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Copper complexes of heterocyclic thioamides and related ligands

Eric S. Raper

Department of Chemical and Life Sciences, The University of Northumbria at Newcastle, Ellison Building, Ellison Place, Newcastle upon Tyne NE1 8ST (UK)

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CONTENTS

Correspondence to: E. S. Raper, Department of Chemical and Life Sciences, The University of Northumbria at Newcastle, Ellison Building, Ellison Place, Newcastle upon Tyne NE1 8ST, UK.

ABSTRACT

The review covers copper complexes of thiazoles, thiadiazoles, thioamides, thiones and imidazole-, thiazole-, pyridine- and quinazoline-thionates. Synthetic and, spectroscopic data are presented but emphasis is placed on detailed discussion of the structural aspects of these species based upon X-ray data.

MAJOR LIGAND ABBREVIATIONS

tz	1,3-thiazole
tdz	1,3,4-thiadiazole
azm	5-acetamido-1,3,4-thiadiazole-2-sulphonamide
bztdz	benzo-1,2,4-thiadiazole
tc	thiochrome
ta	thioacetamide
tap	thioamidopyridine
tu	thiourea
pyrdtH	pyrrolidine-2-thione
$imtH_2$	1,3-imidazoline-2-thione
$imdtH_2$	1,3-imidazolidine-2-thione
$bzimtH_2$	benz-1,3-imidazoline-2-thione
$trztH_2$	1,2,4-triazoline-3(5)-thione
ttztH	1,2,3,4-tetrazoline-5-thione
tmptH	thiomorpholine-2-thione
tcptH	ω-thiocaprolactam
py2tH	pyridine-2-thione
py4tH	pyridine-4-thione
pymtH	pyrimidine-2-thione
$dtucH_2$	dithiouracil
pu6tH	purine-6-thione
pu8tH	purine-8-thione
qntH	quinoline-8-thione
$qnxdtH_2$	quinazoline-2,3-dithione
tztH	1,3-thiazoline-2-thione
tzdtH	1,3-thiazolidine-2-thione
bztztH	benz-1,3-thiazoline-2-thione
rhdtH	rhodanine (1,3-thiazolidine-2-thione-5-one)
oxtH	1,3-oxazoline-2-thione
bzoxtH	benz-1,3-oxazoline-2-thione

Alkyl, aryl, amino and other derivatives are distinguished from the parent heterocycle by the addition of suitable prefixes: me, ph, am etc., to the above abbreviations.

1. INTRODUCTION

It is about 60 years since the preparation of copper(I) complexes of ethylenethiourea, (imidazolidine-2-thione), was first reported [1]. Interest in metal–thioamide coordination chemistry has grown steadily since then, and now virtually matches that in metal–amide systems [2]. In particular, the range of copper complexes involving thione-substituted heterocycles, (Sects. 4 and 5), has grown substantially [3]. Heterocyclic-substituted thioamides, such as the thioamido-pyridines (Sect. 3), together with thiazoles and thiadiazoles (Sect. 2), which are not strictly thioamides, form the remaining major ligand species reviewed here.

Each ligand category possesses sulphur and nitrogen either as the thioamide group, HN–C–S, the N–C–S group, or N=S=N, in a variety of heterocyclic environments, many of which are inherently bioactive. The thioamide group may be directly attached to a heterocycle, as in 2-thioamido-pyridine, or it may involve a combination of exocyclic and heterocyclic environments, as in the imidazole-thiones where the thione sulphur atom is exocyclic and directly attached to a heterocyclic carbon atom. The N–C–S group occurs in the 1,3-thiazoles and 1,3,4-thiadiazoles, the 2,1,3-thiadiazole moiety (N=S=N) has been added for completion.

All of the ligands are potentially S, N, or S,N-donating to copper in terminal or bridging modes and are capable of generating mononuclear, polynuclear and polymeric complexes. Many ligands possess S,N-ambidentate character typical of the classically ambidentate thiocyanate anion [4]. Most of the ligands, or their derivatives, are members of a broad class of thioamides which range from thiourea [5] to thioamido derivatives of amino acids and proteins [6]. Thiourea has an extensive range of copper complexes, some of which are referred to here by way of comparison, as are similar complexes of thioacetamide (see Sect. 3). Apart from these two groups, the presence of a heterocycle is essential for inclusion here as it determines the distinctive chemical and coordination properties of this class of ligand.

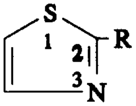
The purpose of this review is to explore the factors which govern the donor behaviour, as well as the reactivity of these ligands, towards copper. Stoichiometric–structural relationships, especially among copper(I) complexes (Sect. 4), the effect of the ligands on the relative stabilities of the oxidation states of the metal (Sects. 2, 3 and 5), together with copper(II)-thione redox chemistry (Sect. 6) are also major themes. The literature in these areas has been reviewed through to the summer of 1992.

In addition, the modelling of copper proteins [7], the dietary significance [8] and the bioregulation of the metal [9], the industrial importance of the metal in electro-plating [10] as well as the protection of the metal in aggressive media [11], have all stimulated much of the work quoted here and elsewhere [12].

2. COMPLEXES OF THIAZOLES AND RELATED LIGANDS

2.1 Introduction

The 1,3-thiazoles, tz, (**I**) are an important class of S,N-containing heterocycles [13] and were identified as such over a century ago [14]. The thiazole skeleton is a constituent of many biomolecules including β-lactam antibiotics such as the penicillins and penems [13], natural products such as thiamin [13] as well as magnetically coupled, (Fe(III)–Cu(II)), cytochrome-C oxidase models [15]. A number of 2-substituted thiazoles and thiazolidines have low toxicity and novel radio protective activity in mice [16]. Competitive coordination sites in tz and benzo-1,3-thiazole, bztz, (**II**) involve the heterocyclic sulphur and nitrogen atoms. These may be increased by 2-substitution, as in 2-amtz, (**Ib**) for example, which is, in principle, flexidentate in nitrogen.

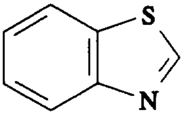


I

(a) R = H = tz

(b) R = NH_2 = 2-amtz

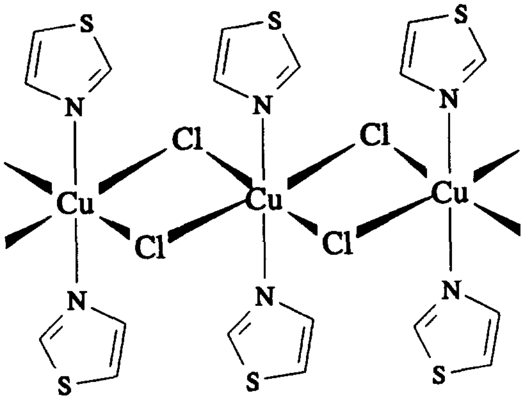
(c) R = Br = 2-Brtz



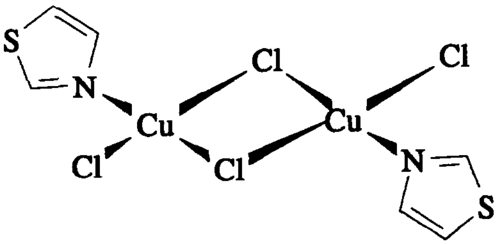
II

2.2 Complexes of 1,3-thiazoles

Complexes have been reported for tz [17], bztz [18], 2-amtz [19] and 2-Brtz [19] with copper and other metals. Stoichiometries include $[Cu(tz)_4X_2]$ ($X = ClO_4$, NO_3), $[Cu(L)_4X_2]$ (L = 2-amtz, 2-Brtz; X = Cl, Br); $[Cu(L)_2Cl_2]$ (L = tz, 2-amtz, 2-Brtz; X = Cl, Br) and $[Cu(tz)Cl_2]$. Syntheses are relatively straightforward in aqueous alcohol with appropriate molar ratios of ligand and metal salt. All of the complexes involve copper(II) with normal room-temperature magnetic moments (μ_B = 1.85–1.90). Structures have been proposed from electronic spectra and metal–ligand attachments deduced from vibrational spectra with ν(Cu–N) in the range 246–276 cm^{-1}. The 1 : 4 (metal–ligand) complexes have tetragonally distorted octahedral structures, with presumably trans ligands, and the 1 : 2 (metal–ligand) complexes have polymeric halogen-bridged structures with terminal ligands and tetragonal (4+2) coordination at the metal (**III**). A halogen-bridged dimeric structure is proposed for [Cu(tz)Cl_2] (**IV**).



III



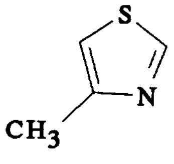
IV

The implied donor in tz is the heterocyclic nitrogen atom. Although the exocyclic amino group in 2-amtz is a possible alternative donor, structural data on the ligand, and its derivatives, suggest that the exocyclic nitrogen atom is trigonal with its pπ electrons subsumed into the π-MO of the heterocycle, (mean C–N = 1.330(5) Å) [20]. This has a consequently deleterious effect on the coordination potential of the exocyclic amino site.

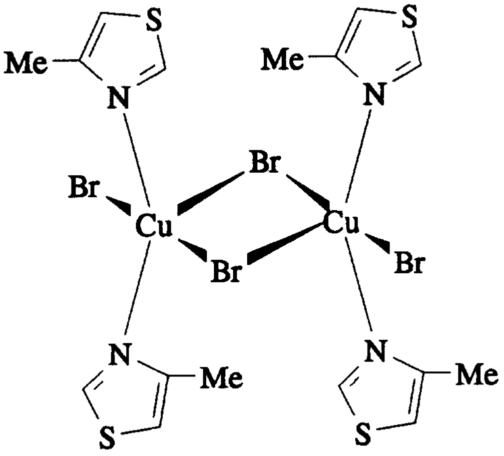
Both tz and bztz have been reported to coordinate with copper(I) halides in saturated aqueous solutions of the appropriate potassium halide, [Cu(bztz)$_2$X] and [Cu(tz)X] (X = Cl, Br, I). Polymeric structures are proposed for these complexes with S-donating bztz and N-donating tz [21].

Heterocycles such as tz are inherently polar with electron distribution within the molecule dominated by the more electronegative nitrogen atom. The heterocyclic nitrogen atom is consequently more nucleophilic than the heterocyclic sulphur and is expected to be the dominant donor.

Definitive evidence for coordination by the heterocyclic nitrogen atom of tz has been provided by the crystal structure of $[Cu(tz)_2Cl_2]$ [22]. The overall arrangement, which confirms the earlier proposal of Underhill and co-workers [17], is a centrosymmetric double halogen-bridged linear polymer (**III**) formed from square-planar $Cu(tz)_2Cl_2$ units. Coordination at the metal is tetragonally distorted (4+2) octahedral. The basal plane is formed from pairs of trans tz and chlorine (Cu–N = 1.990(2); Cu–Cl = 2.332(1) Å) with the metal occupying an inversion centre. The bridging, out-of-plane, Cu–Cl distance is 2.998(1) Å, the $Cu-Cl_{br}-Cu$ angle is 91.89(2)° and the Cu···Cu separation distance is 3.853(4) Å. The room-temperature EPR spectrum of $[Cu(tz)_2Cl_2]$ corresponds to the single-ion ground state with changes in the spectrum at reduced temperature attributed to inequivalent sites in the unit cell. Both $[Cu(tz)_2Cl_2]$ and $[Cu(tz)_2Br_2]$ exhibit low-temperature antiferromagnetic coupling. The relatively small magnitudes of the exchange constants J for the thiazole complexes, relative to the corresponding pyridine complexes, is attributed to an interchain superexchange pathway involving sulphur–sulphur contacts between adjacent thiazole rings.



V

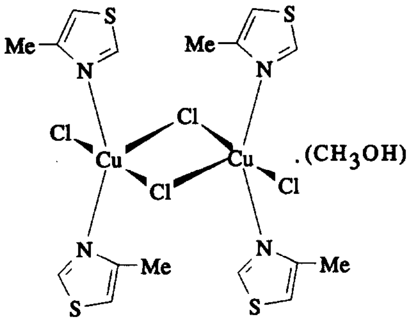


VI
(adapted from [23])

Reaction between anhydrous copper(II) bromide and 4-methylthiazole (4-metz, **V**) in aqueous methanol, yields $[\{Cu(4\text{-metz})_2Br_2\}_2]$ (**VI**) [23]. This centrosymmetric dimeric complex has tetragonal-pyramidal coordination at the metal. The basal plane contains two trans N-donating 4-metz ligands (mean Cu–N = 1.984(5) Å) and two trans bromine atoms, one of which is terminal ($Cu-Br_t = 2.420(1)$ Å) and one is bridging ($Cu-Br_{br} = 2.492(5)$ Å). The apical site is occupied by the other bridging bromine (Cu–Br_{br} = 3.033(1) Å). The metal is displaced from the basal plane in the direction of the apical, bridging bromine. The central, asymmetric Cu_2Br_2 core is strictly planar due to the presence of an inversion centre at the mid-point of the dimer. The metal–metal separation distance is 4.063(2) Å and the Cu–Br–Cu′ bridging angle is 94.16(3)°. The 4-metz ligands are essentially planar and are inclined mutually and to the equatorial atoms in the basal plane. This orientation of the ligand methyl groups hinders further axial coordination at the metal and prevents the formation of polymeric species. The thiazole sulphur atoms, although not involved in coordination to the metal, may form weak, interchain interactions. Low-temperature magnetic susceptibility data indicate weak antiferromagnetic coupling between the copper(II) atoms of the dimer ($J = -1.24\ cm^{-1}$, $g = 2.058$).

In contrast to the copper(II) bromide reaction with 4-metz, the corresponding reaction with copper(II) chloride yields a variety of products depending on the reaction conditions. In the presence of water, the product is a brown precipitate which is presumed to be tetranuclear [Cu_4O(4-metz)$_4Cl_6$] [24]. This product may be virtually eliminated by using freshly distilled methanol in which case the unstable dimer, [{Cu(4-metz)$_2Cl_2$}$_2$], is produced. Allowing this parent complex to stand in solution for 24 h at reduced temperature generates the methanol-solvated dimer **VII**. Attempts to recrystallise the parent dimer and the methanol solvate from dimethylformamide (DMF) or DMF–methanol leads to the isolation of a stable green dimer **VIII**; production of **VIII** from the parent dimer is reversible. The mixed-valent dimer **IX** is produced by dissolving the parent dimer in methanol and sealing the solution under nitrogen after removing some of the solvent. Addition of an excess of 4-metz to **VIII** produces the monomer **X** which may also be obtained from copper(II) chloride with a large excess of the ligand at reduced temperature. The structures and magnetic properties of **VII** and **X** [25], **VIII** [24] and **IX** [26] have been reported.

