be a monomer, with the environment around the Cu^{2+} ion being a square-pyramid with one Br^- ion occupying the apical site and the other Br^- ion at a basal position [126].

Single crystals of di-μ-chlorobis((*N*,*N*′-2-pyridyl-2′-pyridinium) ketone oxime) aquochlorocopper(II) were isolated from an aqueous solution and have been structurally characterized [127]. The structure revealed that di-2-pyridylketone oxime (**105**) does not bridge the metal centres but coordinates separately to the Cu cations through one pyridine nitrogen atom and the nitrogen atom of the Schiff base. The nitrogen atom of the second pyridine ring is protonated and is not involved in coordination. The copper centre has a distorted octahedron geometry and includes Cu–Cl bond lengths up to 3.053(3) Å in the coordination sphere of the copper cation.



(105)

The Cu(II) complex of *N*,*N'*-bis(2-(2-pyridyl)ethyl)-pyridine-2,6-dicarboxamide (**106**), a ligand with two amide moieties, has been isolated and structurally characterized [128]. The copper centre in this distorted square-pyramidal complex is coordinated to two deprotonated amido N donors and is situated 0.41 Å above the mean basal plane.



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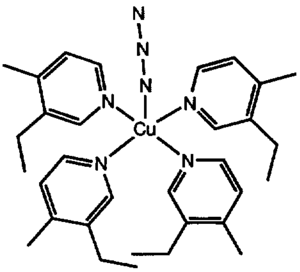

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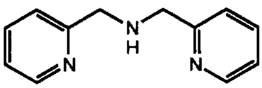


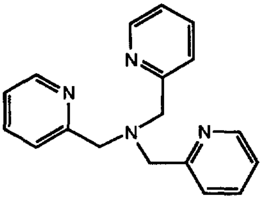
(108)

The complex $[Cu(tren)(DMP)](ClO_4)_2 \cdot CH_3CN$ (where tren is tris(2-aminoethyl)amine, DMP is 4-dimethylaminopyridine) has been synthesized and characterized [129]. The X-ray crystal structure reveals that the copper(II) ion is in a distorted trigonal-bipyramidal geometry with the three primary amine groups of the tren ligand forming the equatorial plane and the tertiary amine and the 4-dimethylaminopyridine molecule on the apical positions.

The preparation and structural characterizations of two new copper(II) azido complexes of 3-ethyl-4-methylpyridine (β-collidine), namely azido tetrakis(β-collidine) copper(II) perchlorate (**107**) and di-μ(1,1)-azido-[diazido-tetrakis(β-collidine)]dicopper(II) are described [130]. The mononuclear structure consists of isolated $[Cu(\beta\text{-collidine})_4(N_3)]^+$ cations and ClO_4^- anions. The copper atom in the cation is in a tetragonal-pyramidal environment with four collidine ligands occupying the basal sites (Cu–N = 2.033(4) Å) and a terminal azido ligand at the apical position with a Cu–N distance of 2.141(6) Å. The dinuclear molecule features monodentate collidine ligands, di-μ(1,1)-azido-bridged Cu_2N_2 rings, terminal azido ligands and distorted square-pyramidal copper(II) coordination geometry.

The solid state structure of bright blue crystals of Cu(**108**)$_2$(BF$_4$)$_2$ shows that two structurally different complex cations are present in the same unit cell, one hexacoordinate and the other pentacoordinate [131]. In the hexacoordinate cation, the two tridentate bis(2′-picolyl)amine ligands (**108**) are trans-facially coordinated with two pyridine nitrogen atoms and the two secondary amine nitrogen atoms situated on four positions in a plane. The remaining two pyridine nitrogen atoms complete the pseudooctahedral geometry. The pentacoordinate cation possesses a square-pyramidal configuration, the two secondary nitrogen atoms being mutually cis, with one ligand equatorially tridentate. The other ligand functions as a didentate ligand, with one of the pyridine nitrogen atoms occupying the equator and the aliphatic nitrogen defining the axial copper position. Its second pyridine is uncoordinated but hydrogen-bonded to the coordinated NH of the other ligand. Solution properties offer no clear distinction between the two cation stereochemistries. The ternary chelates [Cu(**108**)(Acac)]ClO$_4$ and [Cu(**108**)(bpy)(ClO$_4$)$_2$ are also described.

Coordination complexes of tris(2-pyridylmethyl)amine (**109**) were prepared and characterized, including [Cu(**109**)Br]ClO$_4$ [132]. The solid-state structure of Cu(**109**)BrClO$_4$ contains a trigonal-bipyramidal metal ion with halide coordinated in an apical position.



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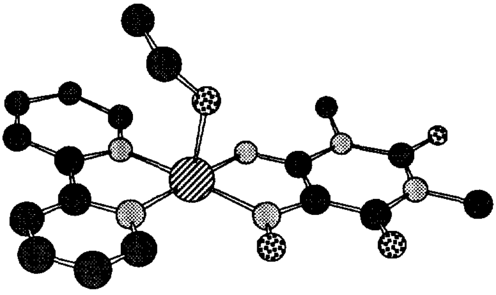


(110)

In absolute ethanol medium, copper(II) nitrate reacts with 6-amino-1,3-dimethyl-5-nitrosouracil (HDANU) and 2,2′-bipyridine to give a mixed complex with the formula [Cu(DANU)(bpy)(EtOH)](NO$_3$) (**110**) [133]. The solid state structure consists of monomeric CuN$_4$O units in which the copper ion displays a 4+1 square-pyramidal coordination. The base of the polyhedron is occupied by four nitrogen atoms, two from bpy and the other two from 5-nitroso and 6-amino groups of the uracil derivative in the N6-mono-deprotonated form, leaving two five-membered chelate rings. An O-coordinated ethanol molecule with a long Cu–O distance (2.248 Å) is located in the apical position of the pyramid, the metallic centre being 0.144 Å above the base of the polyhedron. The nitrate group is out of the coordination sphere, stabilizing the complex by hydrogen bonds formed between the hydrogen atom attached to the ethanolic oxygen and an oxygen atom from the nitrate group.

The oxidation of 35 monosubstituted benzaldehydes by bis(2,2′-bpy)copper(II) permanganate in aqueous acetic acid leads to the formation of the corresponding benzoic acids [134]. The reaction is first order with respect to the complex. The oxidation of the deuterated benzaldehyde (PhCDO) indicated the presence of a substantial kinetic isotope effect. Kinetic studies suggest the presence of an electron-deficient reaction centre in the rate-determining activated complex.

A new copper complex containing 2,2′-dipyridylbenzamide (dpba), Cu(dpba)$(NO_3)_2(CH_3CN)$, has been synthesized and characterized [135]. The copper has a square-pyramidal geometry containing an acetonitrile molecule in the axial site. The redox property of the Cu(dpba)$(NO_3)_2$ complex is different from that of corresponding copper–dpa complex.

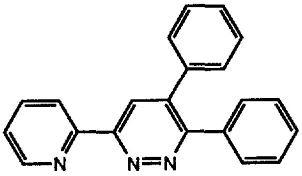
The crystal structures of (3-amino-6,6′-dimethyl-2,2′-bipyridine)dichloro-copper(II) and aqua[3-imido-6-(methoxycarbonyl)-2,2′-bipyridine-6′-carboxylato]copper(II), have been determined [136]. In the complex (3-amino-6,6′-dimethyl-2,2′-bipyridine)dichlorocopper(II) the copper(II) centre exhibits tetrahedral coordination to the bipyridyl nitrogen atoms of the ligand and two chlorine atoms, whereas in aqua[3-imido-6-(methoxycarbonyl)-2,2′-bipyridine-6′-carboxylato] copper(II) the Cu^{II} centre is square-planar with a slight tetrahedral deformation, and coordinates to an imino nitrogen, adjacent pyridyl nitrogen, carboxylate oxygen and a water molecule.

The stability constants of the 1:1 complexes formed between $Cu(Arm)^{2+}$, where Arm = bpy or phen, and methyl phosphate, $CH_3OPO_3^{2-}$, or hydrogen phosphate, $HOPO_3^{2-}$, were determined by potentiometric pH titration in aqueous solution (25 °C; $I=0.1$ M, $NaNO_3$) [137]. The Cu(Arm)$(HOPO_3)$ complexes are slightly more stable (on average by 0.15 log unit) than expected on the basicity of HPO_4^{2-}. This is explained as a consequence of more effective solvation including hydrogen bonding, an interaction not possible with coordinated $CH_3OPO_3^{2-}$ species. The relevance to biological systems is discussed.

A new ligand formation was observed in the complex, $[Cu(C_4H_4N_3O_2)\{N(CN)_2\}(C_{10}H_8N_2)]$, as a result of the nucleophilic addition reaction between methanol and dicyanonitrosomethanide in the inner coordination sphere of a Cu^{II} atom [138]. This new ligand, 3-amino-3-methoxy-2-nitrosoacrylonitrilate (add), $[NHC(OMe)C(CH)NO]^-$, is coordinated as a chelate, forming a five-membered metallocycle with Cu^{II}. The distorted tetragonal-pyramidal coordination is completed by one chelate-coordinated molecule of 2,2′-bipyridine and one end-coordinated dicyanamide anion, $[N(CH)_2]^-$. The four N atoms of the two metallocycles form the base and a fifth N atom, from the dicyanamide anion, forms the apex of the pyramid, creating a $\{CuN_5\}$ chromophore. The structure of $[Cu(add)(bpy)\{N(CN)_2\}]$ consists of discrete molecules.

The crystal structure of $[Cu(C_{12}H_8N_2)_2\{N(CN)_2\}]$–$[C(CN)_3]$ is formed by discrete $[Cu(phen)_2\{N(CN)_2\}]^+$ cations and $[C(CN_3]^-$ anions (phen = 1,10-phenanthroline) [139]. The coordination polyhedron of Cu^{II} is a distorted trigonal-bipyramid with a CuN_5 chromophore.

Copper(II) complexes of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (**111**) with ClO_4^-, BF_4^-, NO_3^-, Cl^- and Br^- as counter ions have been prepared [140]. The crystal structure of the complex $[Cu(\mathbf{111})_2(H_2O)_2][ClO_4]_2$ has been determined. The coordination geometry of the copper ion is elongated octahedral, the equatorial plane being formed by the N_2 nitrogen atoms of both the triazine units and two pyridyl nitrogen atoms and the axial positions being occupied by water molecules. The two **111** ligands are strictly coplanar to each other. The electronic and EPR spectral properties illustrate the strong axial interaction by solvent molecules with the weakly ligated CuN_4 plane. The spectral and electrochemical behaviour of the copper(II) complex of 3-(2-pyridyl)-5,6-bis(*p*-sulfonatophenyl)-1,2,4-triazine, the sulfonato derivative of **111**, in aqueous solution at various pH revealed that it could not act as an efficient catalytically active redox agent.



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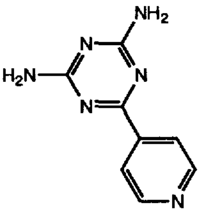

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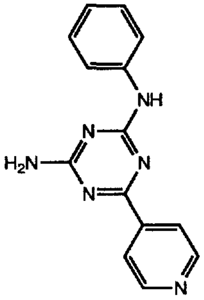
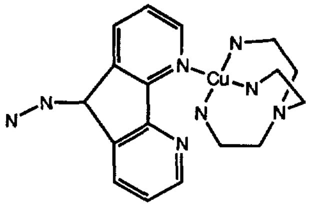


(113)

The crystal structure of two ligands based on 2,4,6-triamino-1,3,5-triazine (**112** and **113**) have been determined and their hydrogen-bonded and π–π stacked supramolecular structures have been analysed [141]. Two copper(II) complexes of these ligands illustrate the formation of metal-ion-directed self-assembled superstructures whose networks are markedly modified as a consequence of the introduction of the coordinated metal centres.

The crystal and molecular structures of green *cis*-$[Cu(NCS)_2(phen)_2]$ containing a distorted octahedral core are reported [142]. The structure shows the geometry is distorted from octahedral stereochemistry because of the 86.9(2)° N–Cu–N bite angle of each 1,10-phenanthroline and because of a slight elongation of the trans positions that are occupied by an N atom from each phenanthroline ligand. The thiocyanate ions coordinate through the nitrogen atoms and are linear (N–C–S = 178.9(6)°) and are at an angle of 161.0(6)° to the Cu atom.

The crystal structure of $[Cu(NCS)(C_{12}H_8N_2)_2][C(CN)_3]$ is reported [143]. The structure comprises discrete $[Cu(phen)_2(NCS)]^+$ cations and $[C(CN)_3]^-$ anions. The coordination polyhedron of Cu^{II} is a distorted trigonal-bipyramid with a CuN_5 chromophore. The compound, tris(2-aminoethyl)amine-4,5-diazafluorene-9-hydrazine copper(II) perchlorate complex, (**114**), has been designed, synthesized and characterized [144]. The X-ray analysis reveals that the copper(II) is coordinated by four nitrogen atoms from tris(2-aminoethyl)amine (tren) and two nitrogen atoms from 4,5-diazfluorene-9-hydrazine (dzfh) to form an unusual (4 + 1 + 1′) six-coordinate geometry. This structure is very rare and is claimed to be a unique example of a tripodal copper(II) complex with an asymmetric didentate phenanthroline derivative. For comparison, the complex, $Cu(tren)(py)ClO_4)_2$ (py is pyridine) was also synthesized and characterized.



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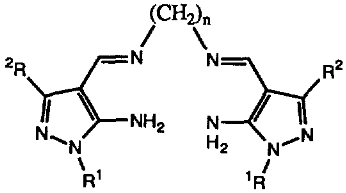


(115)

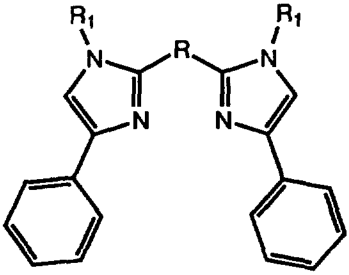
The ligand 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene (L), reacted with copper(II) chloride, cobalt(II) chloride and zinc(II) chloride to form $[CuLCl_2]$, $[CoLCl_2]$ and $[ZnLCl_2]$ respectively [145]. The structures of these metal complexes have been determined by X-ray crystallography. The Co and Zn structures are isomorphous with distorted tetrahedral metal geometries. The coordination sphere of the copper(II) ion in its complex is intermediate between distorted tetrahedral and distorted square-pyramidal geometry, if a weak Cu···O interaction is taken into account.

Two series of copper(II) and nickel(II) complexes [M(**115**)] containing deprotonated tetradentate *N,N′*-bis(5-aminopyrazol-4-ylmethylene)polymethylene diamine ligands (**115**) varying in length *n* ($n=2$–4) of the bridge have been prepared and investigated by ^1H NMR, UV/VIS and ESR spectroscopy and cyclic voltammetry measurements [146]. Complexes [Cu(**115**)] display a gradual alteration of the configuration at the metal centre from planar to pseudo-tetrahedral when the bridge is lengthened from $n=2$ to 4, as indicated by the variations in their ESR spectral parameters. This was also reflected in the electronic spectra, which exhibited a red shift of the ligand-field bands in this series.

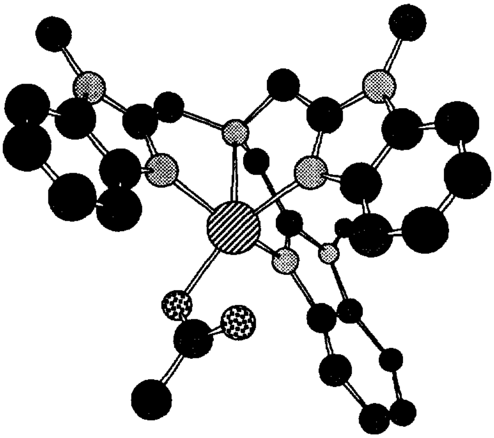
In *mer*-bis[2,6-bis(1-phenyliminoethyl)pyridine-*N,N′,N″*]copper(II) diperchlorate two tridentate N-donor ligands coordinate to a copper(II) centre to give a distorted octahedral environment [147]. The two ligands are approximately orthogonal, with an angle of 89.7(2)° between the two CuN_3 planes. One of the ligands lies further from the Cu atom, its Cu–N–imino distances (mean 2.31 Å) being 0.21 Å longer than the corresponding distances for the second ligand, an effect which is due to Jahn–Teller distortion.

The complexes $[CuL_2(Him)_2]\cdot MeOH$ and $[CuL_2(mim)_2]\cdot H_2O$ (HL = 4-amino-*N*-(thiazol-2-yl)-benzenesulfonamide, Him = imidazole, mim = *N*-methylimidazole) have been prepared and their crystal structures determined [148]. In $[CuL_2(Him)_2]\cdot MeOH$ the metal centre has a very irregular stereochemistry, being coordinated by six nitrogen atoms, two of them from the imidazole ligands and the other four from three sulfonamides, one belonging to an adjacent asymmetric unit. The crystal packing shows stacking interactions between the imidazole and phenyl rings of the sulfonamide. In $[CuL_2(mim)_2]\cdot H_2O$ the coordination geometry is intermediate between square-pyramidal and trigonal-bipyramidal. The *in vitro* O_2^- scavenger activity of the complexes shows that they exhibit high superoxide-dismutase mimetic activity.

Five new sterically hindered bis(imidazole) proligands have been synthesized, including 1,2-bis(1-ethyl-4-phenylimidazol-2-yl)ethane (**116**) [149]. Complexation reactions were attempted with $Cu(BF_4)_2 \cdot 4.5H_2O$ but only (**116**) formed a simple monomeric complex, $[Cu(\mathbf{116})_2][BF_4]_2$. The Cu^{II} is coordinated by four nitrogen atoms, $Cu–N_{av} = 2.01$ Å, in an essentially square-planar environment. In CH_2Cl_2 the complex displays a quasi-reversible $Cu^{II}–Cu^{I}$ couple with an oxidation peak at +0.74 V and a coupled reduction at −0.07 V (scan rate of 0.2 V s^{-1}).



(**116**), R_1=Et



(**117**)

The crystal and molecular structures of $[Cu(imidazole)_4(CF_3SO_3)_2]$ have been determined using three-dimensional X-ray diffraction data [150]. The copper(II) ion is coordinated centrosymmetrically by four imidazole ligands forming an equatorial plane, mean Cu–N = 2.010 Å, and by two trifluoromethanesulfonate ions at the axial sites, Cu–O = 2.593(5) Å. The dihedral angles between the imidazoles and the CuN_4 plane are 88.6° and 59.4°.

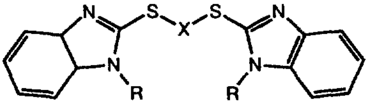
Reaction of $Cu(OAc)_2 \cdot H_2O$ with the tripodal polybenzimidazole ligands tris(*N*-methyl-1-benzimidazole-2-yl)amine and tris(*N*-ethyl-1-benzimidazol-2-yl)amine in the presence of excess of $NaClO_4$ resulted in the formation of mononuclear Cu^{II} complexes $[CuL(OAc)]ClO_4 \cdot 5H_2O$ (**117**) and $[Cu(L)(OAc)]ClO_4 \cdot 1.5H_2O$ respectively [151]. The single-crystal structure of the complex (**117**) was determined by X-ray diffraction. The geometry around Cu is best described as a distorted trigonal-bipyramid comprising four nitrogen atoms from the tripodal ligand and one oxygen atom from the monodentate ligand.

Cu^{II} and Ni^{II} coordination compounds with *N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl)methyl]-1,2-cyclohexanediamine (CDTB) have been prepared and characterized [152]. The crystal structure of $[Cu(CDTB)](ClO_4)_2$ has been determined. The geometry around the Cu atom is highly irregular and can best be described as a cis-distorted octahedron, with four short Cu–N bond distances of 1.988(3) Å and 2.028(3) Å, and two very long Cu–N bond lengths of 2.543(4) Å. The *cis* N–Cu–N chelate angles in the complex range from 68.8(2)° to 141.03°. The cyclic voltammogram of the complex shows a fully reversible one-electron redox wave at $E_{1/2}=0.162$ V *vs* standard calomel electrode, corresponding to the Cu-I/II redox couple.

Mixed-ligand diethylenetriamine copper(II) complexes of the type Cu(LL)(dien)(X), where dien is diethylenetriamine, LL is 2,2′-biimidazole (bimH$_2$), 1,10-phenanthroline, 2,2′-bipyridine and ethylenediamine, and X is ClO$_4$ and CF$_3$SO$_3$, have been synthesized and characterized by elemental analyses and electronic, vibrational and EPR spectroscopic measurements [153]. The crystal and molecular structure of [Cu(bimH$_2$)(dien)](ClO$_4$)$_2$ has been determined using three-dimensional X-ray diffraction data. The copper(II) ion is coordinated by a diethylenetriamine and a biimidazole ligand, forming a distorted CuN$_5$ square-pyramid with one of the imidazole moieties bound at the apical position. The biimidazole is nearly perpendicular to the CuN$_4$ basal plane with a bite angle of 78.6(5)°. Gaussian resolved d–d spectra for these square-pyramidal diethylenetriamine complexes yield a one-electron orbital sequence of $d_{x^2-y^2} \gg d_{z^2} > d_{xy}$ similar to d_{yz}. Bonding properties of these complexes are elucidated and show that biimidazole is a strong π-acceptor, whilst 2,2′-bipyridine and 1,10-phenanthroline do not take part in π-interactions.

The copper(I) and copper(II) complexes with the nitrogen donor ligands bis[(1-methylbenzimidazol-2-yl)methyl]amine (1-BB), bis[2-(1-methylbenzimidazol-2-yl)ethyl]amine (2-BB), *N*-acetyl-2-BB (AcBB), and tris[2-(1-methylbenzimidazol-2-yl)ethyl]nitromethane (TB) have been studied as models for copper nitrite reductase [154]. The copper(II) complexes form adducts with nitrite and azide that have been isolated and characterized. The Cu(II)(1-BB) and Cu(II)–AcBB complexes are basically four-coordinated with weak axial interaction by solvent or counterion molecules, whereas the Cu(II)(2-BB) and Cu(II)–TB complexes prefer to assume five-coordinate structures. A series of solid state structures has been determined. In all the complexes the 1-BB or 2-BB ligands coordinate the Cu(II) cations through their three donor atoms. The complexes with 2-BB appear to be more flexible than those with 1-BB. The nitrito ligand is diden tatein [Cu(2-BB)(NO$_2$)](ClO$_4$)(MeCN) and essentially monodentate in [Cu(1-BB)DMSO–O)(NO$_2$)](ClO$_4$). The copper(I) complexes exhibit nitrite reductase activity and react rapidly with NO$_2^-$ in the presence of stoichiometric amounts of acid to give NO and the corresponding copper(II) complexes. Under the same conditions the reactions between the copper(I) complexes and NO$^+$ yield the same amount of NO, indicating that protonation and dehydration of bound nitrite are faster than its reduction. The NO evolved from the solution was detected and quantified as the [Fe(EDTA)(NO)] complex. The order of reactivity of the Cu(I) complexes in the nitrite reduction process is [Cu(2-BB)]$^+$ > [Cu(1-BB)]$^+$ > [Cu(TB)]$^+$ > [Cu(AcBB)]$^+$.

A new synthetic route towards new bis-benzimidazoles, -benzothiazoles and -benzoxazoles (**118**) from readily available starting materials has been established [155]. These compounds have thioethers at the 2-position of the heterocycle and the resultant carbon–thioether linkage is stable under the conditions of synthesis. Two of the new series have been complexed with copper(II) salts. The bis(benzoxazole) series showed no tendency to complex copper(II). The unusual crystal structure of the copper(II) complex with 1,8-bis(benzimidazol-2-ylsulfanyl)-3,6-dioxaoctane has been determined, indicating a four-coordinate copper(II) atom in a distorted square-planar environment. The two bis(benzimidazole) moieties act as didentate ligands with nitrogen donors. The thioether donors of the chain, although apparently ordered around the copper, are too distant to be regarded as donors, but they probably influence the spectroscopic properties of the copper site and are described as quasi-coordinated.



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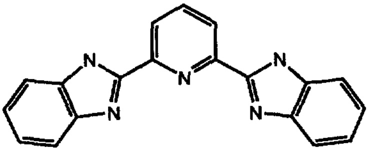


(119)

The crystal structure of the complex $[Cu(\mathbf{119})(H_2O)_2(ONO_2)](NO_3)\cdot H_2O$ (**119** = 2,6-bis(2-benzimidazolyl)pyridine) has been determined by X-ray diffraction methods [156]. The structure is built up of the $[Cu(\mathbf{119})(H_2O)_2(ONO_2)]^+$ cations, NO_3^- anions and crystal lattice water molecules, with a 4+1+1 pseudo-octahedral geometry for the $CuN_3OO'O''$ chromophores. In the EPR spectrum, exchange coupling between Cu(II) chromophores of different orientation is observed.