The monomeric complex **X** contains five-coordinate copper(II) in a severely distorted tetragonal-pyramidal arrangement consisting of two chlorine atoms (Cu–Cl = 2.319(1) and 2.461(1) Å) and three N-donating 4-metz ligands (Cu–N = 2.043(3)–2.066(3) Å). The basal plane contains three heterocyclic nitrogen and one chlorine atoms with the apical site occupied by the second chlorine. The copper atom is displaced from the distorted basal plane in the direction of the apical chlorine. The structure of **VII** is similar to that of **VI** with distorted tetragonal-pyramidal coordination at the metal, involving trans heterocyclic nitrogen (Cu–N = 2.001(3), 2.004(3) Å) and trans chlorine atoms (Cu–Cl_t = 2.303(1), Cu–Cl_{br} = 2.350(1) Å) and an apical bridging chlorine (Cu–Cl_{br} = 2.645(1) Å). The copper(II) atom is displaced from the basal plane in the direction of the apical chlorine. The asymmetric Cu_2Cl_2 core is strictly planar because of an inversion centre at the mid-point of the dimer (Cu···Cu = 3.543(1) Å; Cu–Cl_{br}–Cu′ = 90.15(3)°). The magnetic properties of **VII** show a weak intradimer antiferromagnetic interaction ($2J = -3.40\ cm^{-1}$) and a surprisingly strong interdimer antiferromagnetic interaction ($J' = -1.16\ cm^{-1}$), which is probably transmitted through non-bonded interactions involving adjacent thiazole



VII
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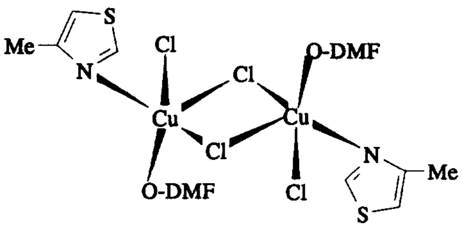

VIII
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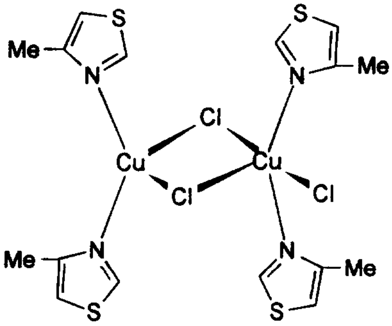

IX
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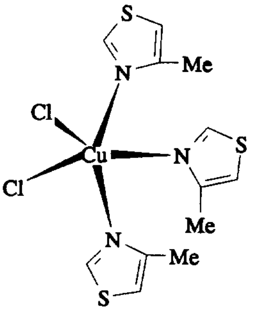
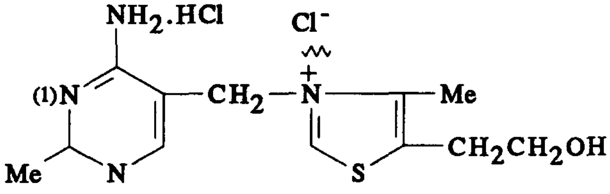


X
(adapted from [25])

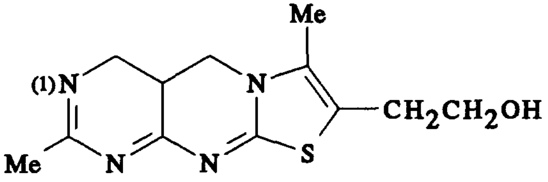
sulphur and terminal chlorine atoms. The DMF dimer **VIII** also has five-coordinate, tetragonal-pyramidal copper(II) with cis chlorine atoms, one N-donating 4-metz and one O-donating DMF molecule in the basal plane as well as an apical bridging chlorine and a central Cu_2Cl_2 core. In the dimeric mixed-valent complex **IX**, the copper(I) atom has pseudo-tetrahedral coordination consisting of two N-donating, terminal, 4-metz ligands, (mean Cu–N = 1.979(4) Å), and two bridging chlorine, (Cu–Cl = 2.340(2), 2.662(2) Å). Angles at the metal (97.67(3)–128.03(19)°) indicate extensive distortion from regular tetrahedral symmetry. Coordination at the copper(II) atom is distorted tetragonal-pyramidal formed from pairs of trans N-donating 4-metz ligands (mean Cu–N = 2.000(4) Å) and chlorine atoms ($Cu–Cl_t$ = 2.298(2); $Cu–Cl_{br}$ = 2.340(2) Å); the apical site is also occupied by bridging chlorine ($Cu–Cl_{br}$ = 2.613(1) Å). The metal is displaced from the basal plane in the direction of the apical chlorine. The central Cu_2Cl_2 core is asymmetric with a "folding" angle of 12.3°, a metal separation distance of 3.244(1) Å and $Cu–Cl_{br}–Cu$ bridging angles of 80.56(5) and 81.61(5)°. The possibility that the mixed-valent dimer **IX** is formed by a one-electron reduction of **VII** has been supported by cyclic voltammetry of **VII**, which shows pseudo-reversible behaviour in dichloromethane ($E_{1/2}$ = +0.59 V) [24].

Hodgson and co-workers have made a substantial contribution to copper–S,N heterocyclic coordination chemistry by establishing the N-donating character of tz and 4-metz, indicating the steric consequences of the 4-methyl group on the coordination geometry at the metal and rationalising magnetic-structural relationships among the complexes. The relevance of this work to biological modelling and catalytic processing has also been noted. Furthermore, it is likely that tz and 4-metz are not unique in their behaviour towards copper(II), related S,N-containing heterocyclic ligands may also be capable of generating chemistry of similar novelty.

The 1,3-thiazolium ion is a constituent of thiamin, vitamin B1 (**XI**). The molecule crystallises as the hydrochloride-chloride and is also known in deprotonated and neutral forms [27].



XI



XII

Interest in the copper–thiamin reaction stems from the possibility that the bio-regulation of the metal involves oxidation of thiamin to thiochrome (**XII**) [28], coupled with reduction and coordination of the metal [29].

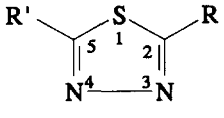
After some initial problems [30], a successful synthesis of $[Cu(thiamin)Cl_2]$ was effected from thiamin hydrochloride and hydrated copper(II) acetate, $[Cu_2(CH_3COO)_4(H_2O)_2]$, in distilled water [31]; thiochrome was identified in the reaction solution. The yellow crystalline complex contains distorted, planar, trigonally coordinated copper(I). The coordination site in the protonated thiamin ion is the pyrimidinium-N(1) atom, the same site as in $[Cd(thiamin)Cl_3]$ [28]. Angles at the metal (106.98(5)–135.96(5)°) and the disparate Cu–Cl distances (2.2002(6); 2.3366(6) Å) are indicative of the distorted geometry. This reaction provides strong support for the suggestion that the biologically ubiquitous thiamin molecule is involved in the bio-regulation of copper [28,29].

The coordination of thiochrome (**XII**, tc) to copper(I) has been reported in the form of a polymeric "stair-type" complex $[Cu_2(tc)_2(ClO_4)_2]$ [32]. This complex was prepared by the addition of tc to a methanolic solution of copper(II) perchlorate hexahydrate to which copper wire had been added then removed prior to the addition of the ligand. The structure of the complex consists of an infinite array of $[Cu_2(tc)_2]^{2+}$ dimers linked, on both sides, by the oxygen atoms of the 2-hydroxyethyl groups of the ligands and interspersed with columns of perchlorate anions which effectively inhibit interchain interactions. The $[Cu_2(tc)_2]^{2+}$ unit is planar and centrosymmetric about the mid-point of the metal–metal vector (Cu···Cu = 2.476(3) Å) with an eight-membered $Cu_2N_4C_2$ central core. Metal geometry is T-shaped with a N_2O donor set consisting of terminal pyrimidino nitrogen, (Cu–N(2) = 1.906(5), Cu–N(3) = 1.905(5) Å) and completed by a bridging neutral oxygen atom from the hydroxyethyl group of the ligand, (Cu–O = 2.262(7) Å). Angles at the metal range from 96.7(2) to 165.9(3)°. Each planar dimeric unit comprises one step in the "stair-type" polymer, the distance between neighbouring steps in the chain being 4.5 Å. The complex exhibits a quasi-reversible cyclic-voltammetry curve in the solid ($E_{1/2} = 0.29$ V vs. Ag/AgCl).

Complexes have also been reported for relatively more elaborate thiazole derivatives. 2-Amino-4-(*p*-methoxyphenylethyl)thiazole [33] and 4-methyl-2-(2-hydroxy-1-naphthylazo)thiazole [34] form 1:1 and 1:2 complexes with copper(II). Deprotonated α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino)benzenesulphonamido-2′-thiazole forms a 1:2 complex with copper(II) [35]. Formation constants have been reported for the copper(II) complex of deprotonated thiazole-2-ylthiourea which is a thiazole-N, thiourea-S chelate [36]. Schiff's bases, formed from 2-amtz and substituted salicylidenes, complex with copper(II) [37]. The bi-heterocycle 2,2′-hydrazothiazole bridges pairs of copper(I) atoms through the thiazole nitrogen atoms [38]. The coordination chemistry of bi-heterocycles, such as 2,2′-bithiazole, towards copper and other metals has been reviewed [39].

2.3 1,3,4-Thiadiazoles

The symmetrical 1,3,4-thiadiazole molecule (tdz, **XIII**) and its major derivatives are extensively used either as the parent ligand or as complexes, including copper complexes, as fungitoxic agents [40]. Thermostable, photostable and heat-oxidation resistant polyamides have been synthesised by melting and polymerising the monomers in the presence of copper complexes of thiadiazole derivatives [41].



XIII

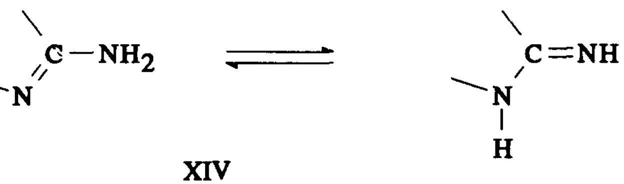
(a) R = R' = H = tdz
(b) R = R' = Me = 2,5-dimetdz
(c) $R = NH_2$, R' = H = 2-amtdz
(d) $R = NH_2$, R' = Me = 2-am-5-Metdz
(e) $R = NH_2$, R' = Ph = 2-am-5-Phtdz

The coordination chemistry of the tdz system has evolved primarily through study of the derivatives (**XIIIb–e**) rather than the parent molecule. The derivatives have considerable coordination potential with heterocyclic sulphur and nitrogen and, in some instances, exocyclic nitrogen as possible donor sites. Copper complexes have been reported for 2-amtdz (**XIIIc**) [42], and its 5-methyl, 2-ammetdz (**XIIId**) [43], and 2-phenyl, 2-amphtdz (**XIIIe**) [44], derivatives; complexes have also been reported for 2,5-dimethyl-1,3,4-thiadiazole (2,5-dimetdz **XIIIb**) [45].

Stoichiometries of the copper(I) complexes of 2-amtdz, [Cu(LH)X] ($X=Cl$, Br, I) and [Cu(LH)$_3$X] ($X=ClO_4$, NO_3), correspond to linear halogen-bridged structures with trigonal, ($N+2X_{br}$) and trigonal-pyramidal ($3N+O$) metal coordination, respectively. The proposed donor site in 2-amtdz is the exocyclic amino nitrogen atom, on the basis of ν(Cu–N) in the region 420–520 cm^{-1} [42(a)]. The copper(II) complexes have conventional room-temperature magnetic moments ($\mu_B=1.86$–1.92) with structures deduced from electronic spectra and metal–ligand attachments deduced from IR spectra. The 2-amtdz complexes [Cu(LH)X$_2$] ($X=Cl$, Br) are presumed to contain six-coordinate metal with bridging 2-amtdz and asymmetric bridging halogen [42(b)] whereas [Cu(LH)$_2$X$_2$] ($X=Cl$, Br) are presumed to have flattened pseudo-tetrahedral stereochemistry with N_2X_2 coordination and additional apical contacts. Bonding is proposed to involve the exocyclic amino nitrogen atom in terminal modes supported by heterocyclic nitrogen donation in bridging environments [43(b)]. Bidentate coordination involving heterocyclic sulphur and exocyclic nitrogen has also been proposed for some [Cu(2-amtdz)$_2$X$_2$) complexes [43].

Polymeric structures, with octahedral metal geometry, are proposed for complexes of 2-ammetdz with amino nitrogen coordination together with one or both heterocyclic nitrogen atoms, as required, for bridging environments [44(b)]. *N,N′*-chelation of the metal is proposed in [Cu(2-amphtdz)$_2$(py)$_2$]SO$_4$ [45(a)]. Heterocyclic nitrogen donation is proposed for 2,5-dimetdz complexes [46].

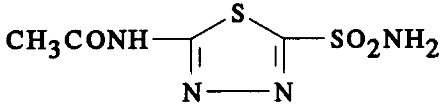
Most of the possible combinations of donor atoms have been proposed for the above tdz complexes. However, the absence of structural evidence presents difficulties in the rationalisation of stoichiometry and structure, especially in the case of 2-amtdz and its derivatives. Resolution of the competitive donor behaviour between heterocyclic and exocyclic nitrogen in 2-amtdz complexes, invariably on the basis of spectroscopic data, is also difficult. Adherence to the exocyclic amino group, as the major donor site, tends to overlook the possibility of amino–imino tautomerism (**XIV**) in the ligands and the presence of substantial pπ–pπ bonding in the exocyclic carbon–nitrogen bond which, as with 2-amtz [20], inevitably minimises the coordination



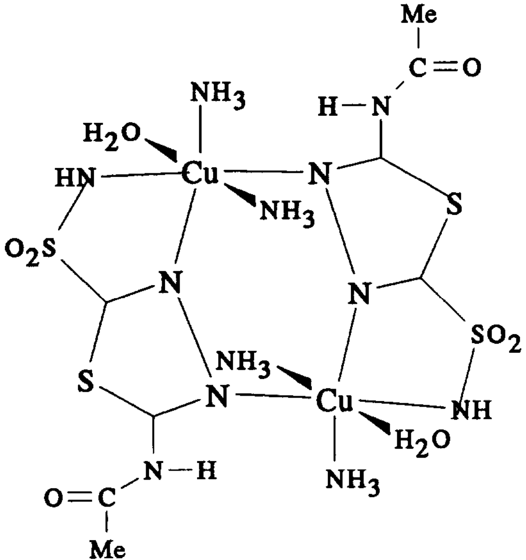
XIV

potential of the group. Consequently, it is not surprising that it is the heterocyclic nitrogen atoms which have been established as the donor sites, at least for a cobalt(II) complex of 2,5-diamino-1,3,4-thiadiazole (am_2tdz) [47].