The influence of the molecular crystalline arrangement upon the state of a Jahn–Teller-active centre has been investigated in crystals of the complex $Cu(mtz)_6(BF_4)_2$, where mtz = 1-methyltetrazole [157]. Crystal structures at 293, 123 and 93 K were determined by X-ray diffraction for the copper complex and also at 293 and 100 K for the analogous zinc complex, $Zn(mtz)_6(BF_4)_2$.

An efficient, catalytic, enantioselective addition of silylketene acetal nucleophiles to (benzyloxy)acetaldehyde using C_2-symmetric bis(oxazolinyl)pyridine Cu(II) complex has been reported [158].

The structure of bis[4-amino-1-methyl-2(1*H*)-pyrimidinone] dichlorocopper(II) consists of discrete $[CuCl_2–(C_5H_7N_3O)_2]$ units [159]. The coordination about the Cu^{II} ion is distorted 4+2 octahedral. The non-equivalent 1-methylcytosine ligands are bonded to the metal through N(3) and more weakly through O(2). The average N–Cu–Cl trans angle is 159.9(1)°.

The crystal structure of tetrakis(cytosine)copper(II) perchlorate dihydrate has been determined [160]. The geometry around the copper centre is a bicapped octahedron (4+2+2*). The adjacent cytosine rings are oriented head-to-tail with respect to each other and are roughly perpendicular to the coordination plane. The exocyclic oxo groups form an interligand, intracomplex hydrogen-bonding network above and below the coordination plane with the exocyclic amino groups of alternate cytosine bases. The EPR and electronic spectra are consistent with the retention of the solid-state structure in solution. The steric effect of the carbonyl group of cytosine is offset by the presence of the intracomplex hydrogen-bonding network.

The kinetics of ascorbic acid oxidation by molecular oxygen, catalysed by bis(histidine)copper(II) (CuL_2^{2+}), was followed in 0.1 M phosphate buffer at pH 7.0

[161]. The oxidation state of the copper ion during the catalysis and the concentration of the ascorbyl radical were followed by ESR and/or by optical spectroscopy and no significant reduction of Cu(II) was observed under vacuum or in the presence of oxygen at ascorbate concentrations <20 mM. Evidence for the binding of ascorbate to CuL_2^{2+} was found by ESR, and a stability constant of 20 M^{-1} was estimated. A mechanism has been suggested which is consistent with the experimental findings and explains some of the contradictory data reported in the past by various authors.

Formation constants of ternary complexes of Cu^{II} with (*S*)-amino-acid amides ((*S*)-phenylalaninamide, (*S*)-prolinamide, and (*S*)-tryptophanamide) and (*R*)- or (*S*)-histidine and (*R*)- or (*S*)-tyrosine were determined potentiometrically in aqueous solution [162]. Significant stereoselectivity was presented by all three amides towards histidine, the diastereoisomeric complexes with "heterochiral" ligands being more stable than those with "homochiral" ligands. The stereoselectivity observed with (*S*)-phenylalaninamide and (*S*)-tryptophanamide are explained on the basis of hydrophobic slacking interactions between 1*H*-imidazole and the aromatic side chain, favoured by the terdentate behaviour of histidine, whereas repulsive effects seem to be prevalent with (*S*)-prolinamide. Only (*S*)-prolinamide and (*S*)-phenylalaninamide show appreciable stereoselectivity with tyrosine, which is didentate, probably on account of repulsive interactions. The results of this study on the stability of ternary complexes in solution have been used to deduce certain aspects of the mechanism of chiral discrimination performed by Cu^{II} complexes of (*S*)-amino-acid amides added to the mobile phase in HPLC.

Aqua[bis(3-aminopropyl)amine-*N*,*N*′,*N*″](glutarato-*O*)copper(II) tetrahydrate, consists of monomeric complex molecules in which the central Cu atom is coordinated by three N atoms from the amine ligand and by one glutarate and one water O atom [163]. The coordination polyhedron is square-pyramidal.

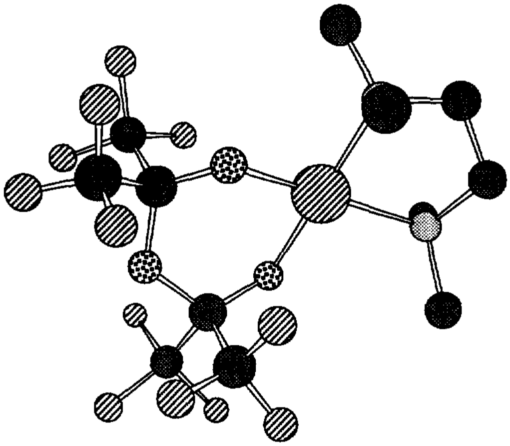
The mononuclear $[Cu(HBPA)_2]^{2+}$ cation within bis[2-(2-pyridylmethylaminomethyl)-phenol]copper(II) diacetate trihydrate, $[Cu(HBPA)_2](CH_3COO)_2 \cdot 3H_2O$, $[Cu(C_{13}H_{14}N_2O)_2](CH_3COO)_2 \cdot 3H_2O$, has a tetragonally elongated coordination polyhedron and represents a rare example of a copper complex in which two phenolic O atoms are axially coordinated to the Cu^{II} centre without deprotonation [164].

3.2.2. *Oxygen coordination*

The structure of tetrakis(dimethyl sulfoxide-*O*)copper(II)bis(perchlorate), $[Cu(C_2H_6OS)_4]^{2+} \cdot 2ClO_4^-$, has been determined and shows a tetrahedrally distorted square-planar arrangement around the central Cu^{II} ion, with all Cu–O bond lengths falling within the range 1.934(6)–1.954(6) Å [165]. One O atom from each of the axial perchlorate anions interacts weakly at distances of 2.466(8) and 2.640(8) Å.

Compounds of the composition $CuX_2(NH_3)_2(H_2O)$ (X = heptanoate, octanoate, nonanoate, decanoate or dodecanoate) were prepared, analysed and characterized by vibrational and electron paramagnetic resonance spectroscopy and by magnetic susceptibility measurements [166]. The crystal and molecular structure of diammineaquabis(decanoato)copper(II) was determined by X-ray diffraction and revealed mononuclear units with (4+2) coordination around the central copper centre.

The complex, [1,1,1,5,5,5-hexafluoro-3-oxa-2,4-bis(trifluoromethyl)-2,4-pentanediolato-*O*,*O*′] - *N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′) copper (II) (**120**), has been shown to contain a condensed dialkoxide ligand which forms a markedly non-planar six-membered chelate ring with a skew-boat conformation [167]. There are two independent molecules in the unit cell. In the first, the absolute conformations of the tetramethylethylenediamine and dialkoxide rings are both Λ and in the second they are Δ and Λ respectively. The mean O–Cu–O angle is 92.6(3)°, with a mean Cu–O bond length of 1.893(3) Å.

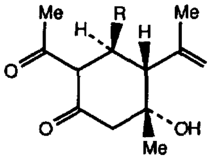


(120)

3.2.3. *Nitrogen and oxygen coordination*

Condensations of tris(2-aminoethyl)amine (tren) with acetylacetone (acac) have been shown to give two different types of complex, depending upon the coexisting metal ions; one contains two tridentate ligands which have β-ketoimine moieties at all primary amino groups of tren, and the other has a pentadentate ligand having a β-ketoimine moiety at one of the three amino groups of tren [168]. In the case of Cu^{2+} the latter structure is obtained, as shown by X-ray crystal structural analysis. The selectivity of the products is discussed in terms of the ionic size and the affinity between the metal ion and the donor atoms.

Mixed-ligand copper(II) complexes with *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) and the β-diketonate moiety of the triketones (**121**), [CuCl(**121**))(tmen)], were synthesized and their solvatochromic properties in organic solvents (due to the acceptor properties of the solvent) investigated [169]. The colour of these five coordinated complexes in the solid state gradually changed from green in [CuCl(**121**)(tmen)] through bluish green, [CuCl(**121**)(tmen)]·CH_2Cl_2, to blue, [CuCl(**121**)(tmen)]·MeOH·CH_2Cl_2. Crystallographic studies showed that this phenomenon arises from an intermolecular hydrogen bond between the coordinated chloride of one complex and the OH group of a triketonate ligand of an adjacent complex and/or cocrystallized MeOH molecule.



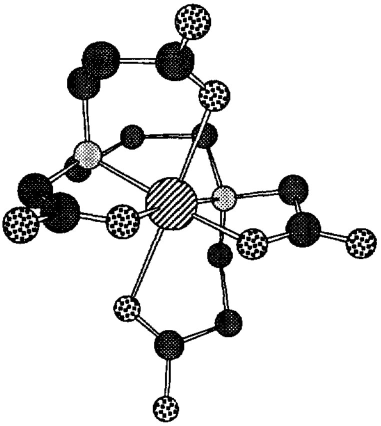
(121)

In order to obtain structural parameters for a comparison with polynuclear metal complexes derived from the $[Cu(C_7H_6N_2O_6)]^{2-}$ complex anion, the X-ray study of disodium [*N*,*N*′-(1,3-propanediyl)bis(oxamato-*N*,*O*)]cuprate(II) hexahydrate has been carried out [170]. The molecular structure parameters are in agreement with the geometrical parameters of derived polynuclear complexes, in particular, with respect to the loss of planarity of the CuN_2O_2 moiety.

Stoichiometric reactions of copper hydroxycarbonates with *trans*-1,2-cyclohexanediaminotetraacetic acid (H_4CDTA) in water under reduced pressure yielded $[Cu(H_2CDTA)]\cdot H_2O$ [171]. The structure of the complex shows the copper(II) atom exhibiting a distorted square-base coordination (type 4+1) by chelation of one H_2CDTA^{2-} ligand through two N and two O (carboxylate) at the square base and one O (carboxylic) at the apex of the coordination polyhedron; a second carboxymethyl group of H_2CDTA^{2-} remains free.

The five-coordinate mixed-chelate copper(II) complexes [Cu(en)(pmdt)]·$(ClO_4)_2$, [Cu(*SS*-chxn)(pmdt)]·$(ClO_4)_2$, [Cu(*S*-bzen)(pmdt)]·$(ClO_4)_2$ and [Cu(*R*-pn)(pmdt)]·$(NO_3)_2$ have been prepared and characterized (where pmdt = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, en = 1,2-diaminoethane, *SS*-chxn = (1*S*,2*S*)-1,2-diaminocyclohexane, *S*-bzen = (*S*)-1,2-diamino-3-phenylpropane and *R*-pn = (*R*)-1,2-diaminopropane) [172]. The geometry and structures of the complexes were studied by visible electronic, CD and ESR spectra and the structures of the first two complexes were determined by X-ray single crystal analyses. The geometry around the copper(II) ion in the first is very close to regular trigonal-bipyramidal, whereas that in the second is intermediate between trigonal-bipyramidal and square-pyramidal. The coordinating geometries of pmdt in the complexes are significantly different from those of some pmdt-containing copper(II) complexes already published.

The hexadentate complex $[Cu(H_2 1,3\text{-pddadp})]\cdot 1.5H_2O$ (**122**) (1,3-pddadp = 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion) has been prepared and isolated and its molecular structure determined by the single-crystal X-ray diffraction technique [173]. The complex is a *trans*(O-6) isomer, in which the copper(II) ion is surrounded octahedrally by two nitrogen and four oxygen atoms of 1,3-pddadp with two protonated β-alaninate rings in trans positions. The copper atom environment is a tetragonally elongated octahedron. A comparison of structures of the copper(II)–edta-type complexes shows an expected variation in their stereochemistry, depending on the structure of the ligand. The 1,3-pddadp ligand encircles the Cu^{II} ion more favourably than the edta ligand, which is capable of forming five-membered chelate rings only.



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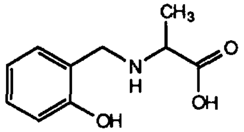
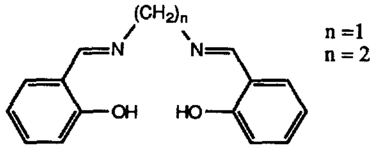


(123)

Copper(II) complexes with reduced Schiff base ligands of amino acids possessing non-polar side chains with salicylaldehyde have been synthesized [174]. Ternary complexes of *N*-(2-hydroxybenzyl)-D,L-alanine (**123**) with imidazole, 1,10-phenanthroline and pyridine have been prepared and characterized. The crystal structures of [(*N*-(2-hydroxybenzyl)-D,L-alanine)(1,10-phenanthroline)Cu(II)] monohydrate and [(*N*-(2-hydroxybenzyl)-D,L-alanine)(imidazole)Cu(II)] have been determined. In the former the copper atom is five coordinate, with **123** acting as a tridentate ONO chelator through the carboxylato and phenolato oxygen atoms and the amine nitrogen. The remaining donors are provided by the phen nitrogen atoms. In the imidazole complex the copper atom is four coordinate, with **123** acting as a tridentate ONO chelator with the neutral imidazole moiety coordinated through nitrogen. In both complexes the ligand has two chiral centres due to the coordination of the amine nitrogen atom. Molecular mechanics calculations show that unfavourable steric interactions would occur in the non-observed *R*,*R* and *S*,*S* diastereomers.

The oxidation of various [CuL] (where L are the dianions of quadridentate Schiff bases derived from salicylaldehyde, and 1,2-diaminoethane, namely 2,2′-[1,2-ethanediylbis(nitrilomethylidene)diphenato] (**124**), its 1,3-propane homologue, (**125**), or from glyoxal and *ortho*-aminophenol, namely 2,2′-[(ethanediimine)diphenato] (**126**), as well as some of their analogues) has been studied by cyclic voltammetry [175]. Anodic sweeps show one, or two, usually irreversible, oxidation peaks originated by the presence of Cu^{II}. The oxidations of the 5-NO_2-substituted derivatives are reversible at high scan rate ($1\ V\ s^{-1}$). The oxidation potentials of the complexes with substituents at the aromatic rings suggest that the electronic influence of such substituents are transmitted to the metal centre via the phenato, rather than the azomethine groups. The complexes of **125** and **126** are oxidized at potentials higher than the corresponding complexes of **124**.

A series of chiral Schiff bases, 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneamino)-1,1′-binaphthyl (**127**), and their complexes [Cu(**127**)] has been prepared [176]. The crystal structure of the racemic form of the complex [Cu(**127**)]



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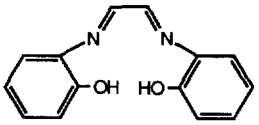
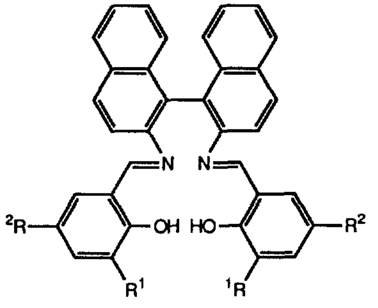


(126)

($R^1 = R^2 = Cl$) has been determined and the complex has been shown to be an active catalyst for the oxidation of alkenes by *tert*-butyl hydroperoxide.



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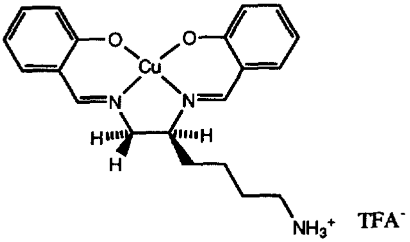
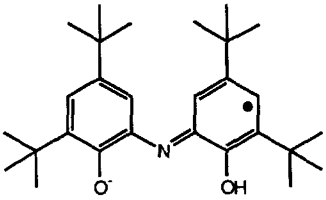


(128)

An original procedure for the efficient synthesis of a functionalized salen copper complex is reported [177]. The mode of binding to DNA of the salen–Cu^{II} complex (**128**) was investigated by viscometry, as well as by absorption, circular, and linear dichroism spectroscopy. The complex can induce DNA strand breakage in the presence of a reducing agent, as revealed by a plasmid cleavage assay. The spectroscopic and biochemical data indicate that the salen·copper(II) complexation induces single-stranded breaks via an interaction within one of the grooves of the double helix.

Stoichiometric quantities of 3,5-*tert*-butylcatechol and aqueous ammonia react in pyridine solution to form 2-amino-4,6-di-*tert*-butylphenol [178]. Under an atmosphere of dioxygen the aminophenol is oxidized to either the corresponding iminosemiquinone or iminobenzoquinone. In the presence of Cu(II) iminosemiquinone condensation with the aminophenol gives the Cat–N–SQ radical ligand (**129**) obtained as the $Cu(py)_2$(**129**) complex. Crystallographic characterization of crystals obtained as the isopropanol solvate show that the expected Jahn–Teller distortion appears in the trans Cu–O lengths of the equatorial plane rather than for the axial Cu–N lengths. Reactions carried out with both Cu(I) and Cu metal require metal oxidation to give the Cu(II) products obtained. With metallic Cu this occurs by a reaction with iminoquinone to give bis(iminosemiquinone)copper(II). Further reaction of this product with aminophenol gives $Cu(py)_2$(**129**) by condensation, and, with O_2, oxidation gives a coordinated azophenolate ligand in Cu(py)(azophenolate) by a unique N–N bond-forming reaction. Cu(py)(azophenolate) has been characterized crystallographically.

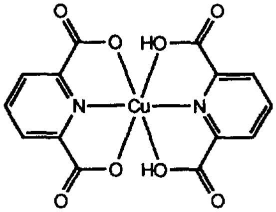


(129)

The structure of di(2-fluorobenzoato-*O*)di(1,3-diaminopropane-*N*,*N*′)copper(II) [$Cutn_2(2FbzO)_2$] (tn = 1,3-diaminopropane; 2FbzO = *ortho*-fluorobenzenoate) was determined by single-crystal X-ray methods [179]. In the complex the chelate rings display a chair conformation and there is trans coordination around the central metal cation; two crystallographically independent complex units are present, representing different modes of conformational isomerism.

The crystal and molecular structure of [$Cu(tedpa)_2$](PF_6)$_2$, where tedpa = *N*,*N*,*N*′,*N*′-tetraethylpyridinecarboxamide, have been determined by X-ray diffraction methods [180]. The compound is built up of cationic [$Cu(tedpa)_2$]$^{2+}$ and PF_6^- groups. The coordination geometry about the copper atom can be described as an elongated and strongly distorted octahedron (CuN_2O_3O' chromophore).

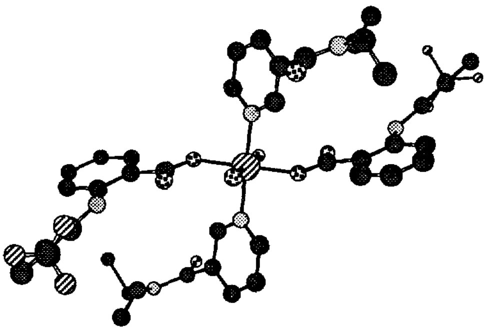
The molecular structure of a new copper dipicolinate, Cu(dipic)(H_2dipic)·H_2O (**130**), and a refinement of the previously reported Cu(dipic)(H_2dipic)·$3H_2O$, where H_2dipic = pyridine-2,6-dicarboxylic acid, have been determined [181]. The Jahn–Teller effect, as operative in six-coordinated Cu^{II} centres surrounded by two planar tridentate ligands, is responsible for the presence of a dianion and a neutral acid molecule in the structure. As opposed to previously reported copper dipicolinates, water molecules do not coordinate and, in the trihydrate, dehydration is facile because interstitial water finds easy dehydration pathways. The monohydrate, however, presents tightly bound water (through hydrogen bonds) and no easy dehydration pathways are available. Five different copper(II) dipicolinates are known; because of the strong tendency of this ligand to form tridentate mononuclear complexes, all of them, except monoclinic Cu(dipic)·$2H_2O$, belong to the class of molecular solids.



(130)

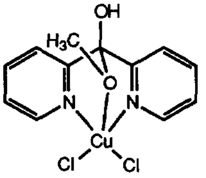
The copper(II) complex of 2,5-diacetylpyridine bis(acetylhydrazone) (H_2dapac) [$Cu(H_2dapac)(OH_2)_2$](NO_3)$_2$·H_2O has been synthesized and structurally characterized by X-ray diffraction methods [182]. The metal atom has a slightly distorted pentagonal-bipyramidal environment, the equatorial positions being occupied by three nitrogen and two oxygen atoms from the hydrazone ligand and the apices by two water molecules. The crystalline cohesion in ensured by a three-dimensional network of hydrogen bonds involving the complex cations, the nitrate anions, and, where present, the uncoordinated water molecules.

As part of a study to gain a better understanding of some aspects of metal ion–drug interactions, new copper(II) flufenamate (flu, *N*(α,α,α,-trifluoro-*m*-tolyl)-anthranilic acid) compounds of the composition $Cu(flu)_2L$ (L = papaverine or caffeine) and $Cu(flu)_2L_2$ (L = nicotine, nicotinamide, *N*,*N*-diethylnicotinamide (Et_2nia), pyridine-2,6-dimethanol or methyl-3-pyridylcarbamate) have been prepared [183]. The spectroscopic properties of $Cu(flu)_2L$ indicate the presence of copper(II) dimers structurally similar to those in copper(II) acetate monohydrate. All the $Cu(flu)_2L_2$ compounds seem to possess octahedral copper(II) stereochemistry with differing tetragonal distortions. An X-ray analysis of $Cu(flu)_2(Et_2nia)_2(H_2O)_2$ (**131**) was carried out, and shows a tetragonal-bipyramidal geometry around the copper(II) atom. The tetragonal plane is created by flufenamate anions bonded to the copper(II) atom via the unidentate carboxylate oxygen atoms (Cu–O(3) = 1.961(2) Å), the pyridine ring nitrogen atoms of the neutral ligand *N*,*N*-diethylnicotinamide (Cu–N(1) = 2.001(3) Å) and axial water molecules (Cu–O(2) = 2.449(4) Å).



(131)

The non-electrolyte dichloro(hydroxy-methoxy-di(2-pyridyl)methane)copper(II) (**132**), resulting from the reaction of di(2-pyridyl)ketone and copper(II) chloride in methanol solution, was isolated and characterized and its structure was determined by X-ray diffraction [184]. The pyridyl nitrogen atoms and the chloride anions virtually form a basal plane in which lies the copper atom, while the oxygen of the methoxy group is in an apical position at a distance of 2.497(3) Å. The nitrogenous base adopts the boat conformation with the pyridyl rings forming a dihedral angle of 108.72(14)°. The nearest interatomic copper distance of 3.940(3) Å precludes copper–copper interactions, while the proximity of copper to the out-of-plane chlorine atoms (3.109(3) Å) suggest weakly bound chloro-bridged dimers. Spectral changes indicate that protic molecules displace the methoxy group and water affords the corresponding 1,1-diol.



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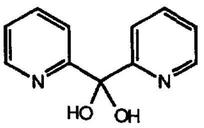


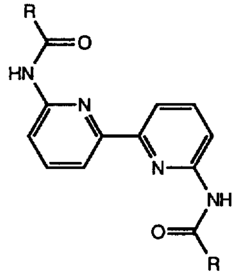
(133)

The reactions of the singly deprotonated di-2-pyridylmethanediol ligand (**133**) with copper(II) and bismuth(III) have been investigated [185]. The reaction of $Cu(OCH_3)_2$ with **133**, H_2O, and acetic acid in a 1:2:2:2 ratio yielded a mononuclear complex $Cu[(2\text{-py})_2CO(OH)]_2(HO_2CCH_3)_2$, whereas the reaction of $Cu(OAC)_2(H_2O)$ with di-2-pyridyl ketone and acetic acid in a 2:1:1 ratio yielded a tetranuclear complex $Cu_4[(2\text{-py})_2CO(OH)]_2(O_2CCH_3)_6(H_2O)_2$. The structures of these complexes were determined by single-crystal X-ray diffraction analyses. Three different bonding modes of the ligand were observed in the complexes. In the mononuclear complex, the ligand functions as a tridentate chelate to the copper centre and forms a hydrogen bond between the OH group and the non-coordinating HO_2CCH_3 molecule. In the tetranuclear complex the ligand functions as a bridging ligand to two metal centres through the oxygen atom binding two copper(II) centres. This complex has an unusual one-dimensional hydrogen-bonded extended structure and its intramolecular magnetic interaction has been found to be dominated by ferromagnetism.

Copper(II) complexes derived from tripodal ligands capable of forming 5,6,6- or 5,5,6-membered chelate ring sequences have been synthesized and characterized [186]. The crystal structures of two complexes $[CuL(O_2C^tBu)]\cdot MeCN$ (HL= (2-hydroxy-5-nitrophenylmethyl)(pyridin-2-ylethyl)(pyridin-2-ylmethyl)amine) and $[CuL(O_2CMe)]\cdot H_2O$ (HL=(2-hydroxy-5-nitrophenylmethyl)bis(pyridin-2-ylmethyl)amine) have been solved. They are neutral, mononuclear copper(II) species in the solid state. In contrast to copper(II) complexes derived from related tripodal ligands forming 6,6,6-membered chelate rings, the present complexes have an axial phenolate–copper(II) bond in their square-pyramidal structures. The formation of this bond is related to the steric factors arising from the flexibility of the ligand pendant arms. The complex $[CuL(O_2CMe)]$ exhibits structural features related to the biosite in galactose oxidase; an acetate coordinates to copper equatorially and a phenolate oxygen atom occupies the axial position.