Acetazolamide (5-acetamido-1,3,4-thiadiazole-2-sulphonamide) ($azmH_2$, **XV**) is a potent inhibitor of carbonic anhydrase. Deprotonation at both the amide sites produces the di-anion azm^{2-}, which complexes with divalent metals in aqueous and aqueous–ethanolic media [48]. With copper(II), a neutral dinuclear complex $[Cu_2(azm)_2]$, together with hydroxo species, are formed in both media. The magnitudes of the stability constants are always greater in the mixed solvent. The crystal structure of $[\{Cu(azm)(NH_3)_2(OH_2)\}_2]\cdot H_2O$ consists of neutral dimers, as well as extensively H-bonded water molecules; the azm^{2-} anion is a terdentate nitrogen donor [49]. The copper(II) atoms in the dimer are bridged by the diazo nitrogen atoms from two azm^{2-} ligands, forming a six-membered ring (**XVI**). The bridging is unusual, however, with one nitrogen atom occupying an equatorial and the other occupying an axial site. The deprotonated sulphonamido nitrogen atom also coordinates to the metal. Each copper(II) atom has tetragonally elongated octahedral geometry with the basal plane consisting of one sulphonamide nitrogen, from one



XV

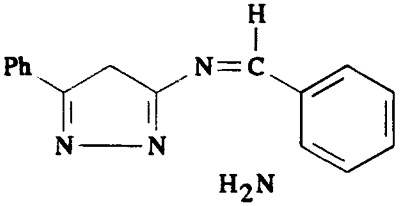


XVI
(adapted from [49])

azm anion, one thiadiazole nitrogen, from an adjacent azm anion, one ammonia nitrogen and one water oxygen atom. The coordination is completed by apical ammonia (Cu–N = 2.825(6) Å), and the second thiadiazole nitrogen atom (Cu–N = 2.546(4) Å), which is also apically coordinated. Equatorial and axial angles at the metal range from 78.7(2) to 98.7(2)° and 162.4(1) to 176.1(2)°, respectively. The equatorial distances (2.011(4)–2.028(4) Å), are relatively similar, in spite of the involvement of four different ligands. The spectroscopic data are consistent with the established structure. Cryogenic magnetic susceptibility measurements indicate the absence of significant metal–metal interactions in the dimer.

The diverse coordination chemistry of H_2azm has been further demonstrated by the structures of two copper(II) complexes of the mono-anion Hazm: [Cu(Hazm-O)$_2$(en)$_2$] and [Cu(Hazm-N)$_2$(pn)$_2$] (en = 1, 2-diaminoethane and pn = 1, 3-diaminopropane). Both complexes are centrosymmetric at the copper atoms with tetragonal geometry consisting of an equatorial CuN_4 arrangement formed from pairs of trans *N,N*-chelating diamines (Cu–N = 2.00–2.05 Å). Pairs of *trans*-Hazm anions complete the coordination, in one complex by means of a sulphonamido-O atom (Cu–O = 2.652(1) Å), and through a thiadiazole-N atom in the other complex (Cu–N = 2.457(2) Å). In neither case is the deprotonated acetamido group involved in the coordination. Electronic and ESR spectra are consistent with tetragonal geometry [50].

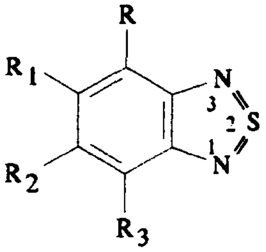
The composition and stability constants of some Schiff's base chelates CuL_2, based on 2-salicylideneamino-5-phenyl-1,3,4-thiadiazolate, [51(a)–(c)] (**XVII**), and 2-amino-5(*o*-hydroxy-phenyl)-1,3,4-thiadiazolate, [51(d)], have been reported.



XVII

2.4 *2,1,3-Thiadiazoles*

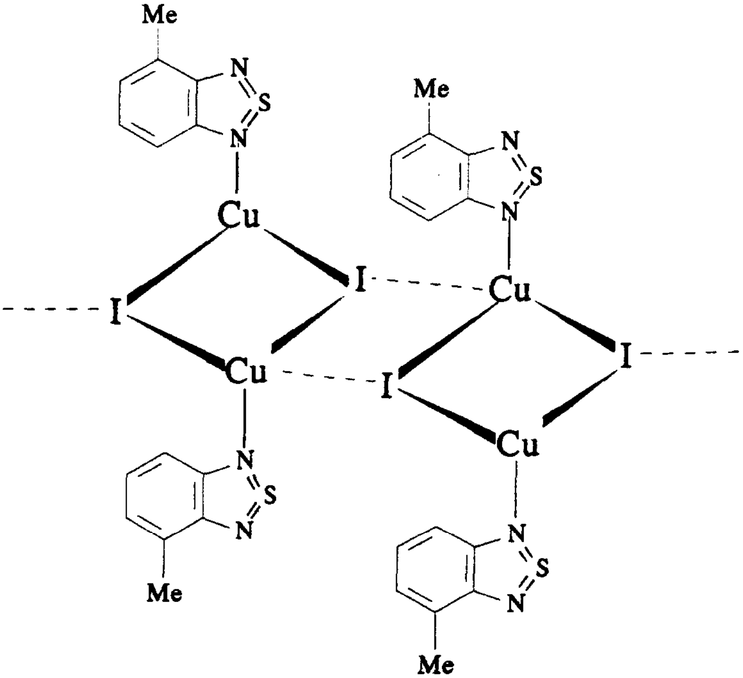
The antimicrobial activity of a number of benzo-2,1,3-thiadiazole (bztdz, **XVIII**) derivatives, and their copper(II) complexes have been studied. Many of the compounds show broad-spectrum activity against bacteria and fungi with the copper(II) complexes generally more active than the parent heterocycles [52]. Dimeric, [{Cu(LH)Cl_2}$_2$] and [{Cu(LH)$_2Cl_2$}$_2$] complexes of bztdz and its methyl derivatives have been prepared and characterised by IR and electronic spectra. The ligands are monodentate and bond to the metal through their heterocyclic nitrogen atoms. The antimicrobial activity of the complexes was also tested [53].



R, R_1, R_2, R_3 = H or Me

XVIII

A number of copper(II) complexes of 4-(2-carboxy-2-aminoethyl)benzo-2,1,3-thiadiazole have also been prepared and characterised by IR and electronic spectra [54]. Heating copper(I) halides with an excess of 4-methylbenzo-2,1,3-thiadiazole (LH) produced complexes of general formula CuX(LH) (X = Cl, Br, I) [55]. The crystal structure of the iodo complex consists of essentially dimeric $Cu_2(LH)_2I_2$ units with a strictly planar, centrosymmetric Cu_2I_2 core (Cu–I = 2.665(1), 2.708(1) Å; Cu–I_{br}–Cu = 119.6(3)°; Cu···Cu = 2.673(1)°) and heterocyclic N(1)-donating ligands (Cu–N = 2.040(4) Å). The central CuI_3N core is pseudo-tetrahedral with angles at



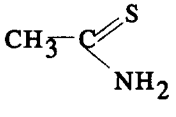
XIX
(adapted from [55])

the metal ranging from 104.9(4) to 119.6(3)°. The fourth coordination site is provided by a bridging iodine in a neighbouring dimer (Cu–I = 2.650(1)P); these contacts generate an infinite chain of edge-sharing tetrahedra (**XIX**).

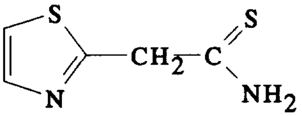
3. COMPLEXES OF HETEROCYCLIC SUBSTITUTED THIOAMIDES

3.1 Introduction

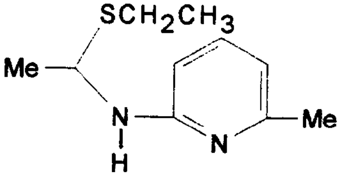
Thioacetamide (ta, **XX**), is an archetypal, simple thioamide which reduces copper(II) and coordinates to copper(I) forming $[Cu(ta)_4]Cl$ in which the metal is tetrahedrally coordinated by four monodentate S-donating ligands, (Cu–S = 2.343(3) Å) [56]. In addition, ta also forms cyclo-tris-μ-thioacetamide-tris-[chlorocopper(I)], $[\{Cu(ta)Cl\}_3]$, which consists of hexagonal rings of alternating copper(I) and thioamide sulphur atoms with the trigonal coordination at the metal completed by chlorine (Cu–S = 2.220(6), 2.251(6); Cu–Cl = 2.226(4) Å), [57].



XX



XXI



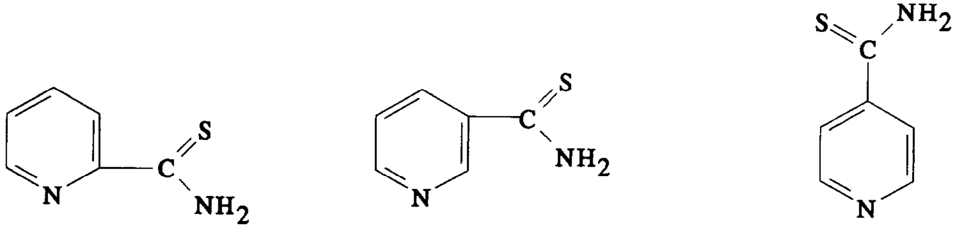
XXII

The ta molecule is the precursor of a range of ligands in which the methyl group, or one of its hydrogen atoms, as well as one of the thioamido protons, may be replaced by a heterocyclic molecule. Examples include, 2-thioacetamido-1,3-thiazole (tatz, **XXI**), which forms $[Cu(tatz)_2Cl]$ with S-donating tatz [58] and *N*-(2-pyridylmethyl)-2-(ethylthio)-acetamide (ptaH, **XXII**), the anion of which forms $Cu(pta)X \cdot nH_2O$, $Cu(pta)X_2$ and $Cu(pta)ClO_4 \cdot 0.5H_2O$, for which N.N.S-terdentate coordination is proposed [59].

Clearly, a potentially rich source of S,N-donating ligands is possible by judicious substitution. Much of the work so far, however, has concentrated mainly on the use of pyridine substituents.

3.2 Pyridine-substituted thioamides

The thioamido-pyridine derivatives (**XXIII**, 2-tap [60(a)], 3-tap [60(b)] and 4-tap [60(c),(d)]) have well-established structures. Their anti-tubercular activity [60(c),(d)] and their use in the electroplating industry [60(a),(b)] have stimulated interest in the coordination chemistry of these molecules.



(a) (b) (c)

XXIII

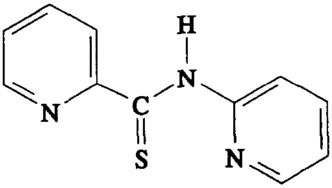
(a) (b)

XXIV

Of the three derivatives, 2-tap clearly has chelating potential with the pyridine-N atom and either the thioamido sulphur or nitrogen atoms involved in S,N- (a) or N,N- (b) chelation (**XXIV**). The remaining derivatives are potentially monodentate or bridging through either the pyridine-N atom and/or the atoms of the side-chain. The copper(I) complexes of 2-tap such as brown $[Cu(2\text{-tap})_2][Cu(SCN)_2]$, as well as the copper(II) complexes $[Cu(2\text{-tap})_2(H_2O)_2](PF_6)_2 \cdot H_2O$ and $[Cu(2\text{-tap})_2(NO_3)(H_2O)](NO_3)$ are S,N-chelated, whereas yellow $[Cu(2\text{-tap})_2][Cu(SCN)_2]$ is N,N-chelated (based on IR data [61]). S,N-coordination and square-planar geometry have been reported for several copper(II) complexes of deprotonated *N*-alkyl-2-thioamido-pyridines [62]; 6-methyl-2-thioamido-pyridine forms $[Cu(LH)_2]^{2+}$ cations with S,N-coordination proposed from IR data [63]. A series of complexes $[Cu(LH)_2Cl_2]$ (LH = 2-tap, 3-tap, 4-tap) have been prepared from copper(II) chloride and the appropriate ligand in 1 : 3 (metal : ligand) ratio in ethanol. Electronic spectra indicate five-coordinate metal and a trigonal-bipyramidal structure for [Cu(2-tap)$_2$Cl$_2$] and tetragonally distorted octahedral stereochemistry for the other two complexes. Infrared spectra indicate S,N-chelation for 2-tap and S,N-bridging in the polymeric complexes of 3-tap and 4-tap [64].

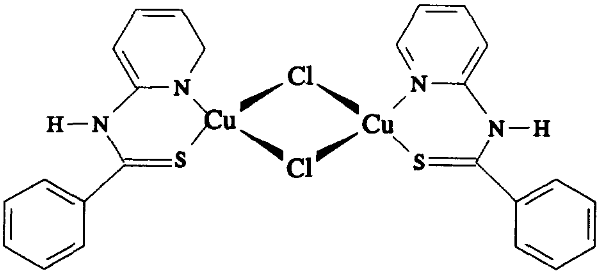
Reduction of copper(II) by substituted thioamidopyridines appears to be variable. The production of copper(II), rather than copper(I) complexes, at least for 2-tap derivatives, is believed to be governed by the nature of the copper(II) salt employed as well as by that of the ligand substituents [61]. S,N-chelation is probable for the invariably deprotonated ligands in such complexes; a square planar environment for the metal has been proposed from a preliminary X-ray study in one instance [65].

Thionation of the corresponding benzamide produces *N*-(pyridin-2-yl)-benzenecarbothioamide (pbctaH, **XXV**). This novel ligand, formally related to ta and potentially S,N-chelating, has thione sulphur and pyridyl nitrogen available for coordination, as well as one weakly acidic thioamido proton [66].