The coordination geometry of the Cu atom in bis(pyridine-2,3-dicarboxylato-*N*,*O*)copper(II), $[Cu(C_7H_5NO_4)_2]$, has been determined as distorted octahedral [187]. The Cu atom is bonded to a carboxylate O atom (at the pyridine 2-position) and the pyridine N atom of two ligands, the four atoms forming the equatorial plane, and via weaker axial contacts to two carboxylic acid O atoms (at the pyridine 3-position) of adjacent molecules.

The copper(II) complex of 6,6′-bis(4-hexylbenzoylamino)-2,2′-bipyridine (**134**) has been used as a new type of functional carrier in efficient and selective up-hill transport of anions across an organic liquid membrane [188]. Reversible deprotonation of the amide groups of the ligand regulated the uptake and release of anions by alteration of the anion affinity of the complex, and affinity switching of the carrier by the pH of external aqueous solution induced efficient up-hill transport of SCN^- and toluene-*p*-sulfonate by coupling with a small pH difference across the membrane. The high thiocyanate selectivity of the carrier was attributed to preferential axial coordination of SCN^- to the complex which possesses an N_2O_2 square-planar structure.



R = 4-hexylphenyl

(134)

Copper complexes with the commercial auxin herbicides 2,3-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)propanoic acid and 2,2′-bipyridine were prepared and their solid state structures determined [189]. The results of this study show that the presence of bpy leads to monomeric forms, as seen by the formation of the complexes $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(bpy)(H_2O)]$ and $[Cu\{Cl_2C_6H_3OCH(Me)CO_2)(bpy)_2]Cl$, whereas its absence leads to the formation of the dinuclear complex $[Cu_2(Cl_2C_6H_3OCH_2CO_2)_4(MeOH)_2]$.

The crystal structure of cyanobis(1,10-phenanthroline)copper(II) tricyanomethanide dihydrate, $[Cu(CN)(C_{12}H_8N_2)_2][C(CN)_3]\cdot 2H_2O$ is formed by discrete $[Cu(phen)_2(CN)]^+$ cations, tcm anions and uncoordinated water molecules (phen = 1,10-phenanthroline, tcm = tricyanomethanide, $C(CN)_3^-$) [190]. The Cu atom is coordinated by four N atoms (from two phen molecules) and by one C atom (from the cyanide group in the equatorial plane) in the form of a distorted trigonal-bipyramid.

The structure of bis(9-dihydroxymethyl-1,10-phenanthroline-2-carboxylato-*N,N′,O*)copper(II) hydrate, $[Cu(C_{14}H_9N_2O_4)_2]\cdot H_2O$, has been determined and shows the stable *gem*-diol ligands are tridentate (two N atoms and one carboxylate O atom) and form a distorted octahedron around the metal centre. The total bite angle of the ligand is approximately 150° [191]. The analogous Co^{II} complex has also been determined and is found to be isostructural with the Cu^{II} complex.

Equimolar (1:1:1) mixed-ligand Cu(II) complexes, with either iminodiacetato (IDA) and *N*-methyl-imidazole (1MeImH) or with *N*-methyl-IDA (MIDA) and ImH, have been prepared and characterized by thermal, spectral, magnetic and X-ray diffraction methods [192]. In [Cu(MIDA)(ImH)] the Cu(II) atom exhibits a flattened square-base pyramidal coordination (type 4+1). The N and two O atoms of the tridentate MIDA and one N of ImH form the square base; one longer Cu–O bond with the next MIDA ligand in the chain complex completes the Cu(II) five-coordination. In [Cu(IDA)(1MeImH)$(H_2O)_2 \cdot H_2O$ (II) the N and two O atoms from IDA and one N from 1MeImH define a square coordination; two longer Cu–OH, bonds complete unsymmetrical elongated octahedral coordination of Cu(II) (type 4+1+1).

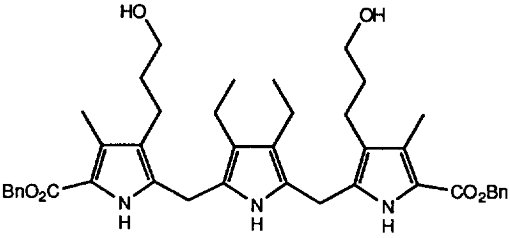
The crystal structure of [Cu(crot)$_2$(im)$_2$(H_2O)] (crot = 2-butenoate (crotonate) anion; im = imidazole) has been determined by X-ray diffraction methods [193]. The compound is built of neutral [Cu(crot)$_2$(im)$_2$(H_2P)] entities linked through hydrogen bonds involving water molecules and carboxylate groups to give a chain structure. The copper atom is involved in a CuN_2O_2O' chromophore and lies in a distorted square-pyramidal environment. Both electronic and EPR spectra are indicative of an essentially $d_{x^2-y^2}$ ground state for the copper(II) ions. No exchange coupling has been detected down to 4.2 K by means of magnetic susceptibility measurements.

The crystal and molecular structures of the complex [Cu(HBIP)(BIP)ONO_2] (HBIP = 3,3-bis(2-imidazolyl)propionic acid) have been determined by X-ray methods [194]. The CuN_4O chromophore could be considered as an intermediate between the trigonal-bipyramid and square-pyramid. Neighbouring molecules of the complex are bound by very strong hydrogen bonds, as short as 2.478 Å, between COO– and COOH groups. Electronic and EPR spectra are consistent with the crystallographic data.

A new ternary complex [Cu(gg)(bzim)]$\cdot 3H_2O$ (gg = glycylglycine^{2-}, bzim = benzimidazole) has been crystallized from aqueous solution [195]. The coordination geometry about the copper is approximately square-planar with the tridentate glycylglycine dianion and the N(1) of the benzimidazole ligand occupying and the corners of the square. The plane of the bzim ligand is twisted 19.0(1)° from the square plane. The three water molecules are involved in a hydrogen bonding network.

Copper(II) complexes of the formula Cu(amtz)$_1H_2P \cdot X_2$, (amtz = 2-acetamido-*N*-(4-methyl-2-thiazolyl); X = NO_3, Cl, Br), were prepared and characterized by elemental analysis, IR and electronic spectroscopy, magnetic susceptibility and molar conductivity measurements [196]. The crystal and molecular structures of the nitrate complex were established by X-ray diffraction. In all the compounds prepared the ligand acts in a didentate fashion. In the nitrate complex the copper atom is five-coordinate in a distorted trigonal-bipyramidal arrangement with the ligand's oxygen atoms in equatorial positions and the nitrogen atoms of the thiazole rings in axial positions.

The reaction of the dibenzyltripyrrane ester (**135**) with Cu(OAc)$_2$ under oxidative conditions was found to give a blue copper Cu(II) tripyrrane complex (**136**) whose structure was determined by X-ray crystallographic analysis [197]. The structure shows that, in the course of metal chelation, the triopyrrane ligand (**135**) is oxidized at one of the two methylene positions to form a bridging methane and at the other an exocyclic keto group forms. This results in the formation of a species with two acidic protons that is able to form an overall neutral complex.



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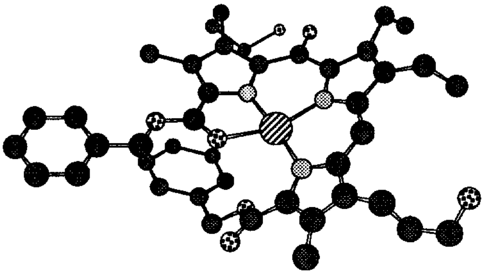


(136)

In absolute methanol, copper(II) nitrate reacted with 1,3-dimethyl-(1*H*,3*H*)-pteridin-2,4-dion (1,3-dimethyllumazine, DMLM) giving a complex with formula $[Cu(DMLM)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ [198]. This compound has been characterized and shows the copper(II) ion occupies an inversion centre and exhibits an elongated octahedral coordination. The equatorial plane consists of two N(5) atoms of the pteridine ligands and two oxygen atoms from water molecules, and the two axial sites are occupied by two O(4) atoms of the ligands. The non-coordinated water molecules and nitrate anions, as well as the pteridine ligands, are involved in a two-dimensional H-bond network, the metal–pteridine moieties being linked to the non-coordinated water molecules and nitrate anions of neighbouring molecules through the O(2) atom of the pteridine ligands. The molecules are packed in planes which are stacked at a mean distance of 3.297 Å to each other. A three-dimensional arrangement is defined by the involvement of the coordinated water molecules in a hydrogen bond with one oxygen atom from the uncoordinated water and another oxygen from the nitrate group of the adjacent layers.

A study of the ternary copper(II) complexes Cu(DA)(AAA), where AA refers to 3,5-diiodo-L-tyrosinate (I_2tyr) or L-tyrosinate (Tyr) and DA refers to 1,10-phenanthroline, 2,2′-bipyridine, 2-(aminomethyl)pyridine (ampty), histamine (hita), or ethylenediamine (ten), has been carried out [199]. Large positive log *K* values have been obtained for the Cu(DA)(I_2tyrOH) and Cu(DA)I_2tyrO$^-$) systems (DA = phen or bpy; OH and O$^-$ refer to the protonated and deprotonated forms of the phenol moiety respectively), indicating that the complexes are stabilized by effective stacking. Differences between the log K values for Cu(DA)(I_2tyr) and Cu(DA)(Tyr) systems indicate that the iodine substituents contribute greatly to the stability enhancement. A distinct CD magnitude anomaly was also observed for the systems with large log K value, supporting the existence of the stacking interaction in Cu(DA)(AA). Two complexes, [Cu(bpy)(I_2tyrO$^-$)(H_2O)$\cdot$2H_2O and [Cu(bpy)(I_2tyrOH)(NO_3)]$\cdot$$CH_3OH$, have been isolated as crystals and analysed by the X-ray diffraction method. The central Cu(II) ion for both complexes has a similar distorted five-coordinate square-pyramidal geometry with the equatorial positions occupied by the two nitrogen atoms of bpy and the nitrogen and oxygen atoms of I_2tyr, and the apical position is occupied by a water molecule or a nitrate ion. The opposite site to the axial water or nitrate oxygen atom is intramolecularly occupied by the side chain aromatic ring, which is approximately parallel to the copper coordination plane directly exhibiting the effective stacking interaction between the aromatic rings in the solid state. Distances between the iodine and one of the pyridine rings of bpy are shorter than the van der Waals distance (3.85 Å), implying that the iodine substituent may be involved in a weak bonding interaction with the pyridine ring. Effects of the iodine substituents on the stacking interactions between the diiodophenol side ring and the coordinated aromatic diamine and their possible biological relevance have been discussed.

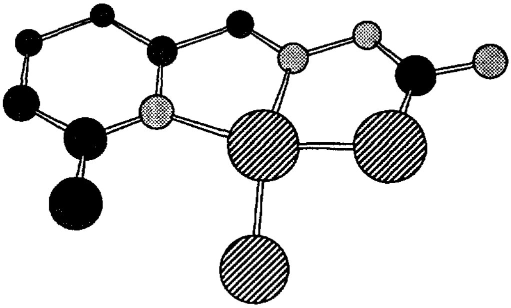
Substituted *o*-phenylenebis(salicylidenaminato) complexes of copper(II), Cu(5-X–saloph), where X = H, CH_3O and Cl have been synthesized and characterized [200]. The complex with X = H, $C_{20}H_{14}N_2O_2Cu$, crystallizes with two molecules in the asymmetric unit with the geometry around copper being essentially square-planar in both, with average Cu–N and Cu–O bond distances being 1.89(2) Å and 1.95(2) Å respectively. The overall chelate conformation is also planar with a moderate "twist" and "sal" groups.

3.2.4. Nitrogen and sulfur coordination

The complexes [$CuX_2(C_7H_8N_4S)$]$\cdot$$H_2O$ ($C_7H_8N_4S$ = pyridine-2-carbaldehyde thiosemicarbazone; X = Cl, Br) have been synthesized and the crystal structure of the bromo compound has been solved [201]. The framework consists of discrete monomeric molecules with five-coordinate square-pyramidal copper(II) ions. One sulfur and two nitrogen atoms of the thiosemicarbazone ligand and one bromide ion are in the basal position, with another bromide ion in the apical one. The chloro complex is isostructural with the bromo one. Considering the electronic delocalization along the thiosemicarbazone ligand and the geometry of its chelating centres, an important influence in the copper orbitals sequence has been shown from the spectroscopic studies and molecular orbital calculations.

Copper(II) complexes of general empirical formulae [Cu(NNS)X]$\cdot$$xH_2O$ (NNS = uninegatively charged tridentate ligand formed by condensation of 6-methylpyridine-2-aldehyde with thiosemicarbazide; X = Cl, Br, NO_3, and CH_3COO; x = 0, 1) and [Cu(NNS)$_2$]$\cdot$0.5H_2O have been prepared and characterized by conductance, magnetic, electronic and infrared spectroscopic measurements [202]. Magnetic and spectral data support a square-planar structure for [Cu(NNS)X]

(X = Cl, Br, NO_3, CH_3COO) and a distorted octahedral structure for $[Cu(NNS)_2]\cdot 0.5H_2O$. The crystal and molecular structures of [Cu(NSS)Cl] have been determined by X-ray diffraction. This complex has a distorted square-planar geometry with the copper(II) ion lying in an approximate plane of four coordinating atoms, three of which come from the 6-methylpyridine-2-carboxaldehyde thiosemicarbazone and the fourth coordination site is occupied by the chloride ligand. The thiosemicarbazone is present as in the thiolate form and is coordinated to the copper(II) ion via the pyridine nitrogen atom, the azomethine nitrogen atom and the mercaptide sulfur atom.



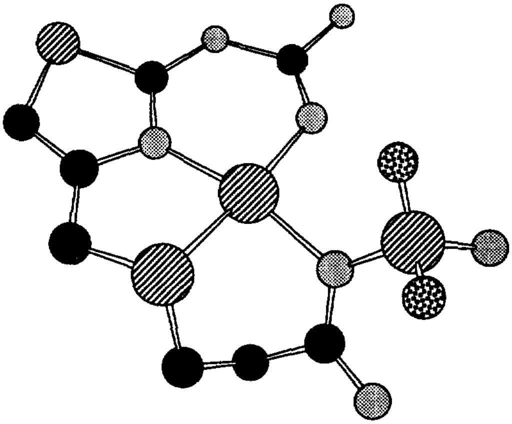
(137)

The complex $[Cu(HL)L]ClO_4$ (HL = methyl 2-pyridyl ketone thiosemicarbazone) have been prepared from the reaction of HL with the copper(II) perchlorate salt. [Cu(HL)L]NCS was also prepared by transmetallation of $[Pb_2(HL)L(NCS)_2]NCS$ with an excess of copper(II) perchlorate [203]. The new complexes have been characterized by spectroscopic techniques and the crystal structure of the copper complex has been determined. The copper atom is six-coordinated by two NNS donor sets from terdentate ligands.

Copper(II) complexes of the general formula [Cu(L–SMe)X] or [Cu(L–SBz)X] (where HL–SMe and HL–SBz respectively represent the 2-acetylpyridine or 2-benzoylpyridine Schiff bases of *S*-methyl- or *S*-benzyldithiocarbazate; X = Cl, Br, NO_3) have been prepared and characterized by a variety of physico-chemical techniques [204]. Magnetic and spectroscopic evidence support square-planar structures for the [Cu(L–SMe)X] (X = Cl, Br) complexes and five-coordinate structures for the $[Cu(L–SBz)NO_3]$ complexes. The structure of $[Cu(AP–SBz)NO_3]$ has been determined by X-ray diffraction studies. The geometry of the complex is a distorted square-pyramid with the NNS tridentate ligand and an oxygen atom of the nitrate ion occupying the basal plane. The fifth coordination position is occupied by another oxygen from the nitrate ion. The anti-fungal and anti-bacterial properties of the Schiff bases and their copper(II) complexes have been evaluated against phytopathogenic fungi and pathogenic bacteria. The fungitoxicity of the five-coordinate $[Cu(Ap–SBz)NO_3]$ complex approaches that of nystatin, whereas the Schiff base HAp–SMe and its copper(II) complex $[Cu(AP–SMe)NO_3]$ display significant antibacterial activity against *E. coli* and *S. aureas*. A similar study has been carried out on complexes of the 2-benzoylpyridine Schiff bases of *S*-methyl- or *S*-benzyldithiocarbazate; X = Cl, Br, NO_3) [205]. The Schiff bases and copper(II) complexes display moderate antifungal activities, but their activities are less than that of the commercially important antifungal agent nystatin.

The redox chemistry of $[CuL]^{2+}$ (L = pdto = 1,8-bis(pyridin-2-yl)-3,6-dithiaoctane, bbdo = 1,8-bis(benzimidazol-2-yl)-3,6-dithiaoctane, pttn = 1,9-bis(pyridin-2-yl)-2,5,8-trithianonane or pttu = 1,11-bis(pyridin-2-yl)-3,6,9-trithiaundecane] in the presence of α-, β- and γ-cyclodextrins in aqueous solution has been extensively investigated by cyclic and differential pulse voltammetric techniques [206]. The addition of cyclodextrins to the complexes results in a substantial decrease in peak currents rather than in peak potentials. The results of this study illustrate the formation of novel and regular arrays around the complex, the number of molecules in the array being dictated by the size of the cyclodextrin rather than the usual inclusion complex formation by cyclodextrins.

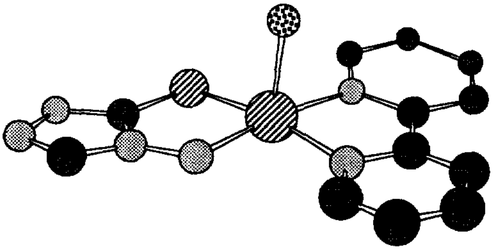
The crystal structure of the complex $[CuL][ClO_4]_2$ (L = 3-{[2-diaminomethyleneamino)thiazol-4-yl]methyl-sulfanyl}-*N*-2-sulfamoylpropionamidine, famotidine) (**138**) has been determined [207]. This work provides a full description of the metal binding sites and reveals the impact of metal coordination on the conformation of the drug molecule and shows that even metal ion binding is not able to change some conformational features of famotidine, which could be an important factor biologically. Potentiometric and spectroscopic data were obtained for the ternary species in the Cu^{2+}–famotidine–histidine system and show that famotidine is a very competitive chelating agent even in the presence of the strongly coordinating amino acid.



(138)

Copper(II) and zinc(II) complexes of two new potentially pentadentate ligands based on methyl 2-aminocyclopent-1-ene-1-dithiocarboxylate with pendant pyrazolyl groups $(Me_2pzCH_2)_2NC_2H_3RNHC_5H_6CSSCH_3$ (R = H, Hmmecd, and R = CH_3, Hmmpcd, both having N_4S donor atoms set) have been reported [208]. The molecular structure of [Cu(mmpcd)]ClO_4 shows a square-pyramidal geometry for the Cu(II) ion. The EPR and electronic spectroscopic studies showed that the copper(II) species doped into zinc(II) complex adopts the zinc(II) trigonal-bipyramidal structure. The cyclic voltammetric measurements indicated one-electron reversible reduction of the copper(II) complex occurring at −0.74 V, whereas irreversible oxidation to copper(III) takes place at +0.75 V (*vs* $Ag/AgNO_3$).

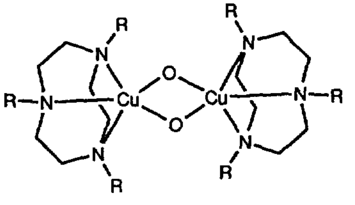
Syntheses and crystal structures of two compounds containing heteroleptic copper(II)–(2,2′-bipyridyl)thione complexes are reported, the thione ligands being 4-amino-1,2,4-triazole-5-thione (atth) $[Cu(by)(atth)(H_2O)](NO_3)_2 \cdot 3H_2O$ (**139**) and 1-(1′-imidazolin-2′-yl)imidazolidine-2-thione (imthim) $[Cu(bpy)(imthim)(NO_3)](NO_3) \cdot H_2O$ [209]. The imthim ligand resulted from copper(II)-promoted ring fusion of two molecules of imidazolidine-2-thione. In $[Cu(bpy)(atth)(H_2O)](NO_3)_2 \cdot 3H_2O$ the copper coordination geometry may best be described as distorted square-pyramidal, with the sulfur and the amino nitrogen of the atth ligand and the two bpy nitrogen atoms in the equatorial plane, and a water oxygen in the apical position. In $[Cu(bpy)(imthim)(NO_3)](NO_3) \cdot H_2O$ the copper coordination geometry is slightly distorted trigonal-bipyramidal, with sulfur, one bpy nitrogen atom and one nitrate oxygen atom in the equatorial plane, and with the second bpy nitrogen atom and an imthim imino nitrogen in the axial positions. Despite the differences in coordination geometries, the Cu–S bond distances are almost identical in the two complexes and the thione ligands remain essentially in their thione form in the complexes (S–C = 1.692(3) Å and 1.688(3) Å).



(139)

3.3. Dinuclear complexes with macrocyclic ligands

The results of experiments designed to probe the mechanism by which the bis(μ-oxo)dicopper complexes $[(LCu)_2(\mu\text{-}O)_2](ClO_4)_2$ (**140**) (L = 1,4,6-tribenzyl-, 1,4,7-triisopropyl-, and 1,4-diisopropyl-7-benzyl-1,4,7-triazacyclononane ligands; $L(Bn_3)$, $L(^{i}Pr_3)$, and $L(^{i}Pr_2Bn)$ respectively) decompose to products arising from macrocyclic ligand *N*-dealkylation have been reported [210]. After removal of copper from the decomposed solutions, analysis of organic products revealed *N*-dealkylated ligands and aldehyde or ketone, and ^{18}O-isotope labelling experiments show that the oxygen atoms in the ketone are derived from the bis(μ-oxo)dicopper core. Thus, the overall *N*-dealkylation is similar to monooxygenase reactions carried out by various metalloenzymes such as cytochrome P450, dopamine β-monooxygenase, and peptidyl glycine α-amidating monooxygenase. Mechanistic studies indicate that the rate-determining step involved the direct, intramolecular attack of the bis(μ-oxo)dicopper core at a ligand substituent C–H bond and that the diamagnetic bis(μ-oxo)dicopper core was behaving as an electrophile during C–H bond scission like the active oxidant in cytochrome P450.



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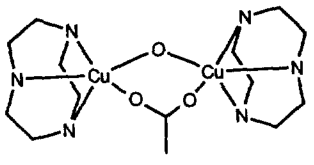
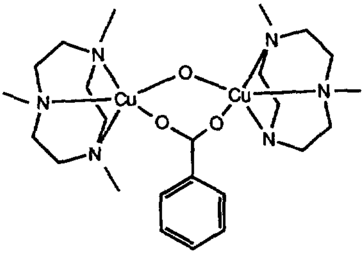


(141)

The novel dinuclear copper(II) complex (**141**) has been prepared by reaction of the macrocyclic ligand with $Cu(MeCO_2)_2 \cdot H_2O$ in ethanolic solution [211]. The crystal structure shows that a pair of copper(II) atoms separated at 3.288(1) Å are bridged by a μ_2-HO—and a μ_2-carboxylato-*O,O′* group. Each copper(II) atom is capped by a ligand, resulting in a distorted trigonal-bipyramidal N_3O_2 coordination environment about the copper(II) atom with the Cu–N bonds at 2.040(5)–2.144(4) Å, and Cu–O bonds at 1.895(2)–1.970(3) Å.

The dinuclear complex $[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5CO_2)][ClO_4]_2$ (**142**, L = 1,4,6-trimethyl-1,4,6-triazacyclononane) has been synthesized and characterized by X-ray crystallography and from temperature-dependent susceptibility measurements. The latter established a moderately strong, intramolecular, antiferromagnetic exchange coupling ($J = -66\ cm^{-1}$) and a magneto-structural correlation between the Cu–O–Cu angle and J for complexes containing a Cu_2(II) μ-hydroxo-μ-carboxylato core [212].