XXV

Appropriate molar ratios of copper(II) chloride dihydrate and pbctaH in methanol produce [Cu(pbctaH)$_2$]Cl$_2$ and [{Cu-(pbctaH)Cl}$_2$]; each complex is significantly contaminated with the other in these syntheses. The complexes are black, diamagnetic and indefinitely air stable. In the mononuclear complex, the metal, which occupies a crystallographic two-fold axis, is pseudo-tetrahedrally coordinated by two S,N-chelating pbctaH ligands (Cu–S = 2.237(1) Å; Cu–N = 1.672(3) Å); angles at the metal range from 95.7(1) to 126.8(1)°. The dinuclear complex **XXVI**, is a dichloro bridged dimer with the central, non-planar Cu$_2$Cl$_2$ core bisected by a crystallographic two-fold axis (Cu–Cl$_{br}$ = 2.353(1) Å; Cu···Cu′ = 3.097(1) Å; Cu–Cl$_{br}$–Cu′ = 80.6(1)°); coordi-

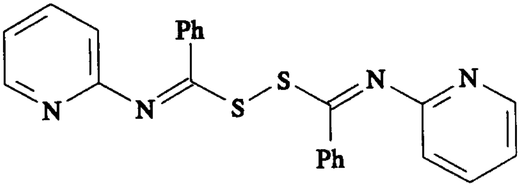


(adapted from [66])

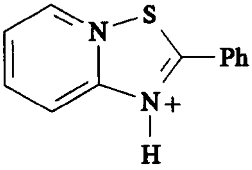
XXVI

nation at the metal is completed by an S,N-chelating pbctaH (Cu–S = 2.192(1) Å; Cu–N = 2.052(3) Å). The authors propose substantial π-bonding of the type Cu = S = C in both complexes because of the relative shortness of the appropriate bond distances.

During the preparation of the above complexes, it is likely that copper(II) chloride oxidises pbctaH to the related bis-imidoyldisulphide **XXVII** (bisdis) and that the excess ligand coordinates to the resultant copper(I) chloride. The disulphide has also been prepared, in low yield, by iodine oxidation of pbctaH in dry dioxan–ether solution containing triethylamine. Attempts to produce complexes of the disulphide by the slow addition of pbctaH to a swamping excess of copper(II) chloride dihydrate produced complexes of the protonated pyridinium disulphide cation $[\text{bisdisH}_2]^{2+}$. An orange product, empirically formulated $Cu_4(\text{bisdisH}_2)\text{-}Cl_6$, is diamagnetic, sparingly soluble in organic solvents and is probably polymeric. A yellow product, empirically formulated $Cu_2(\text{bisdisH}_2)Cl_4$, is paramagnetic ($\mu_B = 1.87$) with an isotropic ESR signal and is believed to be the tetra-chloro cuprate(II) salt of the thiadiazolopyridinium ion (**XXVIII**) with a polymeric structure similar to those of previously reported halo-cuprates [67].



XXVII



XXVIII

The production of stable copper(II) chelates of pbctaH is frustrated by the fundamental redox instability of the copper(II)–thioamide system (see also Sect. 6). A possible solution to this problem lies in substituting alternative, sacrificial, redox sites into the pyridyl ring. The reaction between 4-nitro-*N*-(pyridin-2-yl)benzenecarbothioamide and copper(II) acetate, which gave a bis-chelated copper(II) complex with $\mu_B = 2.01$ and electronic spectra typical of a square-planar structure, indicates that such a strategy may be generally applicable.

4. COMPLEXES OF HETEROCYCLIC THIONES

4.1 Introduction

The structural and coordination chemistry of heterocyclic thione derivatives (**XXIX**) were last reviewed in 1985 [3]. The parent molecules, however, continue to generate interest, especially in relation to their tautomeric (**XXX**) and bioactive properties.

Recent reports have dealt with further aspects of the vibrational activity of the thione derivatives of imidazole and thiazole [68]. Specific studies of thione-thiol tautomerism include: equilibria among pyridine and pyrimidine thione-thiol derivatives in polar and non-polar solvents [69], a theoretical and matrix isolation study of pyridine-2-thione tautomers [70] as well as tautomerism among 2,4-dithiouracil derivatives [71]. Electronic structures and quadrupole coupling among imidazolidine-thione, -one and -selenone derivatives have also been reported [72]. It is evident that the thione-thiol equlibrium is dependent on environmental factors with the thiol form favoured in the gas phase and non-polar solvents, and the thione form favoured in the solid state and polar solvents [70].

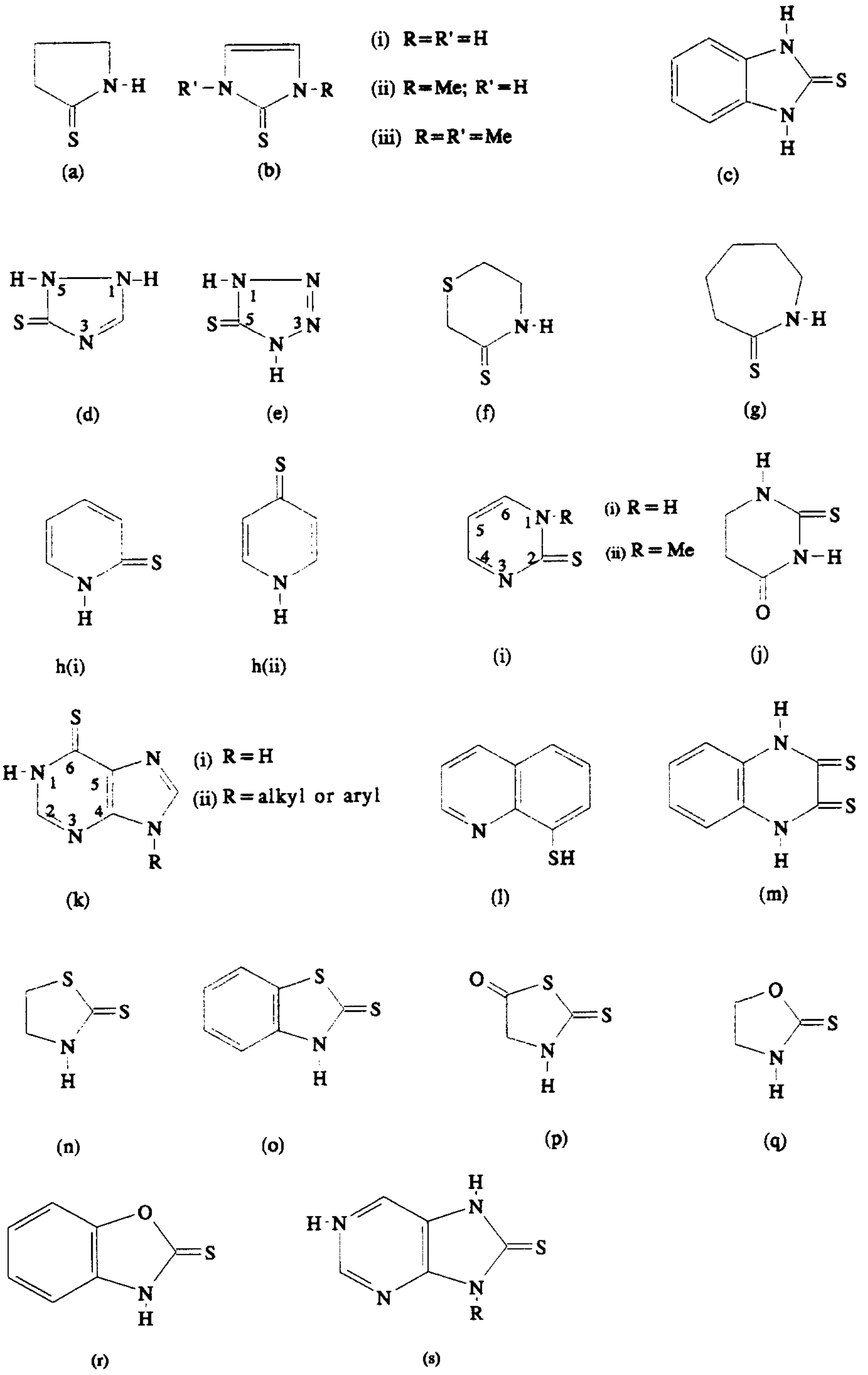
Interest in the bioactivity of the parent molecules has been maintained by reports on the T-cell mediated anti-tumour activity of 6-mercapto-purine (purine-6-thione) [73]; imidazole-thione derivatives have been used as biomimetic models for cysteine proteases [74].

Recent crystallographic studies of thiazole-2(3H)-thione [75] and pyrimidine-2-thione derivatives [76] have supported previous reports that the thione tautomers are dominant in the solid.

The coordination chemistry of heterocyclic thiones, especially with copper(I), continues to attract attention. Specific systems studied include, imidazolidine-2-thiones [77], thiazole-thiones [78], neutral and protonated forms of pyrimidine-2-thione [79] as well as 2-thiouracil [80]. Characterisation of these, and other copper(I) complexes, involves IR, NMR, conductivity and, increasingly, electro-chemical studies. The absence of definitive structural data has inhibited resolution of stoichiometric–structural relationships in many cases. However, since the last review appeared [3], the number of crystal structures of copper(I) complexes of heterocyclic thiones and thionates, with either trigonal or tetrahedral coordination of the metal, has increased significantly. Consequently, the emphasis in this section is placed on the developing structural chemistry of such complexes. A survey of synthetic procedures is also included because of their inherent importance and relevance to the solution chemistry of the copper(II)–heterocyclic thione system.

4.2 Synthetic procedures

In solution, the structural forms adopted by heterocyclic thiones, and consequently the donor sites available for coordination, are dependent on the prevailing reaction conditions (**XXX**).

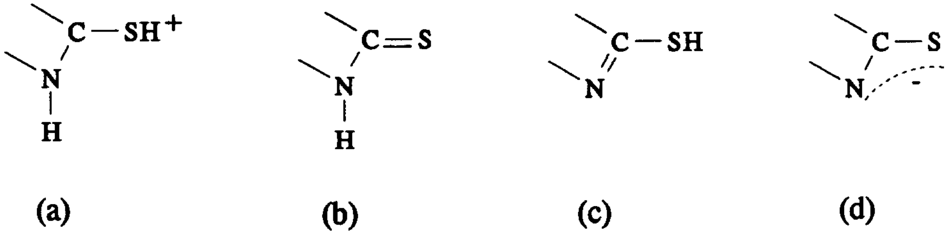

(a) (b) (c) (d) (e) (f) (g) h(i) h(ii) (i) (j) (k) (l) (m) (n) (o) (p) (q) (r) (s)

(b) (i) R=R'=H (ii) R=Me; R'=H (iii) R=R'=Me

(i) (i) R=H (ii) R=Me

(k) (i) R=H (ii) R=alkyl or aryl

XXIX



XXX

In the solid, and in neutral solution, the thione form (**XXXb**) is the dominant tautomer with the thione sulphur atom the favoured donor site [3]. Protonation, in molar acid for example, produces the thionium ion (**XXXa**). Although all available donor sites appear to be blocked in this form, the thioamido proton is clearly labile and thione-S donation to copper invariably occurs [81]. Deprotonation of thiones, by a variety of means, generates the thionate anion (**XXXd**). This species has both the thionate sulphur and the heterocyclic nitrogen atoms available, either singly or collectively, for coordination. Conditions which favour the formation of the thiol form (**XXXc**), and release the heterocyclic nitrogen atom for coordination, are the least understood in this system although non-polar solvents and dilute ligand concentrations are believed to help [69]. With the addition of other potentially tautomeric sites, such as amino–imine and keto–enol, for example, to thione-substituted heterocyclic molecules, the available coordination sites become even more numerous and the structural forms of the ligand more complicated, especially in different reaction media [82].

The factors which affect the structural form of a ligand at the time of coordination, and consequently the outcome of the reaction with copper salts are: the oxidation state of the metal, the coordinating ability of the counter ion, the molar ratios of the reactants and their order of addition as well as the solvent system. Among the many ligands used, 1-methylimidazoline-2(3H)-thione (meimtH, **XXIXbii**) has been successfully complexed with all the common copper salts and, together with pyridine-2-thione (py2tH, **XXIXhi**), meimtH has the most extensively studied structural chemistry. The synthetic procedures succesfully employed with meimtH appropriately illustrate most of the above factors.

The preparation of copper(I) complexes of meimtH from the corresponding copper(I) salts is relatively straightforward. Copper(I) halides in absolute ethanol or 1 : 1 (v : v) acetone : hydrohalic acid and 1 : 2 (metal : ligand) ratios with the ligand added to the metal salt produce colourless $[Cu(meimtH)_2X]$ ($X = Cl,Br,I$). Transient coloured solutions, which occur during the initial stages of the reaction, are probably due to the presence of residual copper(II) [83]. Colourless $[Cu_2(meimtH)_4(SCN)_2]$ was produced by refluxing the reactants in 1 : 4 (metal : ligand) molar ratio in refluxing ethanol: acetonitrile until all the metal salt dissolved [84]. The addition of meimtH to a refluxing solution of copper(I) cyanide in 0.1 M potassium cyanide, in 1:4 (metal:ligand) molar ratio produced $[\{Cu(meimtH)(CN)\}_n]$ [85]. These methods have been succesfully used in the production of halo, thiocyanato and cyano copper(I) complexes of several heterocyclic thiones [86].

The involvement of copper(II) salts widens the range of counter ions and introduces the inherent complexity of the copper(II)–heterocyclic thione interaction. Organo-thiols and thiones (RSH) generally reduce copper(II):

$$2RSH + 2Cu^{2+} \rightarrow 2Cu^{+} + RSSR + 2H^{+}$$

with concomitant ligand oxidation. Addition of the metal salt to a refluxing solution of excess ligand in acetone–acetonitrile produced $[Cu(meimtH)_3](NO_3)$ [87] and $[Cu_2(meimtH)_6](BF_4)_2$ [88] as well as $[Cu_2(meimtH)_5](SO_4)\cdot 3H_2O$ from aqueous acetone [89]. This strategy favours production of the copper(I) complex of the thione (reduced) form of the ligand and minimises the effect of the oxidised form of the ligand on the course of the reaction. An investigation of the reaction between copper(II) chloride dihydrate and meimtH in ethanol has shown that the reaction product depends upon the metal:ligand molar ratio used [90]. A large excess of the ligand produced a green solution. The ESR spectrum of a frozen sample showed the colour to be due to $[Cu(meimtH)_4]^{2+}$ with thione-S ligand donation and implied tetrahedral geometry. Addition of the metal salt to the ligand in 1:3 (metal:ligand) molar ratio produced $[Cu_2(meimtH)_4Cl_2]$, which is dimeric (see p. 118) [83]. A 1:1.5 (metal:ligand) ratio produced the mixed-valent complex $[Cu(I)Cu(II)(meimtH)_2Cl_3]$ with the formula supported by magnetic data ($\mu_B = 1.85$ per copper(II) atom) and an electronic spectral d–d band at 837 nm. A change of solvent system causes the reaction to take a different course. The addition of copper(II) chloride dihydrate in ethanol to meimtH in nitromethane, in 1:2 (metal:ligand) molar ratio, generated a brown solution from which dark-green crystals of $[Cu_2$(2,2′-bis(1-methylimidazolyl)-monosulphide)$Cl_4]$ were obtained. The same complex may be obtained by performing the copper(II) chloride–meimtH reaction in methanol or by the recrystallisation of $[Cu(I)Cu(II)(meimtH)_2Cl_3]$ in nitromethane.