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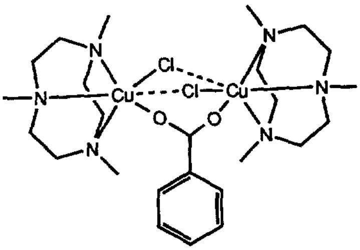


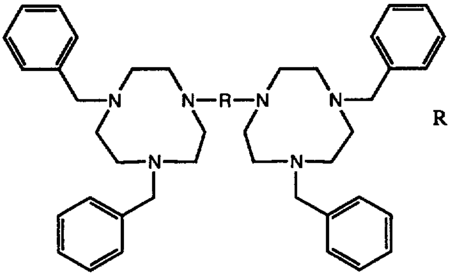
(143)

The dinuclear copper complex $[\{LCu^{II}Cl\}_2(\mu\text{-benzoato})]ClO_4$ (**143**) and its bromo analogue $[\{LCu^{II}Br\}_2(\mu\text{-benzoato})]ClO_4$, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane, which contain one bridging *syn,syn*-benzoate have been prepared in order to investigate further the magneto-structural relationship [213]. The reaction of $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ with piperidine benzoate and the ligand in MeOH affords on addition of $NaClO_4$ green crystals of $[\{LCuX\}_2(\mu\text{-benzoate})]ClO_4$, X = Cl or Br respectively. The X-ray structure of (**143**) shows each copper centre occupies an approximate square-based pyramid with two amine nitrogen atoms cis to each other, the chloro ligand and one benzoate oxygen atom occupying the four basal sites and with the third amine nitrogen atom in the apical site. The *syn,syn*-coordinated benzoate ligand bridges the two basal planes of the Cu^{II} ions and thus connects the $d_{x^2-y^2}$ magnetic orbitals. The large Cu–O–Cu bond angle of 135.6° diminishes the orbital overlap between the metal $d_{x^2-y^2}$ orbital and the p-orbital of the oxygen atom of the bridging carboxylate. This results in the *syn,syn*-mono(carboxylate) bridge between the two square-based pyramidal Cu^{II} ions not providing an affective superexchange pathway, as shown by $J = -1.2\ cm^{-1}$ for (**143**) and $-2.3\ cm^{-1}$ for $[\{LCu^{II}Br\}_2(\mu\text{-benzoato})]ClO_4$.

The structure of $[Cu_2(C_2H_3O_2)_4(C_9H_{17}N_3O_2)_2]$ has been determined and shown to consist of a tetrakis(acetato)-bridged dinuclear copper(II) core with two unidentate N-donor axial ligands, each coordinated via the secondary amine N atom rather than through one of the two amide N atoms [214]. The Cu–Cu distance of 2.702(3) Å is longer than previously reported for copper(II) acetate dimers of this type. Intermolecular hydrogen bonding occurs between the amide O and N atoms.

Magnetic long-range exchange coupling between two unpaired electrons of two copper(II) ions in a square-pyramidal ligand environment ($d_{x^2-y^2}$) which are rigidly separated by > 10 Å by an organic spacer ligand (e.g. a μ-dicarboxylato ligand) has been systematically studied [215]. Temperature-dependent magnetic susceptibility data for all complexes have been measured over the range 2.0–298 K and demonstrate that intramolecular antiferromagnetic exchange coupling of considerable magnitude is possible over distances > 15 Å, provided that the effective magnetic orbitals are favourably aligned.

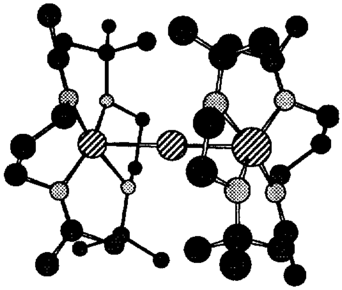
Three alkyl-bridged bis(pentadentate) ligands (**144**), 1,2-bis(*N,N*-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]ethane (tmpdtne), 1,3-bis[*N,N'*-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]propane (tmpdtnp), and 1,4-bis[*N,N'*-bis(2-pyridylmethyl)-1,4,7-triazacyclononyl]butane (tmpdtnb), have been synthesized by reaction of the corresponding bis(tridentate) macrocycles with 2-picolyl chloride at pH ≈ 10 [216]. Copper(II) complexes of the three ligands have been prepared and were found to have the composition $[Cu_2(\mathbf{144})](ClO_4)_4 \cdot xH_2O$, where x = 2 for **144** = tmpdtne and $x = 0$ for L = tmpdtnp and tmpdtnb. Single-crystal X-ray diffraction studies established the molecular structure of the monomeric complex, $[Cu(dmptacn)](ClO_4)_2$, where dmptacn = 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane, and the corresponding dinuclear complex $[Cu_2(tmpdtne)]ClO_4)_4 \cdot 2H_2O$. The UV–VIS spectra of the dinuclear complexes $[Cu_2(tmpdtne)]ClO_4)_4 \cdot 2H_2O$, $[Cu_2(tmpdtnp)](ClO_4)_4$, and $[Cu_2(tmpdtnb)](ClO_4)_4$ show a band in the range 598–602 nm which, for five-coordinate Cu(II) complexes, is indicative of a square-pyramidal geometry. The slightly higher $\lambda_{(max)}$ value of 612 nm for the mononuclear complex suggests more distortion towards trigonal-bipyramidal geometry in solution. These data are in agreement with the solid state structures which show that $[Cu(dmptacn)](ClO_4)_2$ and $[Cu_2(tmpdtne)](ClO_4)_4 \cdot 2H_2O$ are respectively 32% and 11% distorted from square-pyramidal. Variable-temperature magnetic susceptibility measurements show no evidence of exchange coupling between the Cu(II) centres in the dinuclear complexes.



R =CH_2CH_2 tmpdtne
= $CH_2CH_2CH_2$ tmpdtnp
= $CH_2CH_2CH_2CH_2$ tmpdtnb

(144)

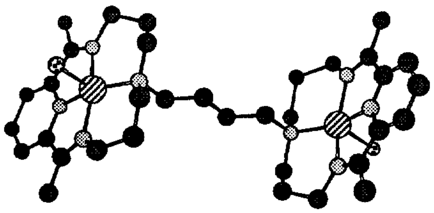
The complex μ-chloro-bis[(1R*,4R*)-5,5,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene-N^1,N^4,N^8,N^{12})(perchlorato-O)copper(II)] perchlorate, (**145**), has a chloride-bridged centrosymmetric confacial dinuclear cation [217]. Each copper(II) ion has a tetrahedrally twisted (±0.30 Å) planar coordination composed of the four atoms of the macrocyclic ligand (mean Cu–N–amine = 2.02(1) and Cu–Ni–imine = 1.99(1) Å), with a weak tetragonal chloride (Cu–Cl = 2.83(1) Å) and perchlorate O-atom (Cu–O = 2.94(1) Å) interactions. The Cu atom is displaced by 0.09 Å from the best N_4 plane towards the chloride ion.



(145)

A new synthetic route has been designed for the preparation of bispolyazamacrocycles in high yields by direct condensation of *N*,*N*′-diboctriazamacrocycle or *N*,*N*′,*N*″-triboctetraazamacrocycles with aromatic biselectrophiles, i.e. *o*-, *m*-, *p*-xylyl and anthracenyl derivatives [218]. The use of a versatile group, such as *tert*-butyloxycarbonyl (Boc), which is easily removed within 1 h by treatment with 6 M HCl or TFA, leads to polyazamacrocycles in which one nitrogen is discriminated from the others. The anthrocenyl and *o*-xylyl dimers were synthesized by reacting diacyl chloride to give the corresponding diamides. Further reduction of the amide groups and elimination of the protecting Boc moieties were carried in a one-pot reaction with BH_3·THF followed by acid treatment. In parallel, exclusive mono-*N*-alkylation of the available secondary amine of the same protected macrocycle with the corresponding dibromoxylene gave the meta and para dimers; the protecting moieties were eliminated in a similar way.

The dicopper(II) complex with the dimacrocyclic ligand $[Cu_2(OH_2)_2L](ClO_4)_4 \cdot 4H_2O$ (L = 7,7′-tetramethylene-bis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadecal(17),2,11,13,15-pentaene]) linked with a tetraethylene chain was chosen for the study of the conformation of polymethylene-bridged dimacrocycles since molecular models suggest that the tetraethylene chain is suitable, being neither too long nor too short, for the formation of both open and closed conformations [219]. Recrystallization of the perchlorate salt of the dicopper(II) complex from water gave purple crystals of the complex with the open conformation (**146**). The two macrocycles are as far apart as possible, in which the tetramethylene chain is staircase-like to minimize the electrostatic repulsion between the Cu^{II} ions. Recrystallization of the perchlorate salt from water containing 100-fold molar excess of NaCl yielded blue crystals of the chloride-anion-coordinated square-pyramidal $[Cu_2Cl_2L](ClO_4)_2 \cdot H_2O$ in the closed conformation (**147**) in which the tetramethylene chain is folded. The chloride ion actually coordinates to the Cu^{II} ions, reducing the electrostatic repulsion between the Cu^{II} centres. Additionally, the two perchlorate anions are located between the macrocycles. In contrast to the open conformation, the tetramethylene bridge is folded in the closed conformation so that the macrocycles have essentially the same structure and face each other, although not completely face-to-face but spread at an angle of ~23° away from each other. The distance between the Cu centres becomes considerably shorter in the closed conformation (7.669(2) Å) compared with the open conformation (9.366(1) Å). The formation of the closed system is favoured by the reduction of the positive charge of the Cu^{II} ions and the location of the perchlorate anions between the Cu^{II} ions. One additional force directing towards the formation of the closed conformation in the solid state arises from a stacking interaction of the pyridine rings.



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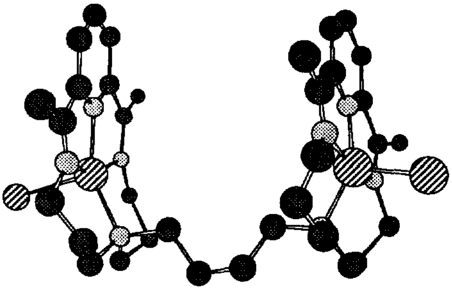
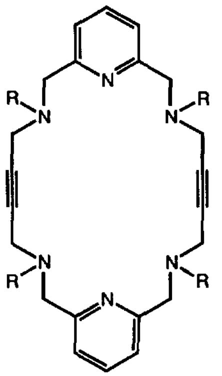
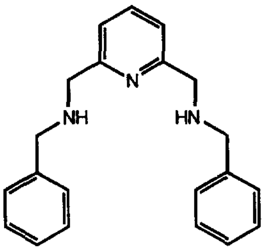


(147)

The first cyanide-selective electrode based on a molecular recognition process has been constructed in which dinuclear metal complexes of lipophilic macrocycles represent a novel class of ionophore in liquid-membrane electrodes [220]. The crystalline complexes $[(\mathbf{148})Cu_2(NO_3)_4]$, $[(\mathbf{149})Cu_2(NO_3)_4]$ and $[(\mathbf{150})Cu(NO_3)_2]$ were obtained by the reaction of the ligands with $Cu(NO_3)_2 \cdot H_2O$ in appropriate stoichiometry. The reaction of $[(L^n)Cu_2(NO_3)_4]$ with KCN (1 equiv.) gave green microcrystalline complexes [(L^n)Cu_2(μ-CN)(NO_3)$_3$]. Weak ν(CN) IR bands at 2205 cm^{-1} and 2208 cm^{-1} were observed for complexes with L^n = (**148**) and L^n = (**149**) respectively. The application of [(L^n)Cu_2(NO_3)$_4$] (L^n = **148**, **149**), [(**150**)Cu(NO_3)$_2$] and (**149**) as ion-selective membranes in liquid-membrane electrodes was studied by measuring potentiometric behaviour. Membranes containing [(**149**)Cu_2(NO_3)$_4$] interacted with CN^-, as evident by the bulk membrane resistance changing by a factor of 4 on exposure to 1 mM KCN solution in a 0.1 M Ca(NO_3)$_2$ background electrolyte. Furthermore, the bright blue membrane adopts the bright green colour of [(**149**)Cu_2(μ-CN)(NO_3)$_3$] when kept in 0.1 M solution for 5 h. Electrodes based on [(**150**)Cu(NO_3)$_2$] show only a slight sensitivity to CN^- and behave more or less as typical anion exchangers with a sensitivity pattern dependent on the lipophilicity of the sample anions.

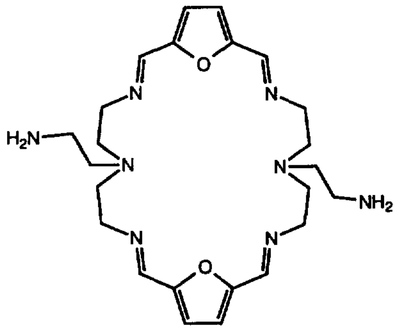


(**148**) R=$C_{16}H_{33}$
(**149**) R=CH_2Ph

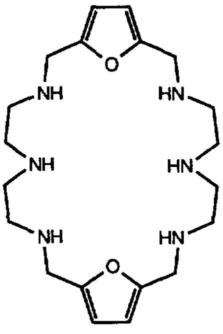


(**150**)

The synthesis, structure and properties of a mono-μ-hydroxo-bridged dinuclear copper(II) complex of the macrocycle (**151**), Cu_2(**151**)(OH)(ClO_4)$_3$ · 1.5H_2O, derived from the cyclocondensation of tris(2-aminoethyl)amine (tren) and 2,5-diformylfuran (dff) are reported [221]. The copper–copper separation is *ca* 3.74 Å and the Cu–OH–Cu angle is *ca* 150°. There is a strong antiferromagnetic interaction between the metals with $-2J = 510$ cm^{-1}.



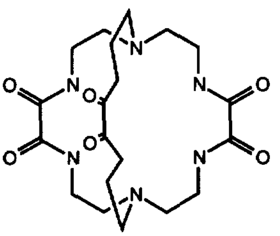
(**151**)



(**152**)

The hexaaza macrocyclic ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo-[(11,14)]octacosa-1(26),11,13,24-tetraene (**152**), forms both mono- and dinuclear complexes, as well as several protonated and hydroxo chelates, with Cu(II) ions [222]. These cationic species can bind inorganic and organic anions through coordination and hydrogen bonding. Stability constants of the mono- and dinuclear Cu(II) complexes of **152** and their interaction with oxalate, malonate, and pyrophosphate anions have been measured potentiometrically. The crystal structures of two new dinuclear Cu(II) complexes, determined by X-ray crystallography, are also reported. In [(**152**)$Cu_2(Cl)_3$]$ClO_4 \cdot 0.5H_2O$] each Cu(II) ion is coordinated by three nitrogen atoms from the diethylenetriamine unit of the macrocyclic ligand and two chloride anions, forming a square-pyramidal geometry, whereas in [(**152**)$Cu_2(Ox)$]$(BF_4)_{1.8}Cl_{0.2}$] the environment of each copper is intermediate between square-pyramidal and trigonal-pyramidal. The oxalate anion bridges in a bis-didentate fashion between the two Cu(II) ions.

The reaction of the bicyclic cryptand 1,4,7,10,13,16,21,24-octaazabicyclo-[8.8.8]hexacosan-5,6,14,15,22,23-hexone (**153**) with copper(II) leads to the dinuclear complex {1,10-bis(2-aminoethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-5,6,14,15-tetronato(4-)}dicopper(II) (**154**) [223,224]. The structure of **154** is made up of centrosymmetric neutral dinuclear copper(II) units. Each copper(II) ion assumes a distorted-octahedral environment. The basal positions are occupied by four nitrogen atoms, two from deprotonated amide groups and two from the tertiary and primary amines; the apical positions are occupied by one amido nitrogen atom from the same dimer and one amido oxygen atom from a neighbouring unit within the stack. The analysis of variable-temperature magnetic susceptibility data reveals the occurrence of a significant intramolecular antiferromagnetic interaction ($J = -47\ cm^{-1}$) in **154**. The analysis of the exchange pathways by extended Hückel calculations shows a strong contribution of the N–C–C–N σ bonds to the coupling between the two copper(II) ions. The triplet exciton-type EPR spectrum of **154** allowed the evaluation of the interdimer interaction (J' approximate to $10^{-3}\ cm^{-1}$), a possible description of **154** as a magnetic alternating chain being ruled out.



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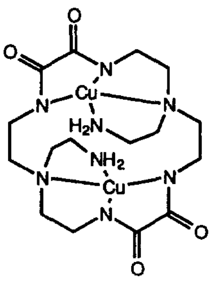

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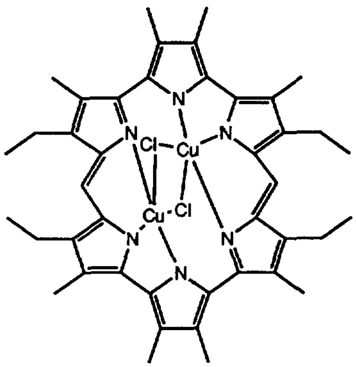
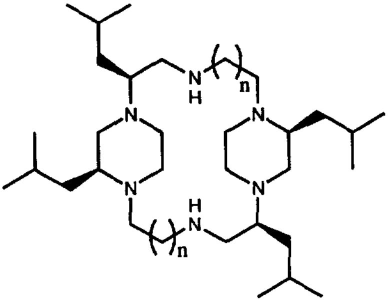


(155)

The preparation of a bis-copper(II) complex of an expanded porphyrin (**155**) is described [225]. A single-crystal X-ray structural analysis of this complex showed the two metal centres to lie within the mean plane of the macrocycle with a rather short interatomic distance of 2.761(1) Å. The two metal centres are formally in the +2 oxidation state and are weakly antiferromagnetically coupled.

Optically active μ-chloro and μ-hydroxo dinuclear copper(II) complexes of the structurally reinforced chiral 18-membered azamacrocycle (2*S*,8*S*,11*S*,27*S*)-2,8,11,17-tetraisobutyl-1,4,7,10,13,16-hexaazatricyclo[14.2.2.2(7,10)]docosane (**156**) and the 20-membered (2*S*,9*S*,12*S*,19*S*)-2,9,12,19-tetraisobutyl-1,4,8,11,14,18-hexaazatricyclo [16.2.2.2(8,11)] have been synthesized and characterized [226]. The X-ray structures of the Cu^{II} complexes of the two macrocycles have been solved with $[Cu_2(\mathbf{156})(\mu\text{-}Cl)(\mu\text{-}OH)](ClO_4)_2$ consisting of a dinuclear system with the two copper centres in an approximate square-planar geometry situated inside the rugby-ball-shaped macrocyclic cavity. Each copper atom is coordinated by two nitrogen atoms of a piperazine ring and a secondary nitrogen atom with a Cu···Cu distance of 2.832(3) Å.



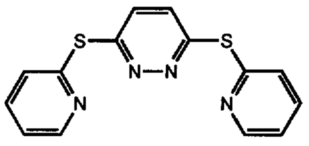
n=1 (**156**)
n=2 20 membered ring

3.4. Dinuclear complexes with acyclic ligands

3.4.1. Nitrogen, sulfur and oxygen coordination

The dinuclear copper(II) complex of the polypyridine ligand *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine (btpa) has been prepared and structurally characterized [227]. The crystal structure shows there is a square-planar arrangement of an oxygen atom of the sulfate ion and three nitrogen atoms of the btpa ligand which bridges the two copper atoms of the centrosymmetric complex cation, Cu···Cu 7.718(4) Å. The structure is disordered with a water molecule sometimes coordinating to the copper atom. Magnetic measurements show no magnetic interaction between the metal centres.

The green hydroxo-bridged dicopper(II) complex $[Cu_2(\mathbf{157})(OH)Cl_3]\cdot 2CH_3CN$ was obtained by aerial oxidation of an acetonitrile solution of a red copper(I)/(**157**) complex, (**157**) = 3,6-bis(2-pyridylthio)pyridazine [228]. The structure has a triple bridged, distorted five-coordinate structure with a Cu–Cu separation of 3.0514(8) Å and a Cu–OH–Cu angle of 106.2(1)°. Variable-temperature magnetic studies indicate moderate antiferromagnetic coupling between the copper centres ($2J=296\,cm^{-1}$). The salt $[H_2\mathbf{158}]^{2+}[CuBr4]^{2-}$ is also reported from an unusual reaction between $CuBr_2$ and (**158**) (where (**158**) = 1,4-bis(2-pyridylthio)phthalazine) in a CH_3CN–$CHCl_3$ mixture. The ligand is protonated at both pyridine nitrogen atoms, leading to an essentially flat cation due to internal hydrogen bonding.



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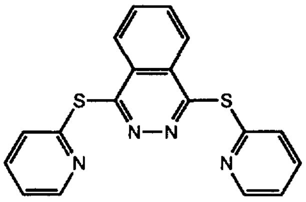
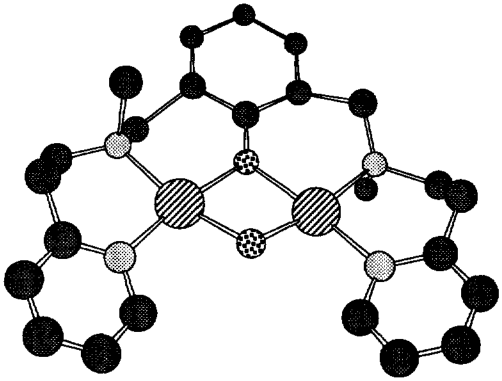


(158)

The structure of di-μ-chloro-bis{chloro[2-(*N*-propylaminomethyl)pyridine-*N*,*N*′]copper(II)}, $[Cu_2Cl_2(C_9H_{14}N_2)_2$-$(\mu$-$Cl)_2]$, has been determined [229]. The geometry about the Cu atom is square-pyramidal. The complex exists as a dimer with the Cu atoms linked by two asymmetric chlorine bridges. The dimeric structure of this complex differs from the polymeric dihalo-bridged chain of $CuLX_2$ complexes, where L is 2-(aminomethyl)pyridine.

A new dinucleating nitrogen-donor ligand has been shown to exhibit tyrosinase-like activity by bringing about aromatic hydroxylation mediated by copper; the phenoxy- and hydroxy-bridged copper(II) complex (**159**) and a novel dihydroxy-bridged copper(II) complex (**160**) are structurally characterized [230]. The reaction of L with $Cu(MeCN)_4ClO_4$ in CH_2Cl_2 under N_2 gave a yellow suspension of an extremely air-sensitive Cu(I) complex. When exposed to O_2 for 12 h, a deep green solution and a bluish-grey precipitate were obtained. Slow evaporation of an acetonitrile solution of the solid at first gave only a few light blue crystals (**160**) and bulk of microcrystalline green compound (**159**). An X-ray structure determination of the green crystals determined the structure to be $[Cu_2L''(OH)][ClO_4]$ (**159**) with two oxygen atoms incorporated—one into the aryl–H bond and the other into a hydroxy bridge. The two copper(II) centres are in almost identical square-planar coordination environments. The free phenol ligand HL″ was isolated by treatment of the complex with ammonia. The X-ray structure of the light blue crystals shows a dicationic $Cu_2(OH)_2$ bridging unit supported by L′, i.e. $[Cu_2L'(OH)_2][ClO_4]_2$ (**160**). Ligand L′ was formed during the synthesis of L and was present as an impurity in the formation of the Cu complex. In **160**, the Cu^{II} centres are square-planar and, in order to adopt the doubly bridged dinuclear structure, the Cu_2O_2 core is bent with a dihedral angle of ~12°. This study demonstrates the synthesis of the first *m*-$CH_2C_6H_4CH_2$ hydroxylation ligand system L within the non-Schiff-base family, providing **160** nitrogen coordination centres at each Cu centre. This finding is of considerable interest in the context of biomimetic studies aimed at the functional properties of tyrosinase.



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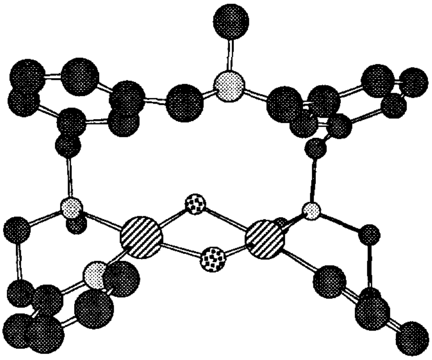
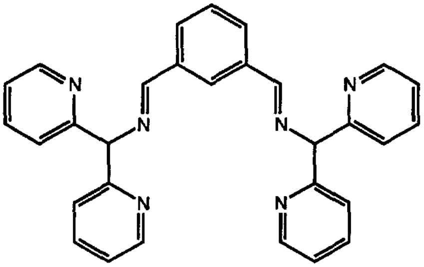


(160)

The compounds bis(methyl 2-pyridyl ketone)carbono- and thiocarbono-hydrazone have been synthesized, their protonation constants obtained through spectrophotometric studies, and their crystal structures determined by X-ray diffractometry [231]. Their complexation behaviour has been studied towards copper and zinc chloride and acetate. The results indicate that they are able to form dimetallic complexes with both copper salts used and zinc acetate; this is confirmed by an X-ray analysis.

New N_6 ligands derived from isophthaldehyde and di(2-pyridyl)methylamine were synthesized, in order to probe the corresponding copper complexes as model systems of tyrosinase [232]. Copper(II) complexes of the N_6 ligands: α,α′-bis(di(2-pyridyl)methylimino)-*m*-xylene (**161**) and α,α′-bis(2-pyridyl)methylamino)-*m*-xylene (**162**) were obtained. $[Cu_2(\mathbf{161})(OCH_3)_2ClO_4]ClO_4$ and $[Cu_2(\mathbf{161})(OH)_2ClO_4]ClO_4$ were isolated by the oxidation reaction of the cuprous species with molecular oxygen in methanol and dichloromethane solutions respectively. Neither of the two dicopper(II) complexes showed insertion of oxygen at the arene ring under the experimental conditions used. $[Cu_2(\mathbf{2})_2Cl_4]\cdot 2H_2O$ was synthesized by the direct reaction of the reduced organic ligand with cupric chloride. X-ray structures are reported: $[Cu_2(\mathbf{161})_2(OCH_3)_2ClO_4$; $[Cu_2(\mathbf{161})(OH)_2ClO_4]ClO_4$; $[Cu_2(\mathbf{162})Cl_4] \cdot 2H_2O$. The coordination geometries of the Cu(II) ion in the first two complexes are best described as tetragonally distorted octahedral, and doubly bridged by methoxo and hydroxo groups, whereas the third is trigonal-bipyramidal. The methoxo complex $[Cu_2(\mathbf{161})_2(OCH_3)_2ClO_4]ClO_4$ is antiferromagnetic, whereas the hydroxo complex $[Cu_2(\mathbf{161})(OH)_2ClO_4]ClO_4$ and the dicopper(II) complex $[Cu_2(\mathbf{162})Cl_4] \cdot 2H_2O$ are paramagnetic.



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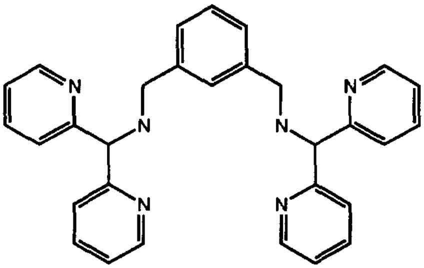


(162)

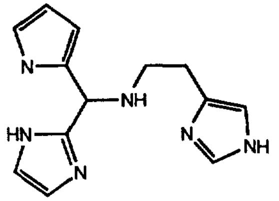
When a mixture of excess $Cu^{I}I$ and 2-benzoylpyridine (2-Bzpy) stands in an ethanolic medium for 2 weeks, an intramolecular oxidative cyclization of 2-Bzpy occurs with formation of the ionic complex [9-oxo-indolo[1,2-a]pyridinium]$^+ \cdot CuI_2^-$ [233]. In contrast, the interaction of $Cu^{I}Br$ and 2-Bzpy in ethanol leads to formation of the dimer $[CuBr(2\text{-}Bzpy)]_2$. The structures of both compounds were established by spectroscopic methods and X-ray diffraction analysis. The structure of [9-oxo-indolo[1,2-a]pyridinium]$^+ \cdot CuI_2^-$ consists of a packing of [9-oxo-indolo[1,2-a]pyridinium]$^+$ cations and CuI_2^- species with the four Cu–I distances varying from 2.669(2) to 2.705(2) Å. The centrosymmetric $[CuBr(2\text{-}Bzpy)]_2$ molecule has a short Cu–Cu distance of 2.696(2) Å.

The syntheses and characterization of a series of dinuclear μ-oxalato complexes of the general type $[(N)_4M(C_2O_4)M(N)_4]^{2-}$, where M is Mn(II), Fe(II), Ni(II), Cu(II) and Zn(I)I, are described [234]. The ligands $(N)_4$ represent the tetradentate ligands *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen, $C_{14}H_{18}N_4$), *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn, $C_{15}H_{20}N_4$) and *N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-dimethyl-1,2-ethanediamine (bispicMe$_2$en, $C_{16}H_{22}N_4$). The crystal structures of five representative complexes have been determined, including the copper(II) complexes $[(bispicen)Cu(C_2O_4)Cu(bispicen)](ClO_4)_2$ and $[(bispicMe_2en)Cu(C_2O_4)Cu(bispicMe_2en)](ClO_4)_2$. The complexes contain six-coordinate metal centres bridged by planar bis-didentate oxalate groups. The small *J*-values of $\approx 2\ cm^{-1}$ for the Cu^{II} complexes are caused by the fact that in these cases the $x^2 - y^2$ orbitals are not the magnetic orbitals.

The structure of blue di-μ-isocyanato-bis[isocyanato(1,10-phenanthroline)-copper(II)] has been found to consist of $[Cu(NCO)_2(phen)]$ subunits (phen = 1,10-phenanthroline) in a distorted planar arrangement, the subunits existing in centrosymmetrically related pairs in the crystal packing [235]. The subunits have a distorted four-coordinate square-planar arrangement of N atoms about the central Cu atom; pairs of these $[Cu(NCO)_2(phen)]$ subunits form dimers by interaction of the fifth position on each Cu centre with an N atom of an isocyanate ligand of the associated subunit. The coordination around each Cu atom is best described as distorted square-pyramidal.

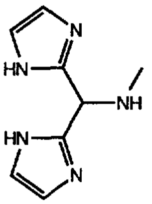
The nitric oxide reduction of $Cu(dmp)_2^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) in solution is reported. This is claimed to be the first quantitative demonstration of NO reduction of a cupric complex [236]. In deaerated solutions of neat H_2O, neat MeOH or MeOH–CH_2Cl_2 mixtures, $Cu(dmp)_2^{2+}$ was very rapidly reduced to $Cu(dmp)_2^{+}$ upon addition of an excess of NO. No reaction is observed in neat CH_2Cl_2 or CH_3CN, indicating the importance of the hydrolytic solvent.

The synthesis and characterization of three dinuclear copper(II) complexes and one mixed-valence tetranuclear cluster with the asymmetric imidazole-containing ligand bis(1,1′-imidazole-2-yl)(4-imidazole-4(5)-yl)-2-azabutane (**163**) are described [237]. The copper complexes analysed by X-ray crystallography are $[Cu_2(\mathbf{163})_2(BF_4)_2](BF_4)_2(H_2O)_4$; $[Cu_2(\mathbf{163})_2(NO_3)_2](H_2O)_4$; $[Cu_2(\mathbf{163})_2(CuBr_3)_2]$. The two Cu(II) ions in all the complexes are coordinated in a square-pyramidal geometry by three imidazole nitrogen atoms and one amine nitrogen donor in the equatorial plane, and each copper ion is weakly coordinated at the axial position by respectively a tetrafluoroborate, a perchlorate, a nitrate, or a tribromocuprate-(I) anion. By comparison of the structural data of the four complexes, a relationship has been established between the donor strength of the anion and some structural features, like the Cu(II)–Cu(II) distance of the dinuclear Cu(II)–Cu(II) unit in the four complexes. EPR spectra of frozen solutions of the perchlorate complex recorded at 77 K show that upon dilution in methanol the dinuclear complex reacts to form a mononuclear species.



(163)

The synthesis, spectroscopy, and structure of three Cu(II) coordination compounds of the ligands bis(imidazol-2-yl)methylaminomethane (**164**) and bis(imidazol-2-yl)methylamine (**165**) are described [238]. Both the ligands **164** and **165** are found to coordinate to Cu^{II} ions in a didentate fashion. In all three complexes the copper(II) ions are coordinated in a distorted octahedral geometry. In $[Cu(H\mathbf{164})Cl_3]_2(H_2O)_2$ and $[Cu(H\mathbf{165})Cl_3]_2(H_2O)_2$ each Cu(II) ion is coordinated by two imidazole nitrogen atoms and four chloride anions. The two mononuclear units are connected by two asymmetric chloride bridges. In $[Cu(H\mathbf{164})_2Cl_2]Cl_2(H_2O)_2$ the Cu(II) ion is coordinated by four imidazole nitrogen atoms and two chloride anions. In the complexes the amine nitrogen donor of the ligand is protonated and not coordinated to the Cu^{II} ion. In all three complexes strong hydrogen bonding is observed between the amine nitrogen donor(s) and the axial coordinated chloride(s). The ligand **164** was also immobilized onto a solid support, resulting in a very Cu^{II}-selective chelating ion-exchange resin with high uptake capacity. The resin retains its high uptake capacity for Cu(II) even in the presence of 1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane as competing ligands in solution.



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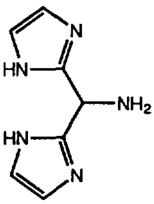


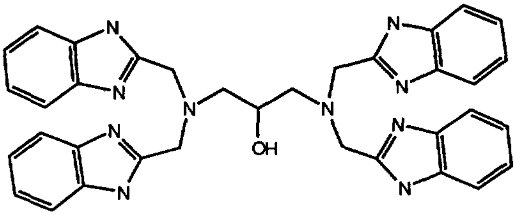
(165)

The magnetic susceptibilities of the compounds [Cu(bbip)(RO)]X (bbip = 1,3-bis(benzimidazol-2-yl)propane; R = CH_3, C_2H_5; X = NO_3, ClO_4) and related alkoxo-bridged copper(II) compounds were determined over the temperature range 80–300 K [239]. The primary factor influencing the exchange couplings for alkoxo-bridged Cu(II) systems is the p character of the hybrid orbitals on the bridging oxygen atom, the p character being measured by the in-plane and out-of-plane tilts of the R–O vector from the bisector of the Cu–O–Cu′ angle, and perhaps also by the bridging angle. This has been taken as evidence for an s pathway for the dominant exchange couplings.

Two dicopper(II) complexes, $[Cu_2(H_2L)(\mu\text{-}N_3)](ClO_4)_2 \cdot 0.5C_2H_5OH$ and $[Cu_2(HL)(\mu\text{-}N_3)(ClO_4)(C_2H_5OH)(H_2O)]$, have been synthesized and characterized, where H_3L is the dinucleating ligand, 2,6-diformyl-4-methylphenol di(benzoylhydrazone) [240]. The crystal structure of $[Cu_2(HL)(\mu\text{-}N_3)(ClO_4)(C_2H_5OH)(H_2O)]$ has been determined. The analysis of variable-temperature magnetic susceptibility data indicates that a medium antiferromagnetic interaction occurred between copper(II) ions in both complexes.

The compound $\{[Cu(bppn)](ClO_4)_2\}_2 \cdot H_2O$ (where bppn = *N*,*N*′-propylenebis-[2-benzoylpyridineiminato]) was prepared by reaction of 2-benzoylpyridine and 1,3-propanediamine with copper perchlorate in ethanol and characterized by X-ray crystallography [241]. The central Cu atom in two crystallographic non-equivalent $[Cu(bppn)]^{2+}$ cations exhibited a slightly distorted tetrahedral geometry, with Cu–N bond distances of 1.967(5)–2.010(5) Å and 1.966(5)–2.000(5) Å. The electronic absorption $\epsilon(646)$ was 194 M^{-1} cm^{-1}. The EPR parameters were in accordance with the respective values of intact Cu_2Zn_2 superoxide dismutase (Cu_2Zn_2SOD). Its electronic property displayed a single quasi-reversible one-electron reduction process at −0.204 V with $\Delta E_p = 84$ mV, suggesting the title complex possesses high superoxide dismutase (SOD) activity.

The structures of five dicopper complexes of dinucleating ligand **166**–H (*N*,*N*,*N*′,*N*′-tetrakis [(2-benzimadazolyl) methyl] - 2-hydroxy-1,3-diaminopropane) with thiocyanate and some other counterions were investigated by the X-ray diffraction method [242]. In $Cu_2(\mathbf{166}\text{–}H)(NCS)_2Cl_2 \cdot 6H_2O \cdot CH_3OH$ one chloride is not coordinated. Distorted square-pyramidal geometry is found for both CuN_3ClN and CuN_3ON coordination sites in which the N_3 tripodal coordination sites come from the two symmetric halves of **166**–H and other nitrogen atoms come from thiocyanate ions. In $Cu_2(\mathbf{166}\text{–}H)(NCS)_2(ClO_4)_2 \cdot 6H_2O \cdot 2EtOH$, the coordination environments for the two copper ions are both CuN_3ON. However, their geometries are different: one is distorted square-pyramidal and the other is distorted trigonal-bipyramid. In $Cu_2(\mathbf{166}\text{–}H)(NCS)_2(ClO_4)_2Cl \cdot H_3O \cdot 3.5H_2O$, the chloride ion does not coordinate to the copper ion, but it is hydrogen bonded to the hydroxy hydrogen. The coordination environments for the two copper ions are both CuN_3ON with distorted square-pyramidal geometries. In $Cu_2(\mathbf{166}\text{–}H)(NCS)Cl_3 \cdot 6H_2O$ one chloride does not coordinate. The coordination environments for the two copper ions are CuN_3ON in severely distorted trigonal-bipyramidal geometry and CuN_3Cl_2 in square-planar geometry. In $Cu_2(\mathbf{166}\text{–}H)(NCS)_3OH \cdot 2H_2O \cdot 3CH_3OH \cdot Et_2O$ the hydroxide ion does not coordinate and the coordination environments for the two copper ions are CuN_3N_2 with a geometry in between square-pyramidal and trigonal-bipyramidal, but slightly closer to square planar, and CuN_3ON in distorted square planar geometry. The distances between the copper ions are in the range 4.45–7.99 Å, indicating negligible interaction between the copper ions. The hydroxy groups of **166**–H in all the complexes all coordinate to copper ions, either in a terminal mode or in a bridging mode. These hydroxy groups do not lose their protons in all cases. All thiocyanate anions coordinate to copper ions through nitrogen atoms. All copper ions in all the complexes are pentacoordinated. The fact that the CuN_3 geometries of the tripodal coordination sites in **166**–H do not allow the formation of a square-planar complex may be the driving force for the formation of pentacoordinated complexes.



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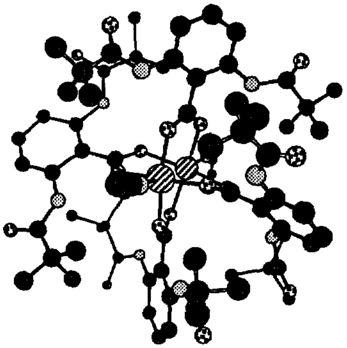
The tetracarboxylatobenzene tetraanion in μ-(1,2,4,5-benzenetetracarboxylato-*O*-1:*O*-4) bis [aqua (4-azaheptane-1,7-diamine-*N*,*N*′,*N*″) copper (II)] octahydrate, $[\{Cu(C_6H_{17}N_3)(H_2O)\}_2(\mu\text{-}C_{10}H_2O_8)] \cdot 8H_2O$ bridges two *N*,*N*′,*N*″-chelated aquacopper entities in a monodentate manner to give rise to square-pyramidal coordination at the metal centres [243]. Hydrogen bonding involving the three N atoms, the four carboxyl O atoms and the five water molecules gives rise to a three-dimensional network structure.

The $[Cu_2(dap)_5](ClO_4)_4$ complex (dap = 1,3-diaminopropane) crystallizes, in almost quantitative yield, from alcoholic solutions containing the ligand and Cu^{II} in a 5:2 molar ratio [244]. As revealed by the crystal structure of $[Cu_2(dap)_5](ClO_4)_4$, a dap molecule bridges two $Cu(dap)_2^{2+}$ units. Each copper atom is five-coordinated in a rather regular square-pyramidal environment, the two nitrogen atoms of the bridging dap occupying the apical positions. The basal planes of the square pyramids form a dihedral angle of 61.7(2)°.

Treatment of benzylethyl ether with a catalytic amount of dinuclear copper(II) complex of 7-azaindole under oxygen atmosphere at 80 °C produced ethyl benzoate in 10 400% yield based on the catalyst [245]. This reaction could also be applied to other ethers (e.g. alkylbenzyl ethers and dialkyl ethers) to give alpha-oxygenated products catalytically.

Using a three-solvent biphasic method, three new fully conjugated, chalcogen-rich, bridged copper(II) complexes have been synthesized for the preparation of molecular conductors and magnetic materials, having the general formula $(Bu_4N(_2\{tto[Cu(L)]_2\}$ (tto = $C_2S_4^{2-}$ = tetrathiooxalato; L = mnt = 1,2-dicyanoethene-1,2-dithiolato, dmid = 2-oxo-1,3-dithiole-4,5-dithiolato [246]. The single-crystal X-ray structures of $(Bu_4N)_2\{tto[cu(mnt)]_2\}$ has been determined and displays perfect planarity. Cyclic voltammetry of the complexes shows each to exhibit two reversible redox processes. Copper(II) benzoate reacts with 2-dimethylaminoethanol in ethanol forming a green copper(II) complex, bis[(2-hydroxyethyl)dimethylammonium[tetrakis(μ-benzoato-*O*:*O*′)bis[(benzoato-*O*)cuprate(II)] [247]. The two Cu atoms, with a Cu···Cu distance of 2.670(2) Å are held together by the four carboxylate groups. Each Cu atom is bound in a square-pyramidal configuration to five carboxylate O atoms. The (2-hydroxyethyl)dimethylammonium cation is hydrogen bonded to the uncoordinated O atom of the unidentate carboxylate group.

The copper(II) dimer complexes $[Cu_2\{OCOC_6H_3Me_2(NHCO^tBu)_6\}_4(MeOH)(H_2O)]$ (**167**) and $[Cu_2\{OCOC_6H_3(NHCO^tBu)_2\text{-}2,6\}_4(MeCN)_2]$ (**168**), containing bulky intramolecularly NH···O hydrogen-bonded carboxylate ligands, were synthesized and characterized [248]. The solid state structure of **167** shows a distorted Cu–O–C–O–Cu structure with a magnetic exchange ($-2J = 302\ cm^{-1}$) between the two Cu^{II} ions, whereas the latter has a twisted Cu–O–C–O–Cu structure, due to the steric congestion of the two bulky amide groups, with a relatively large exchange ($-2J = 460\ cm^{-1}$) through the NH···O hydrogen bonds. The complexes were synthesized by the reaction of $CuSO_4 \cdot 5H_2O$ and the appropriate carboxylic acid in H_2O with recrystallization from MeOH, (**167**), or CH_3CN, (**168**). Each Cu^{II} centre is bonded to four carboxylate oxygen atoms and an MeOH or H_2O oxygen atom in (**167**) or one acetonitrile nitrogen atom in (**168**). The short distance between the carboxylate oxygen and amide nitrogen atom indicates the presence of NH–OH bonds (av. 2.75 Å in **167** and 2.67 Å in **168**).



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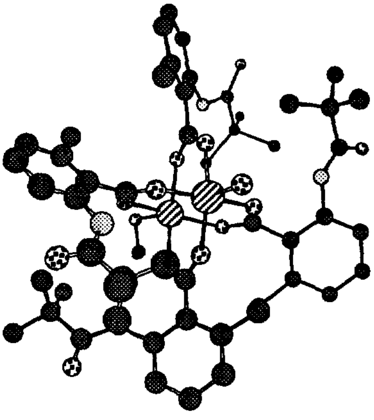


(168)

Copper(II) complexes of high and low melting points, 1,2-bis(*n*-octylsulfinyl) ethane (α-bose and β-bose), have been synthesized [249]. The complexes were assigned the formulae $[Cu_2(\alpha\text{-bose})_4](ClO_4)_4$, $[Cu_2(\beta\text{-bose})_4](ClO_4)_4$, $[Cu_2(\alpha\text{-bose})_2(NO_3)_3](NO_3)\cdot 2H_2O$ and $[Cu_2(\beta\text{-bose})_2(NO_3)_4]\cdot H_2O$, on the basis of their elemental analyses, electrical conductance, magnetic measurements (room and variable temperature) and IR studies.

A series of copper(II) complexes with tridentate Schiff bases, obtained by the 1:1 condensation of a 4-(*p*-*n*-alkoxybenzoyloxy)salicylaldehyde and an aminoalcohol have been prepared and characterized, where the *n*-alkoxy group is *n*-propyloxy, *n*-butyloxy, *n*-hexyloxy, *n*-octyloxy, *n*-hexadecyloxy or *n*-octadecyloxy and the aminoalcohol is 2-aminoethanol, 3-aminopropanol, (*R*)- or (*S*)-2-amino-4-methylpentanol [250]. The 19 complexes thus synthesized can be classified into two groups: the first group contains a 3-aminopropanol residue, are rod-like in shape and involve a dinuclear Cu_2O_2 central core; the second group involves one of the remaining aminoalcohol residues and are likely to have a tetranuclear Cu_4O_4 central core of cubane-like structure and overall disc-like molecular shape.

3.4.2. *Nitrogen and sulfur coordination*

The X-ray crystal structure determination of the copper derivative [bis(6-methyl-2-pyridylmethyl)sulfide-*N*,*N*′,*S*] bis(trifluoromethylsulfonato-*O*)copper(II) dichloromethane solvate, shows that this compound contains monomeric $[Cu(DMPT)OSO_2(CF_3)_2]$ molecules in which the Cu^{II} ion is surrounded by a tridentate DMPT ligand and by a pair of trifluoromethylsulfonato ligands in a distorted tetragonal-pyramidal environment [251].

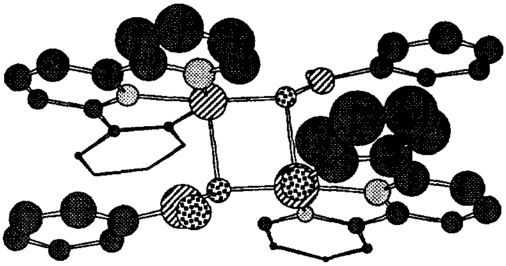
The new quadridentate N_3S-compound di-2-pyridyl ketone thiosemicarbazone (**L**) has been characterized by spectroscopic techniques and single-crystal X-ray analysis [252]. The thiosemicarbazone moiety adopts a configuration with N(1) *cis* to N(3).

The chelating behaviour of the deprotonated compound (L) has been investigated in two dinuclear copper(II) complexes, $[(Cu(L–H)Cl)_2] \cdot 2DMF$ (DMF = dimethylformamide) and $[\{Cu(L–H)(CN)\}_2] \cdot 2MeOH$. The crystal structures of the complexes have been determined: the coordination geometry about the copper(II) in both compounds is distorted square-pyramidal with one pyridine nitrogen atom, the sulfur, the imino nitrogen, and a chloro or cyano group in the basal plane; a pyridine nitrogen atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

3.4.3. Nitrogen and oxygen coordination

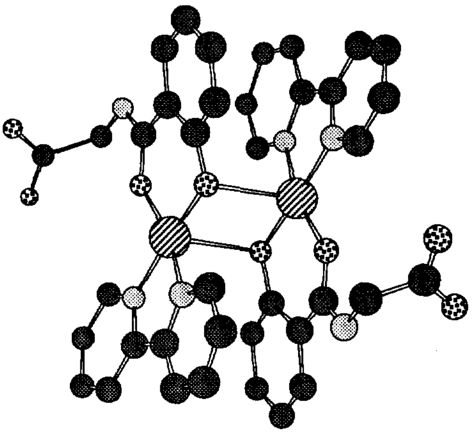
A mixed-ligand, 1:2 complex for copper(II) azide with 3-acetylpyridine, di-μ(1,1)-azido-di(*O*,*O*′-nitrato)tetrakis(3-acetylpyridine)dicopper(II) has been synthesized and characterized by spectroscopic and X-ray crystallographic methods [253]. Spectroscopic results suggest didentate chelate nitrate groups and a μ(1,1) bridging azido ligand. The dimeric molecule, which possesses a crystallographic inversion centre, contains two μ(1,1) bridging azido ligands. Each copper(II) atom in the cyclic Cu_2N_2 ring is further coordinated by two oxygen atoms from a didentate, chelating nitrate group and two nitrogen atoms from the 3-acetylpyridine molecules. The coordination environment of the copper atom may be described as a very distorted tetragonal-bipyramid with a nitrogen atom of an azide group and one oxygen atom of a nitrate group occupying the apical sites. The azido ligands are almost linear.

Reaction of $Cu(BF_4)_2$ with 6-(2-hydroxyphenyl)2,2′-bipyridine (HL) followed by precipitation with aqueous $NaBPh_4$ gave the unexpected product $[Cu_2L_2\{\mu\text{-PhB(OH)O}\}_2]$ (**169**) in which the bridging groups, which are the anions of phenylboric acid, $PhB(OH)_2^-$, are derived from decomposition of the $[BPh_4]^-$ counter-ion [254]. The complex contains two five-coordinated Cu^{II} centres in an elongated square-pyramidal geometry, with a $Cu_2(\mu\text{-O})_2$ core, and appears to be stabilized by an aromatic π–π interaction in which the pendant phenyl ring of each bridging group stacks with one of the pyridyl rings of a ligand. In solution, EPR spectroscopy shows that the dinuclear complex is cleaved to a mononuclear species.