Synthetic procedures in this field, especially those involving copper(II)-thione reactions, are clearly not straightforward. Furthermore, considerable effort has been expended in devising methods to stabilise copper(II) in the presence of thione-thiol-containing ligands (see also Sect. 6). It is possible, in most cases, to prepare a complex of a given ligand; however, the controlled preparation of a specific complex is a different matter.

4.3 Mononuclear complexes

4.3.1 Trigonal coordination

Homoleptic, trigonally coordinated copper(I) with CuS_3 coordination has been established for relatively few ligands (Table 1(a)). In all cases the geometry is signifi-

TABLE 1

Mononuclear trigonal complexes: selected bond lengths (Å) angles (°) and [mean values]
(a) Homoleptic complexes

Complex	Ref.	Cu–S	Angles at the metal
$[Cu(meimtH)_3](NO_3)$	87	2.235 (2)–2.258 (2) [2.249]	114.7 (1)–125.4(1) [119.6]
$[Cu(py2tH)_3](NO_3)$	91	2.213(5)–2.228(5) [2.222]	109.0(2)–131.0(2) [120.0]
$[Cu(imdtH_2)_3]1/2(SO_4)$	92	2.270(4)–2.280(4) [2.276]	119.7(1) [119.7]

(b) Mixed-ligand complexes

Complex	Ref.	Cu–S	Angles at the metal	Cu–X (X = Cl,I,N,Br,P)
$[Cu(NEtimdH)_2Cl]$	93	2.214(2)–2.218(2) [2.216]	118.5(1)–121.4(1) [120.0]	2.258(2)
$[Cu(Me_2imdt)_2Cl]$	94	2.229(3) [2.229]	112.9(1)–134.2(1) [123.5]	2.233(3)
$[Cu(H_4pymtH)_2Cl]$	95	2.206(2) [2.206]	118.3(1)–123.4(1) [120.0]	2.317(3)
$[Cu(tucH_2)_2Cl.DMF$	96	2.225(1)–2.228(1) [2.227]	118.1(1)–120.6(1) [120.0]	2.260(1)
$[Cu(imdtH_2)_2(NCS)]$	97	2.221(1) [2.221]	119.2(1)–121.6(1) [119.5]	1.956(4)
$[Cu(N\text{–}primdtH_2)_2Cl]$	77	2.193(3)–2.223(3) [2.212]	117.3(1)–121.9(1) [120.0]	2.257(2) 2.269(3)
$[Cu(w\text{-}tcp)_2I]$	102	2.238(1)–2.250(1) [2.212]	117.8(1)–121.3(0) [120.0]	2.590(1)
[Cu(totp)(tzdtH)Br][a]	217	2.290(1) [2.290]	113.4(0)–125.8(0) [119.0]	2.413(0) Cu–P = 2.256(1)
$[CuCl(py2tH\text{-}3\text{-}Si(Me_3)\text{–}6\text{–}Si(Et_3)]$	218	2.198(4)–2.204(4) [2.201]	119.0(2)–121.5(2) [120.0]	2.279(4)
[Cu(totp)(pym2tH)Cl][a]	220	2.221(2) [2.221]	114.7(1)–130.9(1) [119.7]	2.293(2) Cu–P = 2.241(2)
[Cu(totp)(py2tH)I][a]	220	2.254(2) [2.254]	118.2(1)–120.7(1) [119.4]	2.563(1) Cu–P = 2.269(2)

[a] totp = tris *o*-tolyl phosphine.

cantly distorted but mean angles (S–Cu–S) cluster around the value for regular trigonal geometry. Metal–sulphur(thione) distances are in the range 2.213(5)–2.280(4) Å (Table 1(a)).

The structures of mixed-ligand complexes (Table 1(b)) are more numerous than the homoleptic variety. As expected, they have distorted geometry with metal–sulphur(thione) distances generally shorter than those of metal–halide, the S–Cu–S angles are usually larger than S–Cu–X, and the metal is usually displaced from the mean plane of the complex.

In all cases, the ligands "tilt" about the coordination plane and "twist" about the Cu–S–C planes to a varying extent, depending on ligand geometry, hydrogen-bonding and other crystal packing requirements. Furthermore, angles at the sulphur(thione) atom (Cu–S–C) are in the region of the tetrahedral value (106.0(2)–113.9(6)°), and ligand carbon–sulphur(thione) distances (1.683(5)–1.807(4) Å) are invariably slightly longer than in the parent molecule. These are common features of heterocyclic-thione complexes [98].

4.3.2 Tetrahedral coordination

Homoleptic complexes with tetrahedral geometry at the metal, monodentate thione S-donating ligands and CuS_4 coordination are known for imidazolidine-2-thione ($imdtH_2$), $[Cu(imdtH_2)_4](NO_3)$ [99] and pyridine-2-thione $[Cu(py2tH)_4](ClO_4)\cdot 2(py2tH)$ [100]. The copper–sulphur distances are invariably longer than those for trigonal geometry (2.273(3)–2.480(3) Å), with the cross-over value in the region of 2.270 Å. The distortion from regular tetrahedral geometry is indicated by the range of angles at the metal (98.3(1)–122.0(1)°). Angles (Cu–S–C) at the thione S-atom range from 101.2(3) to 115.1(3)°, with the mean in the region of the tetrahedral angle. Ligand carbon–sulphur(thione) distances (1.685(4)–1.710(12) Å) are invariably slightly longer than in the parent ligand.

The mixed-ligand complex $[Cu(tzdtH)_2Cl]$ has an unusual structure in which the metal occupies a crystallographic three-fold axis. Consequently, the ligands have a planar, symmetrical, trigonal disposition about the metal (S–Cu–S = 120.0°, Cu–S = 2.319(4) Å, Cu–S–C = 108.8(6)° and C-S(thione) = 1.652(16) Å). The coordination is completed by an apical chlorine (Cu–Cl = 2.402(4) Å) and the $Cu(LH)_3Cl$ units are linked into linear chains by intermolecular contacts, (Cu–Cl′ = 3.862 Å) [101].

Studies of the competitive donor behaviour between heterocyclic-thiones and phosphines towards copper have generated a significant number of mixed ligand complexes [103–110]. Two types of mononuclear complex have been reported, $[Cu(LH)_2(PPh_3)_2]X$ ($X = NO_3$, ClO_4) and $[Cu(LH)(PPh_3)_2X]$ (X = Cl, Br) (LH = py2tH, py4tH, pymtH, pu6tH, tzdtH, meimtH, bzoxtH, bztztH, $bzimtH_2$, $qnotH_2$ and $nbimtH_2$, **XXIX**), which have been characterised by IR, UV-visible and NMR spectra. Preparations invariably involve the copper(I) halide with the ligand and triphenylphosphine in 1:1:2 molar ratio in tetrahydrofuran, for the $[Cu(LH)(PPh_3)_2X]$ complexes [107–109]. The $[Cu(LH)_2(PPh_3)_2]$ complexes have been prepared from either $[Cu(PPh_3)_2(NO_3)]$ [104] or $[Cu(PPh_3)_4](ClO_4)$ [105] in chloroform, ethanol or acetone with addition of the ligand in the same solvent. Other routes have also been used for both mono- [106] and diphosphines [110]. Structural details of the reported crystal structures of these complexes are summarised in Table 2.

TABLE 2

Copper (I) halide–heterocyclic thione–triphenylphosphine mononuclear complexes: selected distances (Å) and angles (°)

Complex	Ref.	Cu–S	Cu-P	Angles at the metal
$[Cu(tzdtH)_2(PPh_3)_2](NO_3)$	104	2.371(1) 2.382(1)	2.292(1) 2.310(1)	101.7(0)–123.2(0)
$[Cu(py2tH)_2(PPh_3)_2](ClO_4)\cdot 2CHCl_3$	105	2.363(1) 2.377(1)	2.301(1) 2.315(1)	101.3(0)–121.5(0)
$[Cu(py2tH)(PPh_3)_2Cl]$	106	2.374(2)	2.301(2) 2.286(2)	99.6(1)–122.4(1)
$[Cu(py2tH)(PPh_3)_2Br]$	107	2.302(4)	2.263(4) 2.267(4)	102.8(1)–125.0(2)
$[Cu(pymtH)(PPh_3)_2Br]$	108	2.345(3)	2.304(3) 2.267(3)	106.5(1)–112.9(1)
$[Cu(meimtH)(PPh_3)_2Br]$	109	2.375(1)	2.268(1) 2.281(1)	98.3(0)–130.9(0)
$[Cu(PPh_3)_2(bzimtH_2)Cl]\ CH_3COCH_3$	103	2.377(1)	2.278(1) 2.295(1)	103.0(0)–121.7(0)
$[Cu(PPh_3)_2(nbzimtH_2)Cl]$	103	2.381(2)	2.265(2) 2.282(2)	100.9(1)–124.8(1)

The mononuclear complexes all adopt severely distorted tetrahedral geometry. Angles at the metal range from 98.3(0) to 130.9(0)°; the largest angle in a given structure generally involves the sterically hindered phosphines. Copper(I)–sulphur(thione) distances (2.302(4)–2.382(1) Å) in any given structure are slightly longer than the corresponding copper(I)–phosphine distances (Cu–P = 2.263(4)–2.315(1) Å). Angles (Cu–S–C) at the thione-S atom are in the range 105.0 to 113.0°; the carbon-sulphur(thione) distances for the py2tH complexes (1.695(8) Å) are generally similar to the corresponding distance in the parent ligand (mean 1.702(11) Å) [100].

The presence of bulky phosphine groups maximises and distorts the coordination at the metal; the number of thione ligands are limited to one or two in a given complex.

4.4 Dinuclear structures

There are a number of structural forms possible for dinuclear copper(I) complexes based on trigonal or tetrahedral geometry. The established structures are illustrated in **XXXIa–h** and selected dimensions are summarised in Table 3.

The $[Cu_2(meimtH)_3]^{2+}$ ion **XXXIa** is formed from two distorted trigonal CuS_3 units by sharing a thione-S atom. The ion is "folded", with a dihedral angle of 107°,

TABLE 3

Dinuclear structures: selected distances (Å) and angles (°)

Complex	Ref.	Structural type (XXXI)	Cu–S	$Cu–S_{br}–Cu$	Angles at the metal	Cu–Cu
$[Cu_2(meimtH)_5](SO_4)\cdot 3H_2O$	89	**a**	2.151(5)– 2.272(4)	94.8(2)	115.0(2)– 125.6(2)	3.308(4)
$[Cu_2(imdtH_2)_4Cl_2]$	99	**b**	2.196(3)– 2.631(3)	137.3(3)	107.2(3)– 132.5(4)[a] 103.2(2)– 117.4(2)[b]	4.506(5)
$[Cu_2(meimtH)_6](BF_4)_2$	88	**c**	2.310(1)– 2.459(1)	77.2(1)	102.8(1)– 117.2(1)	3.007(1)
$[Cu_2(py2tH)_6]Cl_2$	111	**c**	2.284(2)– 2.498(3)	74.3(1)	99.7(1)– 118.7(1)	2.907(2)
$[Cu_2(py2tH)_6]Cl_2$	112	**c**	2.298(3)– 2.538(4)	74.6(1)	100.1(1)– 118.5(1)	2.950(2)
$[Cu_2(py2tH)_6]Br_2$	112	**c**	2.274(3)– 2.534(3)	73.8(1)	100.3(1)– 118.1(1)	2.907(2)
$[Cu_2(imdtH_2)_6](ClO_4)_2$	113	**c**	2.284(1)– 2.490(1)	67.2(1)	95.9(1)– 120.5(1)	2.683(1)
$[Cu_2(meimtH)_4Cl_2]$	83	**d**	2.271(1)– 2.572(1)	73.2(1)	105.5(1)– 105.4(1)	2.914(1)
$[Cu_2(py2tH)_4I_2]$	114	**d**	2.268(2)– 2.457(1)	79.4(1)	96.1(1)– 121.8(1)	3.139(2)

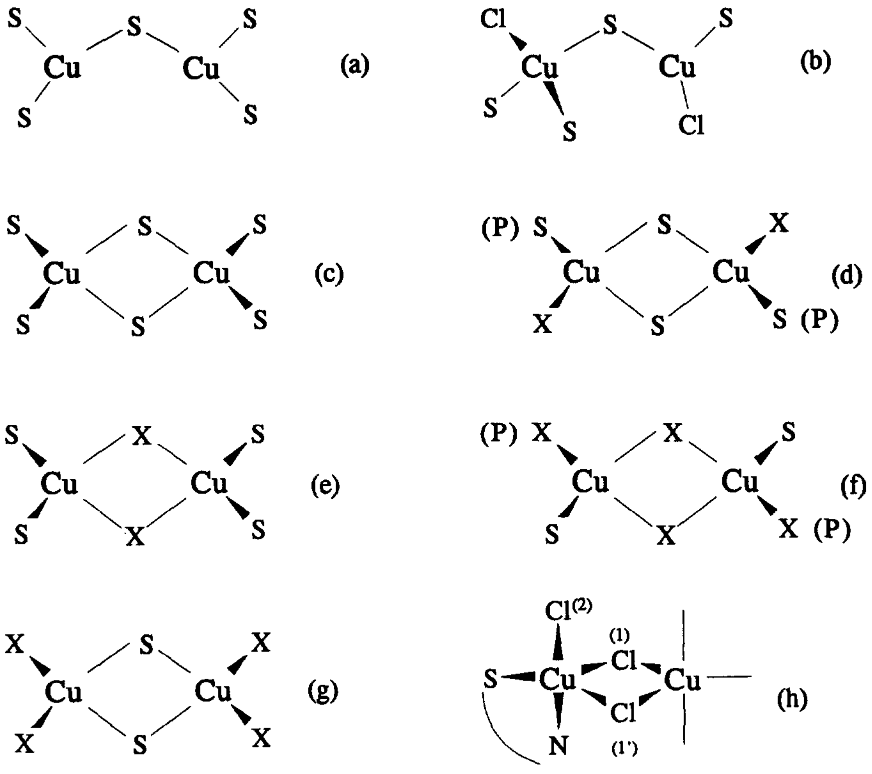
[$Cu_2(meimtH)_4(SCN)_2$]	84	**d**	2.290(1)– 2.457(1)	72.6(1)	95.9(1)– 121.8(1)	2.861(1)
[$Cu_2(py2tH)_2(PPh_3)_2Br_2$]	107	**d**	2.383(1) 2.392(2)	91.5(1)	88.5(1)– 121.3(1)	3.420(3)
[$Cu_2(pymtH)_2(tptp)_2Cl_2$]	115	**d**	2.356(1) 2.470(1)	86.7(0)	93.2(0)– 119.5(0)	3.420(3)
[$Cu_2(tzdtH_2)_2(tptp)_2Cl_2$]	116	**d**	2.386(1) 2.470(1)	87.5(0)	92.5(0)– 119.7(0)	3.359(1)
[$Cu_2(merhod)_4Cl_2$]	118	**e**	2.273(1)– 2.279(2)	[d]	110.1(1)– 126.6(1)	2.906(1)
[$Cu_2(py2tH)_2(tptp)_2I_2$][c]	117	**f**	2.241(1)	[d]	95.9(0)– 120.3(0)	3.119(1)
[$Cu_2(pu6tH)_2Cl_4$]	119	**f**	2.221(1)	[d]	90.17(1)– 126.91(2)	3.501(1)
[$Cu_2(pu6tH)_2Cl_4$]·$2H_2O$	122b	**g**	2.252(2)– 2.733(2)	87.2(1)	92.8(1)– 129.6(1)	3.456(1)
[$Cu_2(mepu6tH)_2Cl_4$]	124	**h**	2.424(1) Cu–N = 1.992(4)	[d]	86.4(1)– 171.9(1)	

[a] Trigonal coordination.

[b] Tetrahedral coordination.

[c] tptp = tris *p*-tolyl phosphine.

[d] Halogen bridged dimer.



XXXI

consequently the bridging atom and the copper(I) atoms are displaced from the Cu_2S_3 coordination sphere. The copper(I)–sulphur(thione) bridging and terminal distances are similar and typical of trigonal geometry (Table 3). The bridging angle and metal separation distances are probably due to ligand geometry rather than metal–metal bonding [89].

In $[Cu_2(imdtH_2)_4Cl_2]$ (**XXXIb**), distorted tetrahedral CuS_3Cl, and trigonal CuS_2Cl, units, share a common thione-S atom. The resultant copper–sulphur(thione) bridging is asymmetrical (2.204(3) and 2.631(3) Å) with no apparent steric reason for the large bridging angle or dissimilar bridging distances; the metal–metal separation distance excludes the possibility of metal–metal bonding (Table 3) [99].

A pair of tetrahedrally coordinated copper(I) atoms may generate structures **XXXIc–g** by the sharing of a common edge. In **XXXIc, d** and **g**, the shared atoms are thione-S with the coordination at the metal either CuS_4, CuS_3X, CuS_2X_2 or CuS_2PCl. In **XXXIe** and **f** the shared atoms are halide and the metal is either $-S_2X_2$, $-SX_3$ or $-SPX_2$ coordinated. The dimensions of the asymmetric Cu_2S_2 cores are discussed later (see Sect. 4.6). The geometry at the metal is invariably distorted in these structures (Table 3). Terminal copper–sulphur(thione) distances (2.268(2)–2.352(1) Å) are invariably shorter than the bridging distances (see Table 5)

Angles (Cu–S–C) at the thione-S atom invariably range from about 100.0(1) to 115.0(1)° and the ligand carbon–sulphur(thione) distances (1.680(3)–1.740(3) Å) are usually slightly longer than those in the parent ligand [83,84,88].

The homoleptic structures (**XXXIc**) are all centrosymmetric with strictly planar, asymmetric Cu_2S_2 cores in which the copper(I) atoms have distorted tetrahedral geometry and S_4 coordination [88,111–113].

In principle, the **XXXId** structures are capable of cis and trans isomerism. In practice, each adopts the trans form because of an inversion centre at the mid-point of the structure. They all have central, asymmetric, Cu_2S_2 cores, (see Sect. 4.6), and distorted geometry at the metal with either S_4, S_3X or S_2PX donor sets; the halo complexes are invariably stabilised by NH···X hydrogen bond formation. In $[Cu_2(meimtH)_4(SCN)_2]$, the metal has an S_4 donor set because of the S-donating thiocyanate, meimtH, is both bridging and terminal with the thiocyanate relegated to a terminal role; terminal thione–S and S–thiocyanate distances are 2.290(1) and 2.332(1) Å, respectively [84].

In the phosphine complexes, the metal has the most irregular geometry of the series which results from the bulky ligands and S_2PX ($X=Cl$ or Br) coordination [107,115,116]. The terminal copper(I)–phosphine distances are closely grouped (2.222(1)–2.229(1) Å), and are invariably shorter than terminal copper(I)–sulphur(thione) distances. In addition, the bridging angles and metal separation distances are also the largest in the series.

$[Cu_2(merhod)_4Cl_2]$ (**XXXIe**) [118] occupies a crystallographic two-fold axis. The central Cu_2Cl_2 core is planar and rhomboid (Cu–Cl = 2.369(1), 2.445(1) Å) and the terminal copper(I)–sulphur(thione) distances are virtually identical (Table 3). $[Cu_2(py2tH)_2(tptp)_2I_2]$ (**XXXIf**) is centrosymmetric with an almost regular Cu_2I_2 central core (Cu–I = 2.690(1), 2.695(1) Å; Cu–I–Cu = 70.8(0)°), together with pairs of trans-terminal phosphine (Cu–P = 2.241(1) Å) and py2tH ligands [117].

Purine-6-thione (**XXIXk**), or 6-mercapto purine as it is generally known, is a synthetic thio-analogue of the natural purine hypoxanthine and is an established clinical agent for the treatment of human leukemias [120]. The formation of a stable copper–pu6tH complex has also been proposed to account for the anti-inflammatory properties of the ligand [121]. The combination of bioactivity and coordination potential has stimulated substantial interest in pu6tH complexes, many of which have been reported [119]. $[Cu_2(pu6tH^+)_2Cl_4]$ [119] and $[Cu_2(pu6tH^+)_2Cl_4]\cdot 2H_2O$ [122], are prepared from the parent ligand and copper(II) dichloride dihydrate in 20% hydrochloric acid. The resultant complexes involve copper(I) and protonated $pu6tH^+$ ligands. Anhydrous $[Cu_2(pu6tH^+)_2Cl_4]$ is a centrosymmetric chlorobridged dimer (**XXXIf**) with a pair of trans-terminal thione S-donating $pu6tH^+$, (Cu–S = 2.221(1) Å), trans-terminal chlorine (Cu–Cl = 2.251(1) Å) and a relatively regular, central Cu_2Cl_2 core (Cu–Cl = 2.465(1), 2.493(1) Å, Cu–Cl–Cu′ = 89.83(2)°). The hydrated complex **XXXIg** is a centrosymmetric thione S-bridged dimer, originally prepared and reported by Caira and Nassimbeni as a non-centrosymmetric (P1) structure [122(a)] and subsequently re-examined and refined in the corresponding centrosymmetric space group ($P\bar{1}$, bar-one) [122(b)]. The data in Table 3 are those of Pope et al. [122(b)]; Hodgson and co-workers [123] report bridging copper–sulphur(thione) distances of 2.253 and 2.734 Å.

A reaction involving 6-thio-9-methyl purine (**XXIXki**) and copper(II) chloride dihydrate in concentrated hydrochloric acid produced $[Cu(II)_2(mepu6tH)_2Cl_4]$ [124]. The complex involves copper(II) and neutral ligands. There is a distinct possibility that the strongly acidic media inhibits the copper(II)–thione redox reaction in this instance. The metal adopts square-based pyramidal (4+1) coordination with the ligand coordinating through the thione-S and imidazole-N(7) atoms as a five-membered chelate **XXXIh**. The thione-S, N(7), Cl(1) and Cl(2) atoms are all coplanar with the copper(II) displaced, out-of-plane, towards the fifth, apical, Cl(1′), ligand. The Cu–Cl(1) bond (2.301(1) Å), which is trans to the thione-S, is significantly longer than Cu–Cl(2) (2.244(1) Å), which is trans to the N(7) atom. The weak, apical Cu–Cl(1′) interaction may explain the elongation in the bridging equatorial bond.

4.5 Tetranuclear and polynuclear structures

The range of polynuclear and polymeric copper complexes of heterocyclic thiones is relatively limited in comparison with thiourea complexes [125]. No trinuclear structure has been reported, but the presence of Cu_3S_3 rings in the thioacetamide complex $[\{Cu(tac)Cl\}_3]$ [57] suggests that a thione analogue is possible.

There are three reported tetranuclear complexes based on a planar-rhomboid, rather than a tetrahedral Cu_4 aggregate; the latter, however, is adopted by both mono- [126] and dithiolates [127], as well as by $[\{Cu(meimt)\}_4]$ [151]. The tetranuclear heterocyclic thione complexes are listed in Table 4, together with selected dimensions; their structures are also illustrated in **XXXII**.

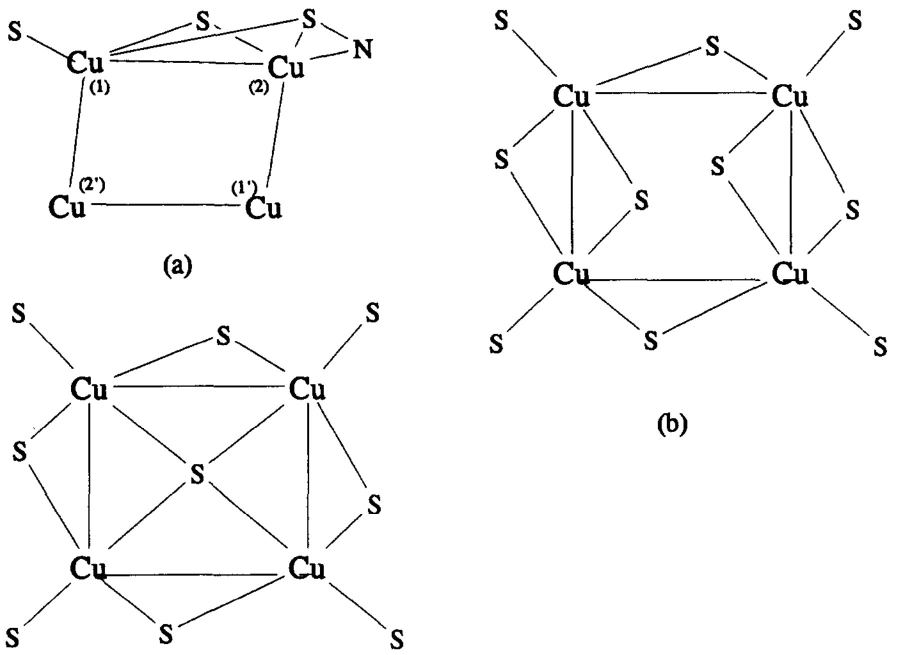
There is no established preparative route to tetranuclear heterocyclic-thione complexes. Red $[Cu_4(mepymtH)_6](BF_4)_4$ [128] and green $[Cu_4(bzimtH_2)_{10}](ClO_4)_4 \cdot 14H_2O$ [130] were prepared by slow addition of the ligand to the metal salt in aqueous mixtures of acetone and ethanol, respectively. In contrast, $[Cu_4(imdtH_2)_9](NO_3)_4 \cdot 6H_2O$ [129] was prepared in distilled water and is colourless. Stoichiometric ratios, (metal : ligand) were in the region of 1 : 3 in all cases. The Cu_4 aggregate is strictly planar in each complex. Although edge dimensions (Cu···Cu) are variable (Table 4), with the largest divergence in the $bzimtH_2$ complex, they are not indicative of metal–metal bonding. Each aggregate accommodates different numbers of ligands. This is caused by variations in both metal geometry and in the combinations of terminal and bridging ligands. Angles at the metal indicate that the geometry is distorted in each instance (Table 4).

A planar Cu_4 core with trigonal metal geometry, four terminal-S and four μ_2-S bridging ligands generates a $[Cu_4(LH)_8]$ core. The $[Cu_4(mepymtH)_6]^{4+}$ ion, however, contains two terminal-S, two μ_2-S bridging and two μ_3-S,N bridging ligands

TABLE 4

Tetranuclear heterocyclic thione complexes: selected distances (Å) and angles (°)

Complex	Ref.	Cu_4 edge dimensions	Cu–S terminal	Cu–S bridging	Angles at the metal
$[Cu_4(mepymtH)_6](BF_4)_4$	128	2.713(1)	2.241(1)	2.264(1)–	103.6(1)–
		2.824(1)		2.356(1)	127.8(1)
				(Cu–N = 2.035(3))	
$[Cu_4(imdtH_2)_9](NO_3)_4 \cdot 6H_2O$	129	2.849(1)	2.243(2)	2.290(2)–	105.1(6)–
		3.362(1)	2.258(2)	2.515(2)	130.2(6)
$[Cu_4(bzimtH_2)_{10}](ClO_4)_4 \cdot 14H_2O$	130	2.681(2)	2.262(2)	2.356(2)–	88.0(1)
		4.216(3)	2.269(3)	2.499(2)	125.3(1)



(a)

(b)

(c)

XXXII

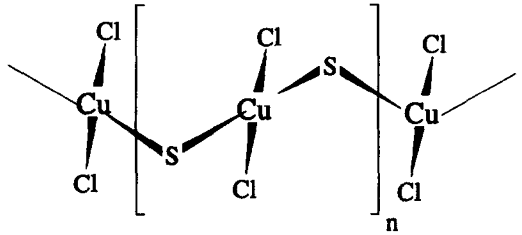
(simplified in **XXXIIa**). The terminal copper(I)–sulphur(thione) distance is normal for trigonal geometry and the μ_2–S and μ_3–S,N bridging is asymmetric (Table 4).

A planar Cu_4 core with tetrahedral metal geometry, eight terminal-S and four μ_2-S bridging ligands generates a $[Cu_4(LH)_{12}]$ core. This system is modified in the case of the $[Cu_4(bzimtH_2)_{10}]^{4+}$ ion by increasing the bridging and decreasing the terminal ligands so that the ion contains four terminal-S and six μ_2-S bridging ligands (**XXXIIb**) [130]. Pairs of bridging ligands are grouped along the short edges (2.681(2) Å), and a single bridging ligand occupies each of the long edges (4.216(3) Å) of the Cu_4 aggregate. All the μ_2-S bridging is asymmetric; that along the short edges generates planar, asymmetric, Cu_2S_2 cores (see Sect. 4.6), and that along the long edges involves a large bridging angle (124.9(1)°). The terminal, copper(I)–sulphur(thione) distances are at the lower limit for tetrahedral geometry (Table 4).