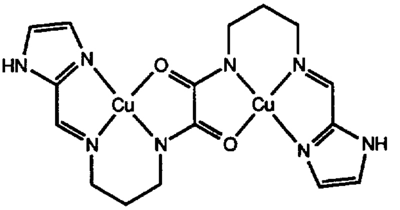
(**169**)

The solution and solid state behaviour of the binary system Cu^{II}–2-hydroxyhippuric acid (2-OHhipH) and the corresponding ternary system with 2,2′-bipyridine (bpy) were investigated through pH-metric titrations and X-ray crystallography [255]. A spectrophotometric pK_a of 5.2(2) was determined for the deprotonation of the phenolic hydroxy group in the ternary system. The structure of $[Cu(bpy)(2\text{-OHhip})]_2 \cdot 8H_2O$ (**170**) was found to consist of dimeric $[Cu(bpy)(2\text{-OHhip})]_2$ units and lattice water molecules. The Cu^{II} atom is pentacoordinated by the two nitrogen atoms of the bpy molecule and the carbonyl and phenolate oxygen atoms of the ligand in the equatorial plane, and by a bridged phenolate oxygen in the apical position, giving rise to a distorted square-pyramidal geometry.



(170)

A novel symmetrical bis-tetradentate Schiff base, H_4L, has been prepared from the condensation of H_2L' [*N*,*N*′-bis(3-aminopropyl)oxamide] with imidazole-2-carbaldehyde [256]. This ligand reacts with copper(II) perchlorate in neutral medium to yield the dinuclear complex $[Cu_2(H_2L)][ClO_4]_2$, (**171**), which has two non-deprotonated imidazolyl moieties. The crystal structure of this compound consists of planar centrosymmetric dinuclear copper(II) cations and two perchlorate anions. The copper(II) ions are bridged by an oxamidate group in a trans conformation, resulting in a copper–copper distance of 5.119 Å. Each copper(II) ion occupies an inner site of the di-deprotonated ligand with a CuN_3O distorted square-planar environment, and bond distances of *ca* 1.95 Å. In **171** each copper(II) ion can additionally accept one donor atom in axial position. Under basic conditions, this donor atom is the deprotonated imidazolate nitrogen atom from another dinuclear $[Cu_2L]$ unit, giving rise, by a self-assembly process, to the formation of the polynuclear copper(II) complex $[(Cu_2L)_n]$. In this complex the copper(II) ions must be alternatively bridged by oxamidate and imidazolate groups. From magnetic susceptibility measurements, both **171** and $[(Cu_2L)_n]$ were found to exhibit strong antiferromagnetic exchange coupling, with J values of $-431\ cm^{-1}$ and $-265\ cm^{-1}$ respectively.



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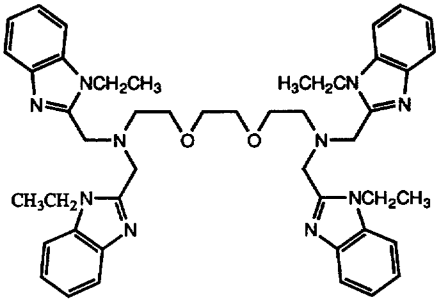


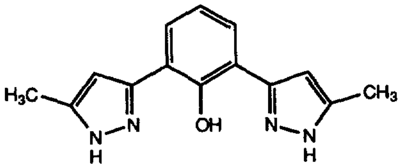
(172)

The ^1H NMR spectra of a series of well-characterized μ-phenoxo and μ-alkoxo spin-coupled dicopper(II) complexes have been investigated [257]. The complexes studied were $[Cu_2(BPMP)(OH)]^{2+}$ (BPMP = 2,6-bis[[bis(2-pyridylmethyl)-amino]methyl]-4-methylphenol), $[Cu_2(CH_3HXTA)(OH)]^{2-}$ (CH_3HXTA = *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxymethylglycine), $[Cu_2(m\text{-XYL})OH)]^{2+}$ (*m*-XYL-2,6-bis[[bis(2-pyridylethyl)amino]methyl]phenol), and $[Cu_2(TBHP)(OAc)]^{2+}$ (TBHP = *N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane). The magnetic interactions of these complexes range from strongly antiferromagnetically to weakly ferromagnetically coupled. The results of this study indicate that ^1H NMR spectroscopy is an excellent tool for probing the solution structures of spin-coupled dicopper(II) centres in model complexes as well as biological systems.

The dinucleating ligand ethylene glycol-bis(β-aminoethyl ether) *N*,*N*,*N*′,*N*′-tetrakis[2-(1-ethylbenzimidazoyl)] (**172**) has been synthesized in good yield by the condensation of 1,2-diaminobenzene with ethylene glycol-bis(β-aminoethyl ether) *N*,*N*,*N*′,*N*′-tetraacetic acid [258]. This ligand was used to synthesize the dinuclear Cu^{II} diacetonitrile complex $[Cu_2(\mathbf{172})(CH_3CN)_2](ClO_4)_4 \cdot 2CH_3CN$. The X-ray structure shows two distinct square-pyramidal Cu^{II} centres with each Cu^{II} ion bound by two benzimidazole nitrogen atoms, one amine nitrogen atom, an ether oxygen atom and one acetonitrile nitrogen atom. The Cu···Cu separation is 5.809 Å. Spectral titration of the complex with sodium acetate or sodium cyanide results in new complexes with terminal acetate or cyano groups. The EPR spectra, the room-temperature magnetic moment of $\mu_{\text{eff}}Cu = 2.16\ \mu_B$ and the X-ray structure show the two Cu^{II} centres are uncoupled.

The structure of blue di-μ-phosphinato-bis[(1,10-phenanthroline)copper(II)] nitrate consists of dimeric $[Cu(H_2PO_2)(phen)]$ subunits (phen = 1,10-phenanthroline) joined by two phosphinato bridging ligands, with each metal centre organized in a distorted planar arrangement [259]. These joined subunits exist as a discrete cation, with the equivalent of two nitrates as counterions. The subunits have a four-coordinate distorted square-planar arrangement of N and O atoms from the 1,10-phenanthroline and phosphinato ligands, with the fifth and sixth positions of the Cu centre occupied by neighbouring O atoms of the nitrate counterions. The coordination stereochemistry around each Cu is best described as tetragonal.

As part of a study to obtain communication between metal centres, a series of phenoxo-bridged homo- and hetero-dinuclear complexes of 4-methyl-2,6-bis(5-methylpyrazo-3-yl)-phenol (**173**) have been synthesized and characterized [260]. Variable-temperature magnetic susceptibility measurements carried out for the homo-dinuclear complexes $[Cu_2(\mathbf{173}-H)_2][ClO_4]_2$, $[Cu_2(\mathbf{173}-H)(acac)_2][ClO_4]$, $[Cu_2(\mathbf{173}-H)(\mu\text{-}OH)Cl_2]$, $[Ni_2(\mathbf{173}-H)_2(H_2O)_4][ClO_4]_2$ and $[Fe_2(\mathbf{173}-H)_4(\mu\text{-}OH)_2]\cdot 4H_2O$ have shown that in all the cases the dinuclear metal centres are antiferromagnetically coupled. The structure of $[Cu_2(\mathbf{173}-H)(acac)_2][ClO_4]\cdot CHCl_3$ consists of two nearly square-planar copper(II) centres supported by a phenoxide bridge. The cryomagnetic behaviour of two phenoxo-bridged dimeric iron(III) complexes derived from a bis(iminomethyl)triphenol and a bis(aminomethyl)triphenol have also been studied.



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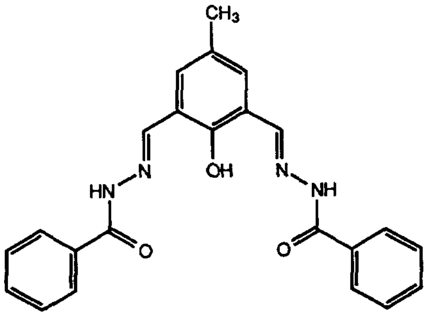

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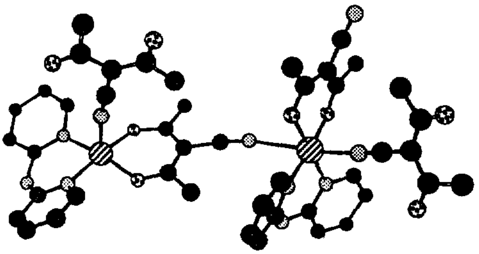
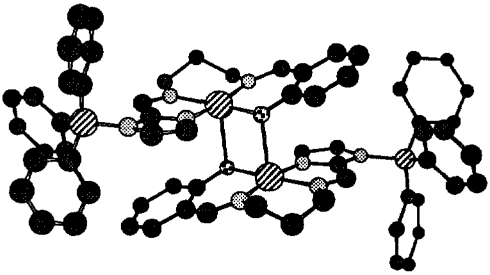


(175)

Three dicopper(II) complexes, $[Cu_2(\mathbf{174}-H)(\mu\text{-}N_3)](ClO_4)_2\cdot 0.5C_2H_5OH$, $[Cu(\mathbf{174}-2H)(\mu\text{-}N_3)(H_2O)(C_2H_5OH)(ClO_4)]$ and $[Cu_2(\mathbf{174}-3H)(\mu\text{-}N_3)]\cdot DMF$ have been synthesized and characterized, where $H_3\mathbf{174}$ is the pentadentate dinucleating ligand 2,6-diformyl-4-methylphenol di(benzoylhydrazone) [261]. Because of the existence of a hydrazide structure in the lateral chain, the ligand **174** can lose one, two or three hydrogen atoms to form the keto form, mixed keto–enol form or enol form of the dinuclear copper(II) complexes respectively. The crystal structure of $[Cu_2(\mathbf{174}-2H)(\mu\text{-}N_3)(H_2O)(C_2H_5OH)(ClO_4)]$ has been determined. The analysis of variable-temperature magnetic susceptibility data indicates that there is an antiferromagnetic interaction between the copper(II) ions in these complexes with the exchange parameters (2J) of $-86.8\ \mathrm{cm}^{-1}$ $-132.4\ \mathrm{cm}^{-1}$ and $-176.7\ \mathrm{cm}^{-1}$ for the complexes respectively.

The addition of dipyridylamine to bis(3-cyano-2,4-pentanedionato)copper(II) Cu(NC–acac)$_2$, has been shown to induce changes in the mode of interaction and the conformation of the NC–acac$^-$ anion [262]. The structure of the resulting dinuclear compound (**175**) was determined from a single microcrystal. In the addition compound {[Cu(NC–acac)dipyamH](NC–acac)}$_2$ when the NC–acac$^-$ acts simultaneously as a chelating and bridging ligand (and assumes the commonly observed U(*Z*,*Z*) conformation), and as weakly an *N*-coordinated unidentate counter-anion (imposing the rarely encountered S(*Z*,*E*) conformation). In the [Cu(NC–acac)dipyamH](NC–acac) entities one of the copper(II) centres is a 4+2 Jahn–Teller complex and the other is a square-based pyramid.

The reaction of Cu^{II}(ClO$_4$)$_2$ with 2-imidazolecarboxaldehyde, 1,3-diaminopropane, salicylaldehyde and NaBPh$_4$ yielded the complex [Cu(LBPh$_3$)]$_2$ (**176**) (LBPh$_3$ = *N*-(salicylidene)-*N*′-(imidazol-2-ylmethylene(-1,3-propanediamine) [263]. The X-ray structure of the complex shows a dinuclear complex and the presence of a B–N bond which is formed by the reaction of BPh$_4^-$ with a nitrogen atom of the imidazolate moiety of the ligand. The structure consists of an oxygen-bridged dimer where the geometry about each copper centre is distorted square-pyramidal with an out-of-plane Cu–O distance of 2.440(3) Å. Basal coordination sites are occupied by three nitrogen atoms and one oxygen atom of the chelated LBPh$_3$ ligand. The link between adjacent metal centres is formed by a self-assembly bridging oxygen atom at a basal site. The chelating Cu(II)–O length of 1.921(3) Å is shorter than the bridging ligand 2.440(3) Å. The Cu···Cu separation is 3.085(4) Å and the Cu–O–Cu angle is 94.35(10)°. The B–N bond is 1.640(6) Å. A weak ferromagnetic exchange interaction is observed between the two copper centres. Although the mechanism for the B–N bond formation is not clear, it is proposed that the triphenylborate radical anion reacts with the imidazolate moiety of the ligand instead of reducing the Cu^{II} ions to Cu^{I}.



(**176**)

A synthetic investigation of copper(II) ibuprofenate (Ibup) addition compounds with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmph) has led to the isolation of dinuclear adducts of the forms [Cu(Ibup)$_2$(bpy)]$_2$·4H$_2$O and [Cu(Ibup)$_2$(phen)]$_2$ and a mononuclear adduct

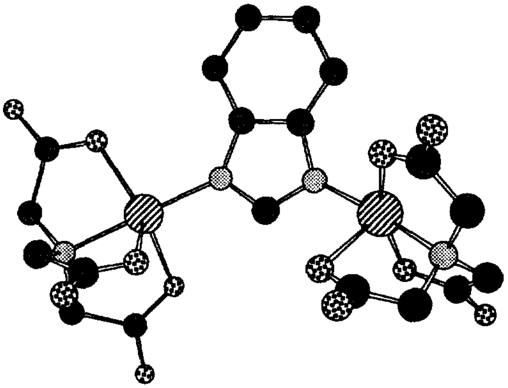
$Cu(Ibup)_2(dmph)$ [264]. Each copper centre is coordinated with two ibuprofenate bridges, a terminal diimine molecule and a monodentate ibuprofenate group complete five-coordination at each metal atom. Spectroscopic data for the dmph complex are consistent with a mononuclear structure having a very distorted square-pyramidal CuN_2O_2+O chromophore. The Cu^{II} atom is coordinated to two nitrogen atoms from a chelating dmph ligand, two carboxylic oxygens of a didentate ibuprofenate ion and an oxygen atom of a monodentate carboxylic group of a second ibuprofenate ion. The effect of the dinuclear complexes on the rate of hydrolysis of bis(*p*-nitrophenyl) phosphate have been examined in aqueous methanol solution at 70 °C and pH 7.4.

The complexes $[Cu(\mu\text{-}L)Cu(bpy)(EtOH)](ClO_4)_2$ and $[Cu(\mu\text{-}^1L)Cu(bpy)(H_2O)](ClO_4)_2 \cdot H_2O$ (where $H_2L = N,N'$-bis(1,3-dimethyl-5-nitrosopyrimidine-2,4-(1*H*,3*H*)-dion-6-yl)propylenediamine; $H_2{}^1L$ arises from H_2L by elimination of a CO molecule from one of the pyrimidine rings) have been obtained from the reaction of the precursor $[Cu(\mu\text{-}HL)Cu(H_2O)_2(CH_3CH_2OH)](ClO_4)_3$ with bpy and $Cu(ClO_4)_2 \cdot 6H_2O$ respectively [265]. The structures of the complexes have been solved by X-ray crystallographic methods. The structure of $[Cu(\mu\text{-}L)Cu(bpy)(EtOH)](ClO_4)_2$ is made up of $[Cu(\mu\text{-}L)Cu(bpy)(EtOH)]^{2+}$ cations and two semi-coordinated perchlorate anions. The [CuL] fragment coordinates to the external Cu ion through the two deprotonated oximate oxygen atoms to afford a dinuclear structure with double syn–syn nitroso-oximate bridge and an intramolecular Cu–Cu distance of 3.731(1) Å. The Cu exhibits a CuN_4O_2 pseudo-octahedral coordination polyhedron, whereas the geometry around the Cu ion is distorted square-pyramidal CuN_2O_2O. The structure of $[Cu(\mu\text{-}^1L)Cu(bpy)(H_2O)](ClO_4)_2 \cdot H_2O$ consists of $[Cu(\mu\text{-}^1L)Cu(bpy)(H_2O)]^{2+}$ cations, two perchlorate anions and one lattice water molecule. The coordination of the $[Cu(^1L)]$ unit to the external Cu ion takes place through the two nitroso-oximate groups with an intramolecular Cu–Cu distance of 3.664(3) Å. The Cu(1) occupying the inner site of the $^1L^{2-}$ ligand exhibits a 4+1 CuN_4O coordination environment, whereas the Cu atom is in a distorted square-pyramidal CuN_2O_3 environment. Both complexes are diamagnetic at room temperature, with $J < -1000\ cm^{-1}$.

A benzimidazolate-bridged dinuclear copper(II) complex with *N,N'*-bis(carboxymethyl)glycine, $Na_3[Cu_2(BCMG)_2Bzim] \cdot 10H_2O$ (**177**) has been synthesized and its structure has been determined by X-ray single-crystal diffraction [266]. The *N,N'*-bis(carboxymethyl)glycinate trivalent anion acts as a tetradentate ligand to copper(II). Each copper atom is complexed by three oxygen atoms from carboxylates, one nitrogen atom from BCMG and one nitrogen atom from the benzimidazolate anion. The benzimidazolate anion bridges two copper atoms (Cu(1), Cu(2)) which are 5.716(7) Å apart. Na^+ ions are complexed by oxygen atoms from water molecules and carboxylates and bridged by several oxygen atoms. The geometry of the coordination around the copper atoms and Na is intermediate between trigonal-bipyramidal and tetragonal-pyramidal, but around Na(1) it is distorted octahedral.

The compound, bis[μ-(1,1)-di(2-pyridyl)-3-butanolato-*N,O*:*N',O*]bis[iodocopper(II)] bis(acetonitrile) solvate, was obtained from copper(I) iodide and the neutral ligand on reaction with oxygen [267]. The olefinic function is unaffected by the oxidation. The coordination at each Cu atom is trigonal-bipyramidal and the coordination polyhedra share a common edge, which is the O···O diagonal of the central Cu_2O_2 ring.

The structure of di-μ-chlorobis[*N*-(2-hydroxyethyl)salicylideneiminato-*N*,*O*,*O*′copper(II)] methanol solvate, $[Cu_2Cl_2(C_9H_{10}NO_2)_2]\cdot CH_3OH$, has been determined from single-crystal X-ray diffraction data [268]. The molecular structure shows the complex is dimeric with a distorted square-pyramidal geometry at each copper centre. The two bridges are formed by Cl atoms giving a Cu–Cu separation of 3.417(1) Å in the dimers.



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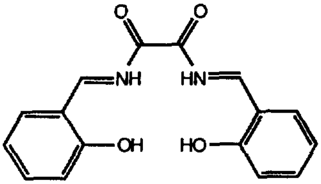

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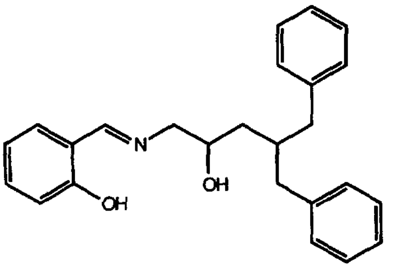
A new *N*,*N*′-disubstituted oxamide ligand *N*,*N*′-bis(2-hydroxybenzyl)oxamide (**178**), the related monomeric copper(II) complex salt $Na_2[Cu($**178**–H$)]\cdot H_2O$ and two oxamidato-bridged dinuclear copper(II) complexes, namely $[Cu_2($**178**–H$)(bpy)]\cdot 2H_2O$ and $[Cu_2($**178**–H$)(py)_4]$ (bpy = 2,2′-bipyridine, py = pyridine), have been synthesized [269]. Single-crystal X-ray analysis revealed that $[Cu_2($**178**–H$)(py)_4]$ has a *trans*-oxamidato-bridged dinuclear copper(II) structure, in which each copper(II) ion exhibits a distorted square-pyramidal surrounding. This complex is rapidly turned into complex $[Cu_2($**178**–H$)(py)_3(H_2O)_2]$ when exposed to the air.

A dicopper(II) complex with a novel unsymmetric dinucleating ligand, **179**, which can provide donor atom, coordination number, and geometric asymmetries at metal centres, $[Cu_2($**179**–2H$)(CH_3COO)]ClO_4\cdot H_2O\cdot 0.5NaClO_4$, was synthesized, where (**179**) is a racemic 1-bis(2-pyridylmethyl)amino-3-salicylideneaminopropan-2-ol [270]. The crystal structure of the complex showed that two stereoisomers are present in the solid state, which is attributed to the presence of an enantiomeric pair of **179**. Dinuclear cations consist of one square-planar site with an NO_3 donor set and one five-coordinate site with an N_3O_2 donor set, which are linked by an endogenous alkoxide bridge of **179** and an exogenous acetate bridge. A powdered sample of the complex shows weak antiferromagnetic interaction (2.60 μ_B/Cu_2 at 300 and 1.81 μ_B/Cu-2 at 5 K).



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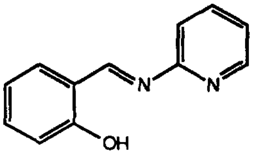
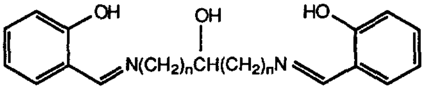


(180)

A survey of 123 copper(II) acetate-type dimeric complex units, determined by X-ray diffraction in the crystal structures containing either a CuO_4O or CuO_4N chromophore, showed that all the distorted square-pyramidal coordination spheres contain a copper atom displaced 0.165–0.225 and 0.184–0.322 Å from the basal O_4 plane in CuO_4O and CuO_4N chromophores respectively [271]. The Cu–Cu distances were in the range of 2.575–2702 and 2.603–2.886 Å for the CuO_4O and CuO_4N chromophores respectively. The apical ligand atoms show large coefficients of variation for the distortion from the perpendicular to the basal O_4 plane. There is highly significant propensity for the copper(II) atoms to move out from the basal O_4 plane upon elongation of the Cu–Cu distance. Strong negative correlations were found between the Cu–O–C and O–C–O angles. The most marked deviations for the observed parameters are caused by the bridges containing a halogenoacetate anion, leading to distorted trigonal-bipyramidal geometry.

The synthesis and characterization of mixed-ligand copper(II) complexes with bridged dicarboxylato groups, of the composition $[(\mathbf{180})Cu]_2L \cdot nH_2O$, where **180** = *N*-pyridylsalicylidenaminato, L = malonato, phthalato and terephthalato, and $n = 8$, 5, 2 respectively, are reported [272]. Ligand **180** coordinates as a monoanionic didentate ligand, whereas the carboxylate coordinates as a monodentate ligand. The stereochemistry around the copper is distorted octahedral for malonato, square-pyramidal for phthalato and square-planar for terphthalato complexes. EPR spectra for polycrystalline complexes at room temperature show non-interaction in the dimeric units. However, the anomalous magnetic moment data suggest intermolecular interactions as an efficient exchange pathway.

The synthesis and characterization of a series of dinuclear copper(II) complexes of ligands formed by the condensation of substituted salicylaldehydes and 1,3-diamino-2-propanol (**181**) and 1,5-diamino-3-pentanol (**182**) and their interaction with both phenols and catechols are reported [273]. Spectroscopic and magnetic data suggest that the neutral phenols and catechols can bind to dinuclear copper(II) complexes without actually coordinating to the copper atoms. The crystal and molecular structures of two dinuclear copper(II) complexes have been solved. The μ-hydroxo-bridged dicopper(II) complex of $[\mathbf{182}]^{3-}$, $[Cu_2(\mathbf{182}\text{–}3H)(OH)]$, consists of neutral molecules with an out-of-plane interaction from a copper in one binuclear unit to the hydroxo group of an adjoining molecule. The 4-ethylphenol adduct of the μ-(O,O′) phenylacetate-bridged dicopper(II) complex of **181**, [Cu_2(**181**–3H)(phenac)(4-ethylphenol)] shows the 4-ethylphenol group is involved in a strong hydrogen bond to one of the phenolic oxygen donor atoms of the [**181**]$^{3-}$ ligand and a weaker hydrogen bond to the adjoining oxygen donor atom of the bridging phenylacetate ion. The other phenolic oxygen donor atom is involved in an out-of-plane interaction to one of the copper atoms.

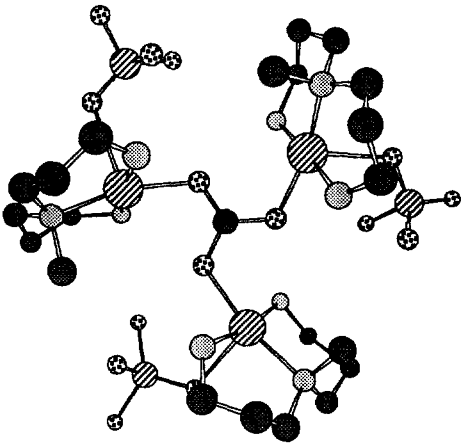


(**181**); n=1
(**182**); n=2

The reaction of $L_2Cu_2OAc_2$ (L = 7-amino-4-methyl-5-aza-3-hepten-2-onato^{1-}, OAc = acetate ion) with NaN_3 and $NaNO_2$ yields $[L_2(N_3)_2Cu_2]$ and $[L_2(NO_2)_2] \cdot H_2O$ respectively which have been characterized by X-ray crystallography [274]. In both cases the structure consists of neutral dinuclear entities resulting from the pairing of two mononuclear units via single-atom bridges connecting an equatorial position of a copper centre to an axial position of the other one. The copper ions adopt a (4+1) square-based geometry in the azido complex, whereas (4+1) and (4+2) environments are present in the nitrito complex. Analysis of the thermal variation of the magnetic susceptibility shows that, in both complexes, the two spins are ferromagnetically coupled within the dimer whereas an antiferromagnetic coupling is operative between dinuclear entities. Both types of interaction are larger in the case of the azido complex ($J = 24\ \mathrm{cm}^{-1}$, $J' = -1.6\ \mathrm{cm}^{-1}$) than for the nitrito complex ($J = 8\ \mathrm{cm}^{-1}$, $J' = -0.2\ \mathrm{cm}^{-1}$).

3.5. *Trinuclear complexes*

The X-ray structure **183** represents a rare example of a ferromagnetic μ_3-L system where L = bis(3-aminopropyl)methylamine and shows a practically equatorial triangle of Cu(II) atoms with a central μ_3-carbonate bridge [275]. Each trinuclear unit consists of three copper atoms in a square-pyramidal environment, of which the apical position is occupied by one oxygen atom of a perchlorate anion and the basal plane is formed by the three nitrogen atoms of the ligand and one oxygen atom of the carbonato ligand. The copper atoms are slightly out of the carbonato plane, the average deviation being 0.189 Å. The CuN_3O planes are tilted with respect to the practically planar CO_3Cu_3 fragments with an average dihedral angle of 61.5°. The magnetic measurements show a ferromagnetic coupling constant of 1.21 $\mathrm{cm}^3\ \mathrm{K}\ \mathrm{mol}^{-1}$ at room temperature and 1.98 $\mathrm{cm}^3\ \mathrm{K}\ \mathrm{mol}^{-1}$ at 5 K. This low J value is partly explained by the large Cu···Cu separation of 4.87 Å.



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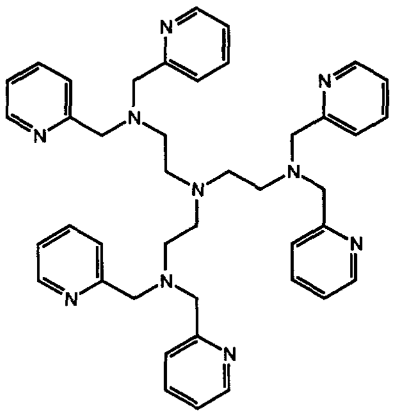
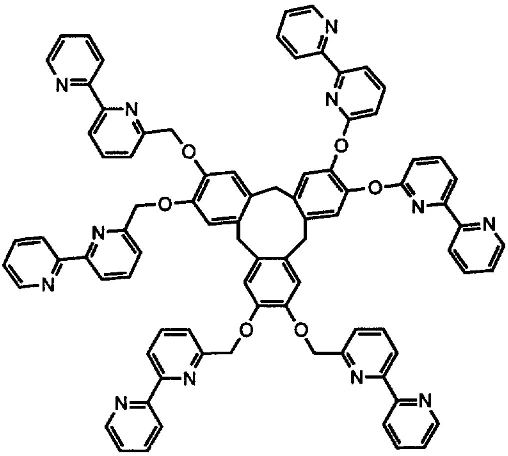


(184)

A novel trinuclear copper(II) complex with a new trinucleating ligand has been synthesized and structurally characterized, and its reactivity with the plasmid pBR322 investigated [276]. The ligand, (**184**), is based on tris(2-aminoethyl)amine, in which the primary amine groups are each substituted with two 2-pyridylmethyl groups. The trinuclear complex, $[Cu_3(\mathbf{184})(NO_3)_2(H_2O)_3](NO_3)_4 \cdot 5H_2O$ has been characterized by X-ray diffractometry. Whereas the three copper(II) ions in $[Cu_3(\mathbf{184})(NO_3)_2(H_2O)_3]^{4+}$ each bind to a tridentate N_3 moiety of **184**, the structure is unsymmetrical owing to the coordination of the "central" alkylamine nitrogen to a single copper(II) ion. The remaining two copper(II) ions coordinate different exogenous ligands: one copper(II) ion coordinates two water molecules; the second binds two nitrate ions with one nitrate coordinating in a monodentate fashion and the other binds to the same copper(II) atom in an anisodidentate geometry. The trinuclear complex, which is formulated as $[Cu^{II}_3(\mathbf{184})(H_2O)_n(OH)_{6-n}]^{n+}$ in aqueous solution, is observed to cleave the plasmid pBR322 efficiently in the presence of hydrogen peroxide or 3-mercapto-propionic acid (MPA). The reaction in the presence of MPA is shown to be O_2-dependent, and is not inhibited by hydroxyl radical scavengers (dimethylsulfoxide or D-mannitol) or superoxide dismutase. However, catalase completely inhibits the reaction, indicating a requirement for H_2O_2. Cleavage of pBR322 by $[Cu^{II}_3(2)(H_2O)_n(OH)_{6-n}]^{n+}$ is equally efficient in the presence of H_2O_2 or MPA, and is comparable with that observed by the well-known reagent $[Co(op)_2]^{2+}$ (op = 1,10-phenanthroline). However, the reaction of $[Cu(op)_2]^{2+}$ with pBR322 in the presence of MPA is much more vigorous, indicating that the reaction mechanisms for the two complexes may be different. $[Cu^{II}_3(2)(H_2O)_n(OH)_{6-n}]^{n+}$ is also observed to cleave pBR322 in a slower process, in the absence of H_2O_2 or MPA, and in a pH-dependent manner.

A series of copper(II) and copper(I) complexes has been synthesized with ligands combining 6-methyl-2,2′-bipyridines with cyclotriveratrylene (**185**) and with catechol (**186**) [277]. The electrochemical, ^1H NMR, and mass spectrometry characterizations of these complexes are described and discussed. The six pendant bipyridines of the ligand (**185**) allow for the formation of two trinuclear copper(I) complexes [(**185**)Cu_3]$(BF_4)_3$ differing only in the conformation vic or int adopted by the ligand to fit the tetrahedral cuprous ions. Similarly, **185** generates two trinuclear copper(II) complexes in which the conformation of the ligand fits the square-planar geometry of cupric ions. In both the cuprous and cupric complexes, a conformational equilibrium exists. Ligand **186** bearing two methylbipyridines has proven to be a useful model of the coordinating sites of ligand **185**. In this case, two homologous copper(I) complexes are obtained, [(**186**)Cu]BF_4 and [(**186**)$_2Cu_2$]$(BF_4)_2$, modelling respectively two possible coordination conformations of ligand **185**. With copper(II), ligand **186** yields only one complex, [(**186**)Cu]$(CF_3SO_3)_2$, which allows for the unambiguous identification of the conformations observed for ligand **185** complexes. The different coordinating modes of ligand **185** in the complexes mentioned are in exchange but exhibit different physical properties, thus representing a new bistable system based on conformational isomerism which exhibits an electrochemical potential hysteresis. An equilibrium constant and thermodynamic data were obtained for this system by variable-temperature cyclic voltammetry. The influence of coordinating *vs* non-coordinating solvents was also studied.



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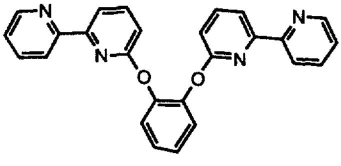

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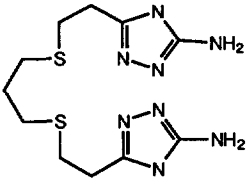


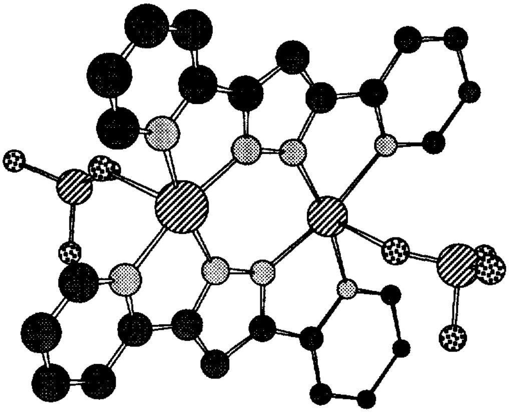
(187)

The syntheses of three new trinuclear copper(II) complexes with the ligand 1,9-bis-(3-amino-4*H*-triazol-5-yl)-3,7-dithianonane (**187**) are described [278]. The X-ray structures of two of them, $[Cu_3(\mathbf{187})_2(H_2O)_2Cl_2]Cl_4(H_2O)_4$ and $[Cu_3(\mathbf{187})_2(ZnCl_4)_2](H_2O)_4$, have been solved. The magnetic properties of these and those of the third related complex, $[Cu_3(\mathbf{187})_2(H_2O)_2Br_2]Br_4(H_2O)_4$, have been studied. The structures consist of linear trinuclear units of three copper(II) ions bridged by two triazole N^1N^2 bridges and one chloride. The central copper ion lies on a centre of symmetry, coordinated by four N and two Cl. The terminal copper ions are coordinated by $N_2S_2Cl_1O_1$ ($Cu_3(\mathbf{187})_2(H_2O)_2Cl_2]Cl_4(H_2O)_4$) and $N_2S_2Cl_2$ ($[Cu_3(\mathbf{187})_2(ZnCl_4)_2Cl_2](H_2O)_4$). The shortest Cu–Cu distances within one complex are 3.5426(1) and 3.620(3) Å for $[Cu_3(\mathbf{187})_2(H_2O)_2Cl_2]Cl_4(H_2O)_4$ and $[Cu_3(\mathbf{187})_2(ZnCl_4)_2Cl_2](H_2O)_4$ respectively.

The first crystal and molecular structures of a transition metal complex containing 1,2-dithiocroconate (1,2-dtcr, dianion of 1,2-dimercaptocyclopent-1-ene-3,4,5-trione), $\{[Cu(bpca)(H_2O)]_2[Cu(1,2\text{-}dtcr)_2]\}\cdot 2H_2O$ (where bpca is the bis(2-pyridylcarbonyl)amide anion), have been determined by single crystal X-ray diffraction methods. The structure is formally built of $[Cu(1,2\text{-}dtcr)_2]^{2-}$ and $[Cu(bpca)(H_2O)]^+$ ions and water of hydration [279]. The copper atom of the anion is situated at a crystallographic inversion centre, bonded to four sulfur atoms in a planar, approximately square arrangement. In the cation the copper equatorial plane is formed by the three nitrogen atoms of the bpca ligand and a water oxygen atom. In addition there is a very weak axial bond to one of the sulfur atoms of a 1,2-dtcr ligand in the anion. Through these latter weak bonds each anion is connected to, and sandwiched between, two cations, resulting in neutral, trinuclear, centrosymmetric formula units. The triple-decker molecules are arranged in stacks along the crystallographic *a*-axis, creating close contacts between the terminal copper atoms and bpca groups of the neighbouring molecules. This intermolecular interaction is, however, too weak to define the structure as a chain compound. The distance between adjacent copper atoms within the trinuclear unit is 4.189(1) Å, whereas the shortest intra-stack metal–metal separation between terminal copper atoms is 5.281(1) Å. Variable-temperature magnetic susceptibility measurements in the temperature range 4.2–140 K reveal that a Curie law is followed; there are three non-interacting copper(II) ions in the formula unit.

3.6. *Tetranuclear complexes*

One copper(II) and two silver(I) complexes with 3,5-bis(2-pyridyl) pyrazole (Hbpypz) have been synthesized and their molecular structures determined by X-ray crystallography [280]. The tetranuclear complex $[Cu_4(bpypz)_4(ClO_4)_4]\cdot 2H_2O$ (**188**) consists of two weakly associated dimeric units coupled via stacking between the pyridine and pyrazole rings with an average spacing of 3.50 Å, which gives rise to charge-transfer absorption bands in the near-UV region. The temperature dependence of the ESR spectrum and magnetic susceptibility indicates the presence of an antiferromagnetic interaction in the system. Whereas Hbpypz is strictly planar in the copper(II) complex, a non-coplanar conformation is observed in both silver(I) complexes, indicative of the unique coordinative versatility of the pyrazole derivative.



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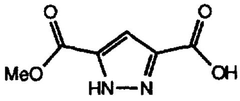
Two weakly antiferromagnetically coupled, tetranuclear copper(II) complexes $[Cu_4(PAP)_2(\mu_2\text{-}1,1\text{-}N_3)_2(\mu_2\text{-}1,3\text{-}N_3)_2(\mu_2\text{-}CH_3OH)_2(N_3)_4]$ (PAP = 1,4-bis-(2′-pyridylamino)phthalazine and $[Cu_4(PAP3Me)_2(\mu_2\text{-}1,1\text{-}N_3)_2(\mu_2\text{-}1,3\text{-}N_3)_2(H_2O)_2(NO_3)_2](NO_3)_2$ (PAP3Me = 1,4-bis-(3′-methyl-2′-pyridyl)aminophthalazine) have been reported as containing a unique structural arrangement with two μ_2-1,1-azide intramolecular bridges, and two μ_2-1,3-azide intermolecular bridges linking pairs of copper(II) centres [281]. The dinuclear complexes $[Cu_2(PPD)(\mu_2\text{-}1,1\text{-}N_3)(N_3)_2(CF_3SO_3)]\text{-}CH_3OH$ and $[Cu_2(PPD)(\cdot_2\text{-}1,1\text{-}N_3)(N_3)_2(H_2O)(ClO_4)]$ (PPD = 3,6-bis-(1′-pyrazlyl)pyridazine) contain pairs of copper centres with intramolecular μ_2-1,1-azide and pyridazine bridges, and exhibit strong antiferromagnetic coupling. A one-dimensional chain structure in $[Cu_2(PPD)(\mu_2\text{-}1,1\text{-}N_3)(N_3)_2(CF_3SO_3)]CH_3OH$ occurs through intermolecular μ_2-1,1-azide bridging interactions. Intramolecular Cu–N_3–Cu bridge angles in the complexes are small (107.9° and 109.4°, respectively), but very large in the dinuclear complexes (122.5 and 123.2° respectively), in keeping with the magnetic properties. The magnetic properties of the tetranuclear complexes indicate the presence of a weak net antiferromagnetic exchange. Magnetically the dinuclear complexes exhibit very strong antiferromagnetic exchange.

A new pyrazolate-bridged tetranuclear copper(II) complex [{Cu(**189**–2H)(H_2O)}$_4$]·12H_2O (**189** = 5-methoxycarbonylpyrazole-3-carboxylic acid) was synthesized and its crystal structure determined [282]. The molecule has C_2 symmetry and consists of four copper atoms bridged by four planar (**189**) ligands through the nitrogen atoms of the pyrazole groups to form a $(\text{-Cu–N–N–})_4$ 12-membered ring. The coordination of each copper is distorted square-planar. The basal plane of each copper atom is nearly parallel to a neighbouring pyrazole plane and perpendicular to another neighbouring pyrazole plane. In the crystal there is a hydrogen-bond network between water molecules and carboxylate groups which may control the packing. The magnetic properties of the complex have also been investigated down to 5 K. The exchange interaction between the copper atoms propagated through the monopyrazolate bridge is antiferromagnetic with $J = -12.34\ \text{cm}^{-1}$.



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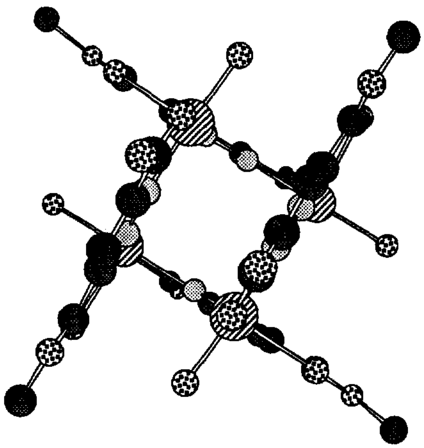
The three-solvent reaction of $(Bu_4N)_2[Zn(dmt)_2]$ (dmt $= C_3S_5^{2-} =$ 3-thioxo-1,2-dithiole-4,5-dithiolato) (CH_2Cl_2), $(Et_4N)_2$tto (tto $= C_2S_4^{2-} =$ tetrathiooxalate) (H_2O), and $CuCl_2 \cdot 2H_2O$ (CH_3OH) yields the anionic tetrameric copper complex $(Bu_4N)_2[Cu(dmt)]_4$ (**190**) [283]. The dianion contains a planar, eight-membered ring core of four Cu atoms and four S atoms. The dmt ligand coordinates for the first time in this particular fashion.



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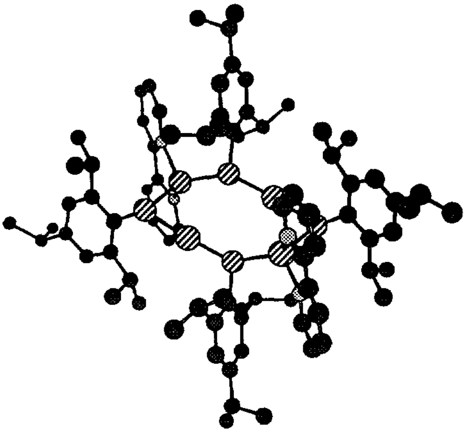

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The oligomeric homoleptical copper(I) chalcogenolate compounds $[CuS(2,4,6\text{-}^iPr_3C_6H_2)]_{(x=4.8)}$ and $[CuSe(2,4,6\text{-}^iPr_3C_6H_2)]_6$ react with 2,2′-bipyridine to yield the tetranuclear complex $[CuS(1,4,6\text{-}^iPr_3C_6H_2)]_4(bpy)_2$ (**191**) and the dinuclear complex $[CuSe(2,4,6\text{-}^iPr_3C_6H_2)]_2(bpy)$ and their structures determined by X-ray analysis [284]. In the eight-membered Cu_4S_4 core of **191** with chair conformation the copper atoms are linked by μ_2-bridging selenolate ligands. Only two copper atoms are coordinated by 2,2′-bipyridine. The corresponding copper(I) selenolate complex forms a folded four-membered Cu_2Se_2 ring with μ_2-bridging selenolate ligands. The Cu–Cu distance of 2.52 Å is relatively short. NMR spectroscopic and cryoscopic measurement of **191** show that this complex dissociates into smaller fragments in solution which undergo rapid exchange reactions. However, corresponding investigations performed on $[CuSe(2,4,6\text{-}^iPr_3C_6H_2)]_2(bpy)$ indicate that the solid state structure is maintained in solution. The electrochemical behaviour of all the complexes was studied in CH_2Cl_2, and in any case no reversible redox processes could be observed.

The compound $[Cu_4(prz)_4(CH_3OH)_2L_2](ClO_4)_2$ (LH = 1,1-di-(2-pyridyl)-1-methoxymethanol, PRXH = pyrazole) is a copper(II) complex in which each dicationic moiety is bridged by two pyrazolate ligands [285]. The solid state structure shows tetrameric dicationic pairs of copper atoms, one square-planar and one square-pyramidal, bridged by an oxygen from the pyridylmethoxymethanol ligand and a pyrazolate moiety, with one example of five coordination completed by a methanol solvent molecule. These dimers are then bridged by two pyrazoles, to give the tetramer. Two perchlorate counter-anions are bound to the tetrameric unit by hydrogen bonds, which stabilize the crystal structure. The copper(II) complex presents antiferromagnetic behaviour with a $2J$ value of $-211.2\ cm^{-1}$.

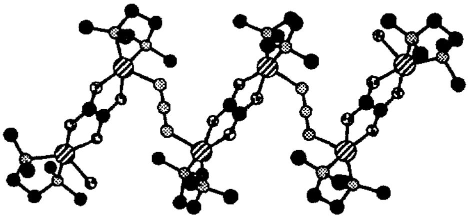
The interaction of Cu(II), Mn(II), Ni(II), Zn(II), Cd(II) and Hg(II) ions with isoorotic and 2-thioisoorotic acids in aqueous ammonia has led to complexes with the general formula $M^{II}(HL^{2-}) \cdot xNH_3 \cdot yH_2O$ [286]. These compounds were characterized by spectral methods (IR, UV–VIS, NIR and EPR), magnetic moments and conductivity measurements. The most common coordination mode of uracil derivatives is an O_4–OCO six-membered chelate ring. The X-ray structure of $[Cu_4(isoorotato)_4(NH_3)_4(H_2O)_2] \cdot 4H_2O$ consists of tetrameric units; each ligand bridging two metallic centres with the N(3) atom linked to one of the copper atoms and the carboxylate group together with the carbonyl oxygen in position 4 chelating to the other; this oxygen also seems to interact weakly with the first copper atom. Each copper atom is strongly coordinated by four atoms in square-planar fashion, N(3) from one ligand, O(4) and the carboxylate oxygen from another one and an ammonia molecule in trans position to O(4). The weak interaction with O(4) of the first ligand and two weakly coordinated water molecules per tetramer complete a "4 + 1" coordination number for two copper atoms and a "4+2" for the other.

The reactions of $[Cu(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) with 3-methyl- and 3,5-dimethyl-1*H*-pyrazoles in light petroleum have been studied [287]. These reactions give the 1:2 adducts of $[Cu(hfac)_2(5\text{-}Hmpz)_2]$ and $[Cu(hfac)_2(3,5\text{-}Hdmpz)_2]$ respectively. The complex $[Cu(hfac)_2(5\text{-}Hmpz)_2]$ changes into complexes $[Cu_4(tfa)_2(\mu_4\text{-}ttpt)_2(5\text{-}Hmpz)_4]$ and $[Cu(hfac)(tfa)(5\text{-}Hmpz)_3]$ (Htfa = trifluoroacetic acid; H_3ttpt = 2,4,6-tris(trifluoromethyl)tetrahydropyran-2,4,6-triol; 5-HMpz = 5-methyl-1*H*-pyrazole), whereas $[Cu(hfac)_2(3,5\text{-}Hdmpz)_2]$ does not change to give similar complexes. The crystal structures of the complexes have been determined. $[Cu(hfac)_2(5\text{-}Hmpz)_2]$ is tetranuclear, and four copper atoms linked together two tridentate ttpt ligands are arranged in a parallelogram giving a geometry about the Cu atoms of a distorted square-pyramid with the coordination type being CuO_5 and CuN_2O_3 respectively. $[Cu(hfac)_2(3,5\text{-}Hdmpz)_2]$ is mononuclear and the geometry about the copper atom is a distorted tetragonal bipyramid.

3.7. *Hexanuclear complexes*

The compound $[Cu_6(tmen)_6(\mu\text{-}N_3)_2(\mu\text{-}C_2O_4)_3(H_2O)_2][ClO_4]_4 \cdot 2H_2O$ (**192**) where tmen is *N,N,N′,N′*-tetramethylethane-1,2-diamine, was synthesized and characterized

[288]. Its crystal structure was determined by single-crystal X-ray analysis. The magnetic behaviour was recorded between 300 and 4 K, showing strong antiferromagnetic coupling with $J=-289(2)\ \mathrm{cm}^{-1}$, $g=2.03(1)$. Polycrystalline powder ESR spectra were recorded at various temperatures and showed the broad room-temperature signal having $g=1.12$ vanishing at approximately 55 K.



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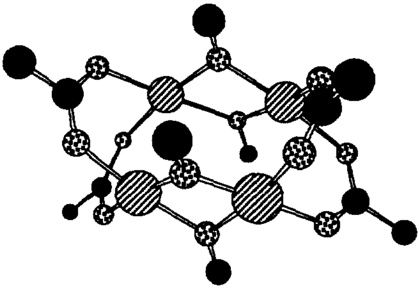
3.8. Cluster complexes

The tetranuclear copper(II) complex $[\{Cu(O_2CMe)(OMe)\}_4]$ (**193**) has been found to contain an unusual open cubane Cu_4O_4 framework defined by two interpenetrating copper and oxygen planes rather than two tetrahedra; it also shows strong antiferromagnetic coupling [289].



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As part of a study to synthesize new molecule-based magnetic materials, the magnetic behaviour of the clusters $[(PhSiO_2)_6Cu_6(O_2SiPh)_6]\cdot 6EtOH$, $Na_4[PhSiO_2)_{12}Cu_4]\cdot 8^nBuOH$, and $K_4[(C_2H_3SiO_2)_{12}Cu_4]\cdot 6^nBuOH$ has been investigated by combined magnetic susceptibility measurements and variable-temperature EPR techniques [290]. The six copper(II) ions in the core of the hexanuclear cluster are ferromagnetically coupled with $J=-42\ \mathrm{cm}^{-1}$, which arises as a result of the geometry at the bridging siloxanolate oxygen atoms. Large antiferromagnetic Cu–Cu interactions (J similar to $200\ \mathrm{cm}^{-1}$) and an $S=0$ ground state have been detected in the tetranuclear clusters as a consequence of the larger Cu–O–Cu angles.