In the $[Cu_4(imdtH_2)_9]^{4+}$ ion, tetrahedral geometry is achieved by a combination of four terminal-S, four μ_2-S bridging and one central μ_4-S bridging ligands (**XXXIIc**) [129]. The terminal copper(I)–sulphur(thione) distances are normal for tetrahedral geometry; the μ_2-S bridging is asymmetric and produces a sequence of long and short copper–sulphur bonds around the periphery of the Cu_4 aggregate, which may be electronic, rather than steric, in character. The central μ_4-S bridging ligand is unusual with relatively long copper(I)–sulphur(thione) distances (2.515(2), 2.480(2) Å); three-centre, two-electron molecular orbitals have been used to rationalise this electron-deficient system.

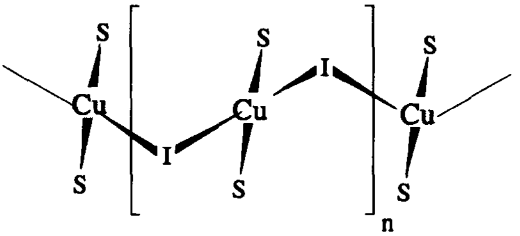
The adoption of a rhomboid, rather than a tetrahedral Cu_4 aggregate, by these thione-S coordinated species is novel. Although the Cu_4 rhomboid aggregate does resemble the basic Cu_2X_2 "step" in the tetranuclear $[\{CuClPPh_3\}_4]$ complexes [131], it clearly represents an alternative distribution for tetranuclear copper(I) atoms which, so far, appears to be limited to neutral heterocyclic thione ligands.

The structures of two bridged, helical, copper(I)–thione–halide polymers have been reported. $[\{Cu(pu8tH^+)Cl_2\}_n]$, prepared from molar hydrochloric acid solutions of purine-8-thione and copper(II) chloride dihydrate, contains the protonated ligand and copper(I). Metal geometry is distorted tetrahedral and consists of terminal chlorine (2.271(2), 2.423(2) Å), and asymmetrically bridging thionium sulphur, (2.289(2), 2.375(2)) (**XXXIIIa**) [132]. In $[\{Cu(rhod)_2I\}_n]$, the metal has terminal thione-S (Cu–S = 2.278(1), 2.299(1) Å), and asymmetrically bridging iodine (Cu–I = 2.657(1), 2.814(1) Å) (**XXXIIIb**). Angles at the metal (100.1(1)–120.0(1)°), are consistent with trigonal pyramidal geometry [133]. Polymeric I–Cu–I chains linked through additional copper(I)–iodine contacts generate a two-dimensional polymeric network with three-coordinate iodine and four-coordinate copper(I) in $[\{Cu(merhod)I\}_n]$ (**XXXIV**) (Cu–I = 2.683(2), 2.627(2) 2.665(2) Å; Cu–S = 2.301(3) Å) [134].



(adapted from [132])

(a)

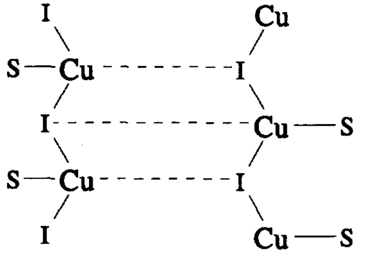


(adapted from [133])

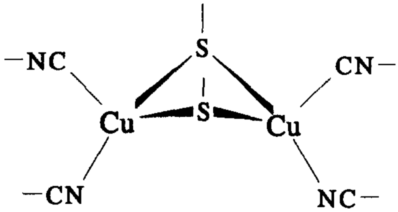
(b)

XXXIII

The asymmetric unit in the two-dimensional polymer $[\{Cu(mimtH)CN\}_n]$ (**XXXV**) [85] consists of pairs of, respectively, copper(I), meimtH and cyanide. Each copper(I) atom has distorted tetrahedral geometry, (98.4(1)–120.2(1)°), and a S_2CN donor set involving four independent ligands. The thione ligands bridge pairs of copper(I) and generate a non-planar Cu_2S_2 core, (see Sect. 4.6). The bridging cyanide ligands are virtually linear (Cu–C = 1.907(4), Cu–N = 1.993(4) Å; Cu–C–N = 175.2(4)°, mean dimensions) and generate relatively long copper(I)–copper(I) contacts (5.027 Å). The asymmetric unit is linked by cyano bridges to symmetry-related units so that the effective structural unit involves six copper(I) atoms, four bridging cyano and four bridging meimtH groups extended into a two-dimensional polymeric array by sharing their copper(I) atoms.



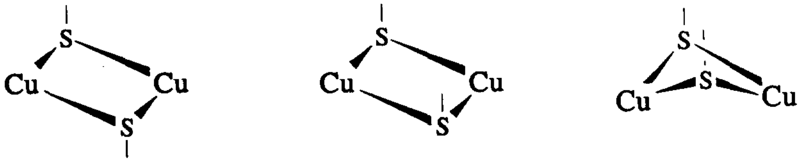
XXXIV



XXXV

4.6 Cu_2S_2 cores

Copper(I) readily forms rhomboid, Cu_2X_2, cores with halide, (see Sect. 4.5) [117–119] and also with the nitrogen atom of a bridging isocyanate ion in $[\{Cu(NCO)(py)_2\}_2]$ [135]. Of primary interest here are the Cu_2S_2 rhomboid cores formed with bridging thione-S atoms.



(a) (b) (c)

XXXVI

Two structural forms are possible (**XXXVIa,b**). In the most commonly observed structure, **XXXVIa**, the core has an inversion centre at its mid-point with the ligands adopting a trans, or 2-anti, disposition. In principle, the cis, or 2-syn form, **XXXVIb**, may also be planar but the two reported examples (Table 5) contain non-planar, folded, cores (**XXXVIc**) with dihedral angles about the bridging sulphur atoms in

TABLE 5

Cu_2S_2 core dimensions (Å and degree)

Complex	Ref.	Cu–S bridging	$Cu–S_{br}–Cu$	$S_{br}–Cu–S_{br}$	Cu···Cu
$[Cu_2(meimtH)_6](BF_4)_2$	88	2.358(1) 2.459(1)	77.2(1)	110.1(1)	3.007(1)
$[Cu_2(py2tH)_6]Cl_2$	111	2.308(1) 2.498(1)	74.3(1)	105.7(1)	2.907(2)
$[Cu_2(py2tH)_6]Cl_2$	112	2.320(3) 2.538(4)	74.6(1)	105.4(1)	2.950(2)
$[Cu_2(py2tH)_6]Br_2$	112	2.297(3) 2.534(3)	73.8(1)	106.2(1)	2.907(2)
$[Cu_2(imdtH_2)_6](ClO_4)_2$	113	2.362(1) 2.490(1)	67.2(1)	112.8(1)	2.686(1)
$[Cu_2(meimtH)_4Cl_2]_2$	83	2.301(1) 2.572(1)	73.2(1)	106.8(1)	2.914(1)
$[Cu_2(py2tH)_4I_2]^a$	114	2.328(1) 2.577(1)	79.4(1)	96.1(1)	3.139(1)
$[Cu_2(meimtH)_4(SCN)_2]$	84	2.377(1) 2.457(1)	72.6(1)	107.4(1)	2.861(1)
$[\{Cu(meimtH)CN\}_n]^a$	85	2.344(1); 2.565(1) 2.366(1); 2.556(1)	79.1(1) 79.7(1)	98.4(1) 98.7(1)	3.145(1)
$[Cu_4(bzimtH_2)_{10}](ClO_4)_4 \cdot 14H_2O$	130	2.356(2); 2.373(2) 2.369(2); 2.499(3)	69.1(1) 66.8(1)	109.3(1) 113.3(1)	2.681(2)
$[Cu_2(py2tH)_2(PPh_3)_2Br_2]$	107	2.383(1) 2.392(2)	91.5(1)	88.5(1)	3.420(3)
$[Cu_2(pymtH)_2(tptp)_2Cl_2]$	115	2.356(1) 2.470(1)	86.7(0)	93.2(0)	3.316(1)
$[Cu_2(tzdtH)_2(tptp)_2Cl_2]$	116	2.386(1) 2.470(1)	87.5(0)	92.5(0)	3.508(1)

[a] Non-planar cores.

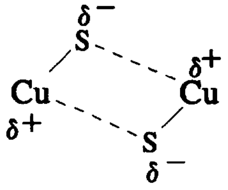
the region of 30°. In $[Cu_2(py2tH)_4I_2]$, a two-fold rotation axis bisects the centre of the core while $[\{Cu(mimtH)CN\}_n]$ is non-centrosymetric.

All of the cores contain an alternating sequence of long (2.369(2)–2.577(1) Å) and short (2.297(3)–2.386(1) Å) bridging copper(I)–sulphur(thione) distances. Angles at the metal range from 88.5(1) to 121.8(2)° and show significant distortion from regular tetrahedral geometry. The bridging angles at the thione-S atoms are narrow and in the range 66.8(1)–91.5(1)°; the ideal bridging angle for two tetrahedra sharing a common edge is 70.5° [136]. Metal–metal separation distances are in the range 2.681(1)–3.508(1) Å with the smallest values close to the separation distance in the parent metal (2.550 Å) [137(a)]. Distances between the bridging thione-S atoms (3.729(1)–3.916(2) Å) are greater than the corresponding van der Waals' distance for the atoms (3.550 Å) [137(b)], at least in the case of the meimtH complexes [84].

Distances between the metal atoms and the bridging thione-S atoms are clearly related to the bridging angle, $Cu–S_{br}–Cu$ (Table 5) [136]. In the relatively compact $[Cu_2(imdtH_2)_6]^{2+}$ ion, the bridging angle (67.2(1)°) generates a metal–metal distance of 2.686(1) Å and a distance between the bridging thione-S atoms of 4.403(3) Å. The largest bridging angle (91.5(1)°) generates separation distances of 3.420(3) and 3.332(3) Å between the copper(I) and bridging thione-S atoms of the relatively bulky $[Cu_2(py2tH)_2(PPh_3)_2Br_2]^{2+}$ ion.

Much has been made of the possibility of metal–metal bonding among copper(I) aggregates with a variety of ligands, [126,136,138,139]. It is probable that the steric requirements of the bridging ligands, rather than metal–metal bonding, are primarily responsible for the rather large variation (ca. 24°) in bridging angle in these Cu_2S_2 cores. Similarly, although the need to accommodate electron-rich bridging thione-S atoms determines asymmetric copper(I)–sulphur bridging in Cu_2S_2 cores, the significant variation among bridging distances (Table 5) is also most likely due to a combination of the steric requirements of the bridging ligands, H-bonding and crystal packing requirements.

Since the ligands are invariably normal to the plane of the Cu_2S_2 cores, they are unable to use two electron pairs and sp^2 hybrid orbitals in the formation of copper(I)–sulphur–copper(I) bridges. The bonding model generally used to rationalise sulphur bridging was originally proposed by Amma and co-workers for the centrosymmetric Cu_2S_2 core in $[Cu_2(tu)_6]\,(BF_4)_2$ [140]. This scheme involves "tetrahedral" metal orbitals with a normally non-bonding sulphur(tu) sp^2 hybrid orbital and electron pair, for the "short" copper(I)–sulphur distances, and a thioketonic (C=S) pπ-MO, for the "long" bridging distances. Conventional electron pair donation is acceptable for the "short" bridging distances, which are within the range expected for copper(I)–sulphur(thione) distances and pseudo-tetrahedral geometry. Molecular-orbital involvement appears to be less realistic for the "long" distances. Alternatively, the "long" distances may be considered primarily in terms of ion-dipole interactions (**XXXVII**). Such a scheme is inherently more flexible than that which involves the geometrically restricting thioketonic pπ-MO and is more capable of accommodating the reported variations in bridging angle and distance.

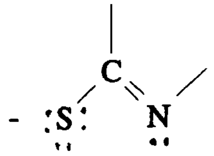


XXXVII

5. COMPLEXES OF HETEROCYCLIC THIONATES

5.1 Introduction

Deprotonation of heterocyclic-thiones (**XXXb**) produces the corresponding "thionate" anion (**XXXd**) in which an electron pair on the heterocyclic trigonal nitrogen and three electron pairs on the thionate sulphur generate considerable coordination potential (**XXXVIII**).

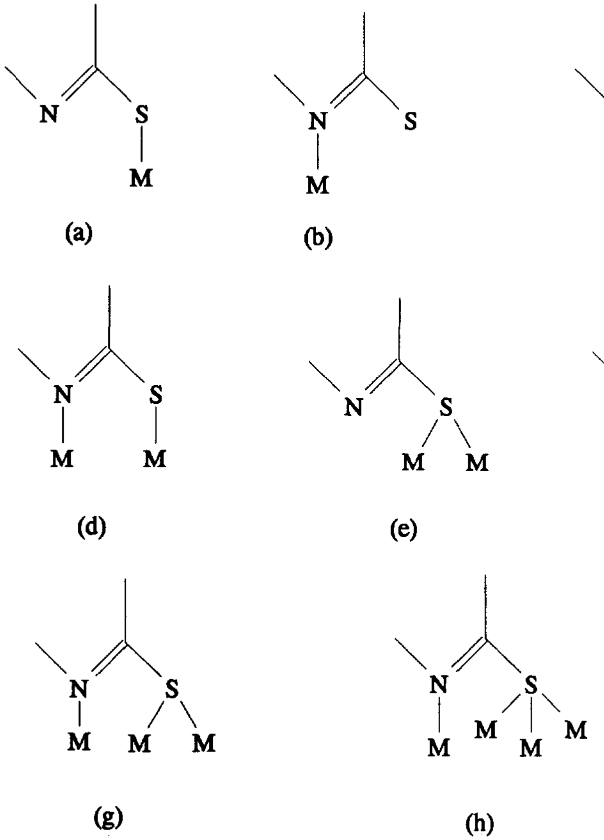


XXXVIII

With pK_a values ranging from about 5 to 11, deprotonation is possible over a wide pH range [3]. BztztH may be deprotonated in aqueous ethanol [141], while the imidazole-thiones may require aqueous alkali [142]. More elegant deprotonation methods are now being used. These are based on non-aqueous solvents with metallic sodium, lithium alkyls and organic bases [143–150] as well as electrochemical routes [151].