The tetranuclear $CuOBr_xCl_{6-x}(OPPh_3)_4$ complexes (where $x=0$, 0.2, 0.5, 1.0, 1.5, 2.0, 2.2, 2.5, 2.8, 3.2, 3.5, 3.8, 4.0, 4.5, 5.0, 5.5, 5.7, 5.8, 6.0) were prepared and studied by IR spectra and powder diffraction measurements [291]. The dependence of the tetrahedral OCu_4 core vibration and the cubic lattice parameter on x for $Cu_4OBr_xCl_{6-x}(OPPh_3)_4$ complexes indicates an increase of the $Cu_4OBr_xCl_{6-x}$ core size with increasing number of larger bromine atoms, without observable change of the symmetry. Single-crystal structure determination of the $Cu_4OBr_3Cl_3(OPPh_3)_4$ complex confirmed the structural type with a central oxygen atom being tetrahedrally coordinated to four copper(II) atoms and the copper atoms bridged in pairs by six halide atoms. The bridging positions are occupied by halide atoms X = Br,Cl statistically in the ratio 0.5:0.5 with interatomic Cu–X distances of 2.461(2) Å. The ligands OPPh complete the trigonal-bipyramidal coordination of the copper atoms.

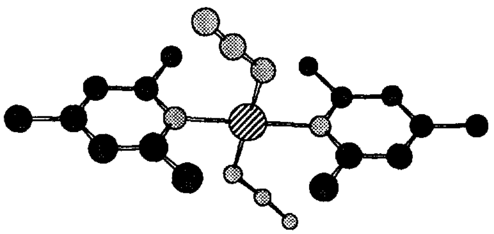
A novel double-cubane copper complex $[Cu_8L_8CMe)_4][ClO_4]_4$ has been prepared, and structurally and magnetically characterized (L = the monoanion of the hydrated, *gem*-diol form of di-2-pyridyl ketone) [292]. Solid di-2-pyridylketone and $NaClO_4 \cdot H_2O$ were added to a warm solution of $[Cu_2(O_2CMe_4)_4(H_2O)_2]$ (2:1:1) in H_2O and the complex added in 30% yield as green crystals. The X-ray structure of the complex shows the cluster consists of a distorted double cubane which are doubly bridged by two syn,anti acetate groups. An antiferromagnetic exchange is observed between the Cu^{II} ions.

3.9. Polymeric complexes

The copper(II) complexes of singly and doubly deprotonated 2,3-pyrazinedicarboxylic acid (pyzdcH(2)) have been prepared and their crystal structures determined [293]. In $[Cu(pyzdcH)_2]_x \cdot 2xH_2O$, extended chains of copper ions are linked by double-bridging $pyzdcH^-$ groups, whereas in $[Cu(pyzdc)(H_2O)_2]_x \cdot 2xH_2O$, $pyzdc^{2-}$ ligands bridge metal centres to form extended linear chains.

Two new 1:1 ligand complexes of copper(II) azide with disubstituted pyridine ligands *catena*-di-μ(1,3)-azido-[di-μ(1,1)-azidobis(2,3-lutidine) dicopper(II)] (**194**) and *catena*-di-μ(1,1)-azido[di-μ(1,1)-azidobis(2-methyl-5-ethylpyridine)dicopper(II)], have been synthesized and characterized by spectroscopic and X-ray crystallographic methods [294]. The polymeric complex (**194**) features monodentate 2,3-lutidine ligands, centrosymmetric di-μ(1,3)-azido bridges which link the centrosymmetric dinuclear $Cu_2(2,3\text{-lut})_2(N_3)_2$ moieties to form sheets. The structure of the second complex shows that the copper(II) centres are pentacoordinated via four nitrogen atoms from the azido ligands and one N from the organic molecule and both azido ligands function as μ(2,2) bridges forming chains of polyhedra. The IR absorption spectra reveal that each of these complexes contains two independent azide ligands.

An example of a 4,4′-bipyridine (γ-bpy) clathrate in its copper(II) complex has been established [295]. The crystal structure of $[Cu(\gamma\text{-bpy})(H_2O)_2(ClO_4)_2]_n \cdot (\gamma\text{-bpy})_n$, comprises γ-bpy-bridged linear polymeric $[Cu(\gamma\text{-bpy})(H_2O)_2(ClO_4)_2(ClO_4)_2]_n$ chains, where the copper atom is coordinated in an elongated octahedral environment by two nitrogen atoms of the bridging γ-bpy ligands (Cu–N = 1.998(4) Å) and two water molecules (Cu–O = 1.968(3) Å) at the equatorial positions, and two perchlorate oxygen atoms at the axial positions (Cu–O =



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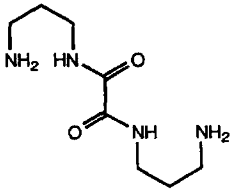
2.414(4) Å). The chains are interconnected by hydrogen bonds between the aqua ligands and the uncoordinated perchlorate oxygen atoms to form two-dimensional layers with cavities each enclosing a γ-bpy molecule. Hydrogen bonding between the aqua ligands and the nitrogen atoms of the solvate γ-bpy molecules further extends the structure into a three-dimensional network in the solid.

N,*N*′-Bis(3-aminopropyl)oxamide (**195**), which can adopt cis and trans conformations, reacted with copper(II) salts in its deprotonated form to yield the compounds [Cu(**195**)], [Cu_3(**195**)$_2$(NO_3)$_2$]·H_2O, [Cu_2(**195**)(NO_3)$_2$] and [Cu_2(**195**)(O_2CMe)$_2$]·$2H_2O$ [296]. The structure of [Cu(**195**)] consists of oxamidate ligands in a cis conformation coordinated to the copper atom through its four nitrogen atoms. The copper geometry is close to square-planar. The amidate-copper bond distance (1.955(6) Å) is significantly shorter than that involving the amine group (1.999(7) Å). The structures of [Cu_2(**195**))NO_3)$_2$] and [Cu_2(**195**)(O_2CMe)$_2$]·$2H_2O$ comprise centrosymmetric trans oxamidate-bridged copper(II) dinuclear units which are linked by asymmetric bis(monodentate) nitrate and acetate ligands to yield a sheet-like polymer and an alternating chain respectively. The coordination geometry around each copper atom is distorted square-pyramidal: the equatorial plane comprises the oxygen and nitrogen atoms of the amide, the nitrogen atom of the amine group and an oxygen atom from nitrate or acetate ligands. The copper–copper separations across the oxamidate are 5.190(1) Å and 5.244(1) Å for [Cu_2(**195**)(NO_3)$_2$] and [Cu_2(**195**)(O_2CMe)$_2$]·$2H_2O$ respectively, and those across the nitrate and acetato groups are 5.116(1) Å and 3.350(1) Å. Variable-temperature magnetic susceptibility measurements show a Curie law behaviour for [Cu(**195**)] and the occurrence of a strong antiferromagnetic coupling through the oxamidate bridge with $J > -300\ \mathrm{cm}^{-1}$ for the other three complexes.



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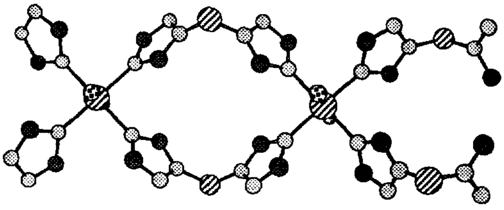

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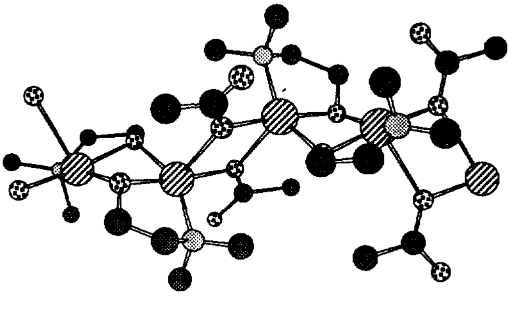
When the labile cobalt complex $[Co\{HB(C_2H_2N_3)_3\}_2]$ is reacted with an excess of $CuCl_2$ in hot water light blue crystals of $[Cu_2Cl_2\{\mu_3\text{-}HB(C_2H_2N_3)_3\}_2 \cdot 2H_2O]_\infty$ (**196**) or deep blue crystals of $\{[Cu_2\{\mu_4\text{-}HB(C_2H_2N_3)_3\}(\mu\text{-}OH)_2]Cl \cdot 6H_2O\}_\infty$, are formed, depending on the reaction time [297]. The latter complex can also be obtained from $[Cu\{HB(C_2H_2N_3)_3\}_2]$ and $CuCl_2$ in aqueous ammonia. The 2D double-layer-type coordination polymer **196** contains two different Cu(II) centres in the lattice which are distinguished only by the direction of the Jahn–Teller distortion. In the 3D coordination polymer, one of the two different Cu centres is chelated by the three endodentate nitrogen donor, while the other Cu centre is coordinated by three exodentate nitrogen atoms. The coordination sphere is completed in both cases by two hydroxo bridges to symmetry-related Cu centres. The metal–ligand connectivity creates infinite channels with helical walls which contain the solvated chloride anions.

Treatment of $[Cu(MeCN)_4]BF_4$ with mixtures of pyz and cnge in MeCN afforded the complex $[Cu(cnge)(MeCN)(pyz)]BF_4 \cdot 0.5pyz$ (pyz = pyrazine, cnge = 2-cyanoguanidine) [298]. Single-crystal X-ray structural analysis has shown this complex to contain a one-dimensional zigzag cationic chain based on four-coordinate tetrahedral copper(I) with each metal atom ligated by two bridging pyz molecules and terminal MeCN and cnge molecules. The uncoordinated pyz molecule connects parallel copper(I) chains via N···H–N bonds involving the amino moieties of ligating cnge molecules. Oxidation of this polymer with $NOBF_4$ in CH_2Cl_2 yielded $Cu(pyz)(cnge)(BF_4)_2$ which on recrystallization from MeCN lost one cnge molecule affording $[Cu(MeCN)_4(pyz)][BF_4]_2$. The crystal structure of this complex showed a one-dimensional linear cationic chain based on six-coordinate copper(II), the tetragonally distorted octahedral coordination geometry of which comprises two bridging pyz molecules (equatorial) and four terminal MeCN molecules (two equatorial, two axial).

Three new polynuclear copper(II) complexes with aminoalcoholate and acetate as ligands, $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2]$ (**197**) $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(H_2O)_2]$ and $[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ (Hbdmmp = 2,6-bis(dimethylaminomethyl)-4-methylphenol), have been synthesized and their structures were determined by X-ray diffraction analysis [299]. In the solid state **197** has a one-dimensional structure linked by covalent bonds, whereas $[Cu_2(O_2CMe)_2(OCH_2CH_2NMe_2)_2(H_2O)_2]$ has an extended structure linked by both covalent and hydrogen bonds. Examination of the solution behaviour of the compounds by ^1H NMR spectroscopy has shown that **197** exists as a mixture of oligomers and undergoes a dynamic process in solution which can be attributed to the formation of weak intermolecular Cu···O bonds through the acetate ligands, whereas no dynamic behaviour of $[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ was observed. The magnetic properties of **197** and $[Cu_4(\mu_4\text{-}O)(bdmmp)_2Br_4]$ were examined via magnetic susceptibility measurements which showed that both compounds are dominated by antiferromagnetism.

Long-range antiferromagnetic to ferromagnetic states have been observed for a family of layered compounds, $Cu_2(OH)_3X \cdot mH_2O$ (X = *n*-alkylcarboxylate) depending on the layer spacing (up to *ca* 28 Å); in contrast, the analogous *n*-alkylsulfate



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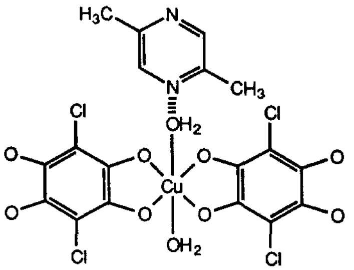
derivatives, $X = C_nH_{2n+1}SO_4^-$, are predominantly three-dimensional antiferromagnets [300]. It is proposed that the mechanism of exchange between layers is basically dipolar, and that the organic spaces only serve to separate the magnetic layers.

New copper(II) intercalation compounds, $\{[Cu(CA)(H_2O)_2](G)\}_n$ (H_2CA = chloranilic acid; G = 2,5-dimethylpyrazine (dmpyz) (**198**) and phenazine (phz) have been synthesized and characterized [301]. For all the compounds, the crystal structures consist of one-dimensional $[Cu(CA)(H_2O)_2]_m$ chains and uncoordinated guest molecules (G). Each copper atom for all three structures displays a six-coordinate geometry with the two bis-chelating CA^{2-} anions and water molecules providing infinite, nearly coplanar linear chains running along the *a*-direction. These chains are linked by hydrogen bonds between the coordinated water and the oxygen atoms of CA^{2-} on the adjacent chain, forming extended layers. The guest molecules are intercalated between the $\{[Cu(CA)(H_2O)_2]_k\}_l$ layers which are supported with $N \cdots H_2O$ hydrogen bonding. The guest molecules are stacked against each other with an interplanar distance of *ca* 3.2 Å perpendicular to the $[Cu(CA)(H_2O)_2]_m$ chain. This study shows that both hydrogen bonding and stack capability of a guest molecule are responsible for building the unique intercalated structures observed.



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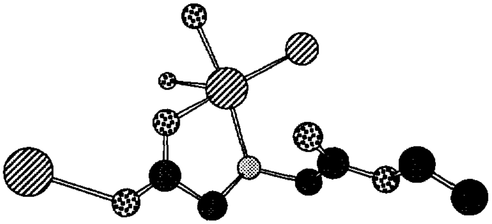
The crystal structure of the one-dimensional complex $[Cu(DCMB)(CA)]_n$, where DCMB = 3,3′-dicarbomethoxy-2,2′-bipyridine, CA = dianion of chloranilic acid, has been determined by X-ray diffraction at room temperature [302]. The copper atoms are coordinated in a distorted octahedral arrangement by two nitrogen atoms of

DCMB and four oxygen atoms of the bridging bis-chelating CA ligands, forming infinite "zigzag" chains of Cu^{2+}, and the chloranilate dianions. The magnetic susceptibility of the compound has been investigated between 280–4.2 K.

Two layered copper(II) hydroxyphosphonates $Cu_{2.5}(O_3P(CH_2)_2NH_3)(OH)_2(SO_4)$ were prepared from copper sulfate or nitrate, (2-aminoethyl)phosphonic acid, and sodium hydroxide in water [303]. In both cases, the anion of the starting copper salt was retained in the structure. For the first compound, the sulfate groups were present in the interlayer space, in a manner similar to that observed in layered double hydroxides.

Three polymeric copper(II) complexes of a flexible double betaine, $[\{Cu(L)X_2(H_2O)\}_n]\cdot 2nH_2O$ (X = Cl, Br) and $[\{Cu(L)(H_2O)_4\}_n](ClO_4)_{2n}\cdot 2nH_2O$ ($L = (O_2CCH)\text{-}O\text{-}(Me_3N^+)CH_2CH_2CH(Me_3N^+)CO_2$), have been prepared and characterized by single-crystal X-ray analysis [304]. The crystal structure of $[\{Cu(L)X_2(H_2O)\}_n]\cdot 2nH_2O$ (X = Cl, Br) features an infinite zigzag chain composed of an alternate arrangement of metal atoms and double betaine ligands, with each Cu(II) atom in a distorted CuX_2O_3 (X = Cl, Br) square-pyramidal geometry, and hydrogen bonding between adjacent chains leads to a layer structure. $[\{Cu(L)(H_2O)_4\}_n](ClO_4)_{2n}\cdot 2nH_2O$ exhibits a layer structure in which neighbouring chains constructed from the metal atoms and the double betaine ligands are cross-linked by hydrogen bonding between the aqua ligands. The Cu(II) atom is coordinated in a CuO_6 octahedral geometry with Jahn–Teller distortion.

The dimethylester of iminodiacetic acid ($NH(CH_2CO_2CH_3)_2$) has been shown to react with $CuCl_2\cdot 2H_2O$ in aqueous ethanol to yield $[Cu(idae)Cl(H_2O)]$ (**199**) (idae = *O*-ethyliminodiacetato) [305]. The original ligand is monohydrolysed and transesterificated by ethanol. When the reaction with copper chloride was carried out in methanol the corresponding methylmonoester copper compound was the reaction product. The X-ray diffraction structure of **199** was obtained and shows the copper(II) atom is in a distorted octahedral geometry, with a fac coordination of the ligand. A chloride ion, a water molecule and a carboxylate oxygen from another molecule complete the coordination sphere. The compound presents a monodimensional zigzag chain structure where the carboxylate oxygen of one ligand bridges two adjacent copper atoms. The chirality of the N and Cu atoms alternates in the chains.



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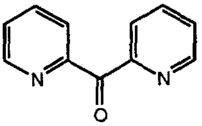
Two copper(II) complexes with the ortho-substituted phenoxyacetic acid, (2-acetylphenoxy)acetic acid (RCO_2H), have been prepared and their crystal structures determined by X-ray diffraction [306]. Both are polymers based on tetracarboxylato-bridged dimer units of the copper acetate hydrate type. In one, *catena*-tetrakis-μ-[(2-acetylphenoxy)acetato-*O*,*O′*]-bis[copper(II)], $[Cu_2(RCO_2)_2]_n$, is extended into a polymer via the axial dimer sites through the acetyl carbonyl oxygen atoms of adjacent units (Cu–Cu, 2.640(6) Å); in the second complex, an adduct with 2-aminopyrimidine (2-AP), *catena*-(2-aminopyrimidine-*N*,*N′*)-tetrakis-μ-[(2-acetylphenoxy)acetato-*O*,*O′*]-bis[copper(II)], $[Cu_2(RCO_2)_4(2AP)]_n$, forms a zigzag chain polymer through the heteronitrogen atoms of the 2-aminopyrimidine ring (Cu–Cu, 2.6775(7) Å). These chains are stabilized by the presence of hydrogen bonding between the 2-amino group of 2-aminopyrimidine and the carboxyl oxygens of adjacent dimers.

Di-2-pyridyl ketone (**200**) can complex metal ions in its activated $[(NC_5H_4)_2C(OR)(OH)]$ or non-activated forms [307]. In its activated form the dinucleating hydroxy group and the chelating groups of the ligand bind to two different metal centres, as evident in the compounds $[\{Cu_2[(NC_5H_4)_2C(OEt)O]Cl_3(EtOH)\}_2]$ and $[\{Cu_2[(NC_5H_4)_2C(OMe)O]Cl_3\}_\infty]$ (which also possess halide bridges), and lead to the formation of one-dimensional systems. In its non-activated form it acts as a simple didentate chelate. The X-ray analysis of $[\{Cu(\mathbf{200})(NO_3)_2\}_\infty]$ revealed an anion-bridged structure where bridging nitrate groups link the copper centres. The π-stacking interactions of these compounds influences the crystal packing arrangements.



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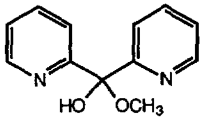

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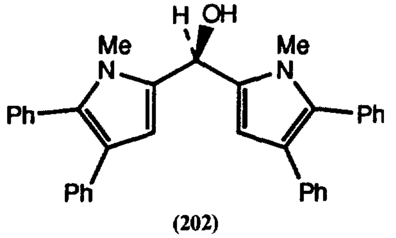
The synthesis, crystal structure and properties of compound $[Cu_4(dpk\cdot CH_3O)_2Cl_6]_n$ (dpk·CH_3OH = unimethylated diol of di-2-pyridyl ketone (**201**)) has been reported [308]. The synthesis of the complex has been achieved by the reaction of $CuCl_2$ with dpk in methanol. The base-catalysed addition results in the formation of a unimethylated diol which may deprotonate. Variable-temperature magnetic susceptibility measurements indicate the presence of a ferromagnetic behaviour with antiferromagnetic coupling below 15 K. The polycrystalline powder EPR spectra were indicative of a bulk concentration of copper ions having strong ferromagnetic interaction.

A new chlorocuprate(II), $[(C_2H_5)_4N]_2Cu_5Cl_{12}$, was prepared by reaction of $CuCl_2\cdot 2H_2O$ and $(C_2H_5)_4NCl$ in 1,1,2-trichloroethane–ethanol followed by water–ethanol evaporation [309]. The crystal structure, solved by single-crystal X-ray diffraction at room temperature consists of a two-dimensional network of $[(Cu_5Cl_{12})^{2-}]_\infty$ chains, alternating with layers of the organic cations. The anionic sheets are built up by aggregation of infinite zigzag chains of alternating tetranuclear and mononuclear sub-sequences. An infinite helical chain of $[Cu^{II}(\text{diethylenetrithiodiacetate})]_n\cdot n(H_2O)$ has been synthesized with a topology analogous to that of collagen fibres [310]. The copper(II) centres are antiferromagnetically coupled with $-J = 5.4\ \mathrm{cm}^{-1}$.

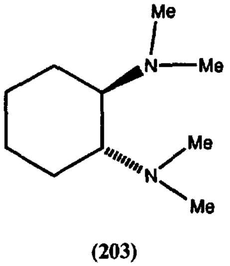
The complexes $[CuL(H_2O)] \cdot H_2O$ (H_2L = L-Leu–D-Phe) and [CuL] (H_2L = L-Leu–L-Phe) have been prepared and structurally characterized [311]. In both, the coordination of the Cu is a distorted square-pyramid with the dipeptide occupying three basal positions, the fourth being occupied by a carboxyl oxygen of an adjacent molecule. A water molecule and a peptide oxygen of another complex complete the coordination of copper in the apical position in the two complexes respectively. Thus, the dipeptide also acts as a bridging ligand between the metal centres so that both compounds exhibit a polymeric structure in the solid state. In both, the phenyl group of the dipeptide is far apart from the metal, since it is on the same side as the apical ligand. In contrast, an interaction between the phenyl residue with Cu in 2 is found in solution. The behaviour is interpreted as being due to breaking of the polymeric structure detected in the crystal. The interaction between the copper(II) ion and the aromatic ring is evaluated by means of a molecular orbital approach carried out on the simplified model $[Cu(OH)_2(NH_3)_2]$ interacting with a benzene molecule.

4. Mixed valence complexes

The new biimidazole, bis(1-methyl-4,5-diphenylimidaz-2-oyl)carbinol, (**202**), has been synthesized and used to form the novel tetrameric complex $[Cu_4(\mathbf{202})_2(BimO)_2]^{4+}$ [312]. The structure consists of an $(N\text{-}im)_2Cu^{II}(OR)_2Cu^{II}(N\text{-}im)_2$ centre with a $Cu^{II} \cdots Cu^{II}$ separation of 2.998(4) Å and two $Cu^{I}(N\text{-}im)_2$ moieties *ca* 5 Å from the Cu_2 centre, each with an N–Cu–N angle of 169.3(4)°.



(202)



(203)

Whereas the reaction of metal complexes with dioxygen generally proceeds in 1:1, 2:1 or 4:1 (metal:O_2) stoichiometry, the reaction of $[(\mathbf{203})Cu(MeCN)_4]$, where (**203**) = *N*-permethylated (1*R*,2*R*)-cyclohexanediamine, has been shown to react to give the structurally characterized 3:1 product [313]. Structural, spectroscopic and redox properties of the product indicate that in the process of O_2 bond cleavage the three Cu^I sites are oxidized by a total of four electrons, forming a mixed valence cluster with bridging oxide ligands that stabilize one of the copper sites in its normally inaccessible trivalent site. The X-ray structure of the product shows that one Cu–O bond in the cluster in unusually short at 1.84 Å, at least 0.15 Å shorter than the other Cu–O bond distances, indicating a higher relative oxidation level. The structure is consistent with the formal description of the complex as a mixed valence cluster containing two Cu^{II} ions and a single Cu^{III} ion bridged by two μ_3-oxo ligands. Magnetic measurements support an electronic description in which the two $S=1/2$ Cu^{II} atoms are ferromagnetically coupled, whereas the Cu^{III} site is diamagnetic (low spin d^8) because of its square-planar coordination and strong ligand fields. The relevance of this synthetic complex to the reduction of O_2 at the trinuclear active sites of multicopper oxidases is discussed. The purple mixed-valence CuA centre in nitrous-oxide reductase has been analysed by EPR spectroscopy of the copper-63-, copper-65-, and both copper-65- and $[^{15}N]$histidine-enriched enzyme [314].

The structure of the complex 1,4,8,12-tetraazacyclopentadecane copper(II) tribromocuprate(I) has been determined as a mixed valence compound [315]. The compound was one of the products of the reaction of $Cu(15\text{-aneN}_4)Br_2$ with $CoBr_2 \cdot 6H_2O$ in water–acetone solvent ($15\text{-aneN}_4 =$ 1,4,8,12-tetraazacyclopentadecane) and contains chains of alternating $Cu(15\text{-aneN}_4)^{2+}$ cations and $CuBr_3^{2-}$ anions.

The mixed-valence complex $[Cu^{II}(DMF)_4][Cu^{I}_4(SCN)_4(CN)_2]$ has been synthesized using a direct method of interaction and characterized by X-ray crystallography [316]. The complex consists of layers formed by polymeric $[Cu^{I}_4(SCN)_4(CN)_2]_n^{2-}$ anions and the $[Cu^{II}(DMF)_4]^{2+}$ cations disposed between anionic layers.

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