Copper(I) complexes of empirical composition CuL (L = pyrdt, imt, meimt, bzimt, ttzt, py2t, me2pymt, bztzt, tzdt, tdzt, rdt, bzoxt) have been reported [3]. In the absence of definitive structural data most are presumed to be polymeric with S,N-bridging ligands. Copper(II) complexes, CuL_2, with square-planar geometry deduced from electronic spectra have been reported for a number of heterocyclic-thionato derivatives including those of 1,2,4-triazoline-5-thionate [152] and 1,3,4-thiadiazole-2,5-dithionate [153]. With preparations frequently involving copper(II) salts and given the complicating nature of the thione-copper(II) redox reaction, it is perhaps not surprising that complexes have been reported with suspect formulae and anomalous magnetic behaviour [3]. Because of these problems, some of the earlier studies are now being carefully repeated [90].

In contrast to the extensive structural chemistry of organo-thiolates [154,155], that of heterocyclic thionates is still relatively underdeveloped, especially with respect to complexes of high nuclearity. However, most of the coordination modes shown in **XXXIX** have been structurally established, at least for bztzt and py2t, with elements other than copper.



XXXIX

[n-Bu$_4$] [Zn(bztzt)$_3$(H$_2$O)] contains both monodentate-S and monodentate-N (**XXXIXa, b**) [156] and the four-membered chelate (**XXXIXc**) occurs in the [Ni(bztzt)$_3$]$^-$ anion [143]. A range of bridging modes (**XXXIX d–h**) has been established among organometallic complexes. Monodentate μ_1-S,N bridging (**XXXIXd**) occurs in the dinuclear species, [{M(bztzt)$_2$}$_2$] for platinum(II) [144] and palladium(II) [145]. The bidentate species μ_2-S (**XXXIXe**) and μ_2-S,N, (**XXXIXf**) bridge pairs of atoms in [Os$_3$H(CO)$_{10}$(tzdt)] [146], and [Re$_2$(6-mepy2t)$_2$(CO)$_6$] [147], respectively. Terdentate μ_3-S,N (**XXXIXg**) bridges homo- and hetero-trinuclear aggregates in [Rh$_3$(py2t)$_2$(CO)$_6$](ClO$_4$) [148] and [(cod)$_2$Rh$_2$(bztzt)$_2$Ag(ClO4)] [149], respectively (cod = cyclo-1,5-octadiene). Quadridentate, μ_4-S,N bridging (**XXXIXh**) has been reported in the octanuclear aggregate, [Ag$_5$(Rpy2t)$_6$](Ag(NO$_3$))$_2$·2CH$_3$OH, (Rpy2t = 3-(Dimethyl-phenyl)silyl-2-pyridinethionate) [150]. Some of the above coordination modes have also been established for copper with a limited range of thionate ligands.

5.2 Imidazole-thionato complexes

Relatively large stability constants have been reported for imidazoline-2-thionato derivatives with copper as part of a programme which correlated metal-binding ability with antibacterial activity [157]. Attempts to mimic the binding sites in "blue" copper proteins have resulted in highly coloured copper complexes involving the meimt anion [158,159]. A reaction, involving tetrakis-acetonitrile copper(I) perchlorate, hydrated copper(II) acetate and meimtH in (1 : 1 v : v) acetonitrile–methanol followed by the addition of sodium tetraphenylborate and recrystallisation from acetonitrile produced a dark blue crystalline solid [Cu(II)$_2$Cu(I)$_{10}$(meimt)$_{10}$(MeCN)$_4$](BPh$_4$)$_2$·4MeCN, [160]. This centrosymmetric mixed-valent copper aggregate contains a ring of eight four-coordinate copper(I) atoms with either S$_4$ or S$_3$N donor sets, (Cu–S$_{br}$ = 2.280(2)–2.645(2) Å; Cu–N = 1.977(4), 1.984(4) Å); which also generate four Cu$_2$S$_2$ rings, (Cu···Cu = 2.547(1)–2.724(1) Å). Two further copper(I) sites are three coordinate and the two copper(II) sites are five-coordinate by a trans N$_2$S$_2$ donor set and an acetonitrile molecule. The meimt anion generates μ_2-S, μ_3-S,N and μ_4-S,N bridges (**XXXIXe,g,h**) between the copper(I) atoms. The copper(II) atoms are magnetically free from other interactions and the complex has electronic, (λ_{max} = 635 nm) and ESR spectra similar to those of copper "blue" proteins.

A detailed study of the reactions of hydrated copper acetate and meimtH in various solvents has shown that the [Cu(II)$_2$Cu(I)$_{10}$(solvent)$_4$]$^{2+}$ species is remarkably stable in solution and does not require monovalent copper for its formation [90]. The mixed-valent aggregate is also an intermediate product in the formation of tetranuclear [{Cu(meimt)}$_4$] by electrochemical oxidation of copper in the presence of meimtH in acetonitrile [151]

$$Cu(s) \rightarrow Cu^+ + e \text{ (anode)}$$

$$meimtH + e \rightarrow meimt^- + \tfrac{1}{2} H_2 \text{ (cathode)}$$

followed by

$4Cu^{+} + 4meimt^{-} \rightarrow [\{Cu(meimt)\}_4]$

The tetranuclear complex contains a four-fold inversion axis and a slightly flattened Cu_4 tetrahedron. Metal separation distances are 2.671(2) Å, along four of the edges and 3.132(2) Å along the remaining two opposing edges of the tetrahedron; internal angles, between the shorter copper distances, are 71.8(1)°. The deprotonated ligands form μ_3-S,N bridges with Cu_3 aggregates on each of the isosceles triangular faces of the tetrahedron **XXXIXg**. The thionato-S atom asymmetrically bridges two copper(I) atoms ($Cu–S_{br} = 2.307(2)$, 2.233(2) Å) with the heterocyclic nitrogen atom bonded to a third copper(I) (Cu–N = 1.995(6) Å). Each copper(I) atom has a S_2N donor set formed from three different ligands, and irregular trigonal-planar coordination with angles at the metal in the range 109.3(2)–129.9(1)°. The exocyclic thioketonic distance 1.751(7) Å shows significant lengthening relative to the free ligand value (mean C–S = 1.685(2) Å) [98], which suggests that the negative charge on the meimt anion is predominantly centred on the thionate-S atom (**XXXVIII**). This may also account for the fact that the bonds to copper(I) (mean 2.270(2) Å), are shorter than those formed by the neutral bridging ligand, (mean 2.436(1) Å, Table 5). The complex also exhibits ligand-centred irreversible redox behaviour in acetonitrile.

5.3. *Thiazole-thionato complexes*

Thiazolidine-2-thionate, $tzdt^{-}$, forms both [Cu(tzdt)] [161] and $[Cu(tzdt)_2]$ [162]. The latter is reported to have a reduced room-temperature magnetic moment ($\mu_B = 0.79$). A variety of ill-defined amorphous complexes have also been reported for the bztzt anion. These include the copper(I) complexes: [Cu(bztzt)] and [Cu(bztzt)-(bztzH)] [163] as well as $[Cu(bztzt)(bztzt\text{-}bztzt)_{\frac{1}{2}}]$ [164], and $[Cu(bztztH)_2\text{-}(bztzt\text{-}bztzt)_{\frac{1}{2}}Cl]$ [164], (bztzt-bztzt = bis(benzo-1,3-thiazol-2-yl)disulphide) and a copper(II) complex $[Cu(bztzt)_2]$ [165].

A careful study of the reactions of bztzH and related heterocyclic-thiones in aqueous ethanol and absolute ethanol accounts for the above and other anomalous formulations [166]. The parent ligand, bztztH, is unchanged in absolute ethanol but is deprotonated in aqueous ethanol and other mixed solvents. Furthermore, in the presence of copper(II) salts, the ligand is oxidised to the disulphide $(bztzt)_2$

$CuX_2 + 2bztztH = [Cu(bztzt)] + \frac{1}{2}(bztzt)_2 + 2HX$

This reaction accounts for the presence of the insoluble disulphide in the above formulae. The “cupric” complex $[Cu(bztzt)_2]$ has also been shown to contain copper(I) [165]. Addition of bztztH in ethanol to an aqueous solution of copper(II) sulphate pentahydrate produced insoluble [Cu(bztzt)]. The addition of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) in hot acetone to a suspension of [Cu(bztzt)] in the same solvent produced crystalline [Cu_2(bztzt)$_2$(dppe)$_3$]; a similar reaction with dppm (dppm = 1,2-bis(diphenylphosphino)methane) produced [Cu(bztzt)dppm].

Structurally, [Cu_2(bztzt)$_2$(dppe)$_3$] is a centrosymmetric dppe-bridged dimer in which each copper(I) atom has distorted tetrahedral geometry and a P_3S donor set consisting of one phosphorus atom from the bridging dppe, two phosphorus atoms from the chelating dppe with the exocyclic sulphur from the bztzt anion completing the coordination sphere. Angles at the metal range from 89.3(3) to 118.6(4)°, copper(I)–phosphorus distances range from 2.282(7) to 2.344(9) Å with copper(I)–sulphur distances of 2.314(6) and 2.322(7) Å [166].

5.4. *Pyridine-thionato complexes*

A diamagnetic insoluble polymer [{Cu(py2t)}$_n$] [167] and tetranuclear [{Cu(py2t)}$_4$], characterised by mass spectra and obtained by treatment of orange [Cu(py2tH)$_3$Cl] with an aqueous ethanolic solution of sodium acetate [111], have been reported. A heterocubane structure has been proposed for the tetranuclear complex [111].

Hexanuclear [{Cu(py2t)}$_6$] has been prepared from tetrakis-(acetonitrile)copper(I) hexafluorophosphate and py2tH in acetone and an argon atmosphere [168]. The structure contains a distorted octahedron of copper(I) (Cu–Cu = 2.795(1)–3.160(1); mean 2.950(1) Å), the overall pattern of metal–metal distances consists of two large transoid "equilateral" triangular faces and six smaller, essentially isosceles, triangular faces. Each copper(I) atom has distorted trigonal geometry, with angles at the metal ranging from 109.7(2) to 124.8(2)°, and an S_2N-donor set. The ligands are μ_3-S_2N donating to Cu_3 aggregates about each of the six smaller triangular faces of the octahedron **XXXIXg** (Cu–S_{br} = 2.220(2)–2.257(2); mean 2.403 Å; Cu–N = 2.024(6)–2.041(7); mean 2.034 Å). Ligand thioketonic distances, (1.751(7)–1.778(8); mean 1.764 Å) are significantly longer than in the parent ligand, (mean C=S = 1.702(11) Å) [100] and in the trigonal copper(I) complexes of the parent ligand, (Table 1). As was observed for the meimt anion, in [{Cu(meimt)}$_4$] the dimensions of the py2t anion in [{Cu(py2t)}$_6$] are consistent with the electron distribution in **XXXVIII**. A ^{1}H NMR study of the reaction solution revealed the presence of several low-molecular-weight species in the early stages of the reaction. Similarly, the sterically hindered ligands in hexanuclear [{Cu(Rpy2t)}$_6$] (R = SiMe$_3$) are also μ_3-S_2N donating to Cu_3 aggregates **XXXIXg** about the triangular faces of a distorted Cu_6 octahedron (Cu–Cu = 3.139(1); Cu–S = 2.236(2)–2.254(2); Cu–N = 2.019(9) and 2.041(5) Å). Each copper(I) atom has distorted trigonal geometry with angles at the metal in the range 82.6(1)–119.2(2)°, and an S_2N donor set formed from three ligands [219].

5.5 *Quinazoline-2,3-dithionato complexes*

The qnxdt^{2-} anion is readily derived from the corresponding dithione **XXIXm** [169]. The ligand has a $N_2C_2S_2$ core similar to that of dithiomaleonitrile. It has other similarities to dithiolene ligands, such as the ability to form S,S-chelates and to stabilise the less-common oxidation states [170].

The crystal structures, UV-visible spectra and electrochemical properties of $(PPh_4)_2[Cu(II)(qnxdt)_2]$ and $(PPh_4)[Cu(III)(qnxdt)_2]$ have been reported [171]. Both bis-chelated anions contain essentially planar CuS_4 cores with the major structural difference between them limited to the copper–sulphur bond lengths (mean Cu(III)–S = 2.187(1); mean Cu(II)–S = 2.260(1) Å). A similar relationship between copper–sulphur bond distance occurs in the corresponding complexes of dithiooxamide [172] and dithiomaleonitrile [173]. Furthermore, the mean copper–sulphur bond length in the $[Cu(toluene\text{-}3,4\text{-}dithiolate)_2]^-$ anion (2.164(2) Å) [174] provides further confirmation of the expected trend towards shorter copper(III)–sulphur distances. The observed structural differences between the $qnxdt^-$ complexes are in agreement with the molecular orbital schemes which have been proposed for square-planar metal complexes of unsaturated 1,2-dithiolates [171]. Thioketonic ligand dimensions show that the copper(III) complex has significantly shorter carbon–carbon (mean C(1)–C(2) = 1.439(3) Å) and longer thioketonic (mean C–S = 1.748(3) Å) distances than the corresponding copper(II) complex (mean C(1)–C(2) = 1.459(3); mean C–S = 1.739(3) Å).

The electrochemical properties of the $qnxdt^{2-}$ complexes have been studied by cyclic voltammetry in DMF. Two redox processes have been observed at $E_{\frac{1}{2}} = -0.18$ and -1.28 V vs. SCE. The first process corresponds to the $[Cu(qnxdt)_2]^-/[Cu(qnxdt)_2]^{2-}$ couple and is fully reversible. The second couple corresponds to the $[Cu(qnxdt)_2]^{2-}/[Cu(qnxdt)_2]^{3-}$ couple and is quasi-reversible. Differences in electrochemical behaviour have been attributed to the structural relationships between the complexes [171].

6. COPPER(II)-THIONE REDOX SYSTEMS

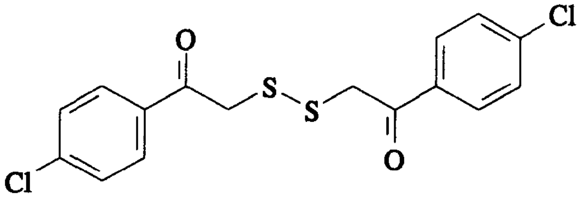
6.1 Introduction

The oxidation of thioamides and organo-thiols (RSH) by metal ions is of both chemical [175] and biochemical interest [176]. Typical examples include the oxidation of thiols to the corresponding disulphides by copper(II) and iron(III) [177].

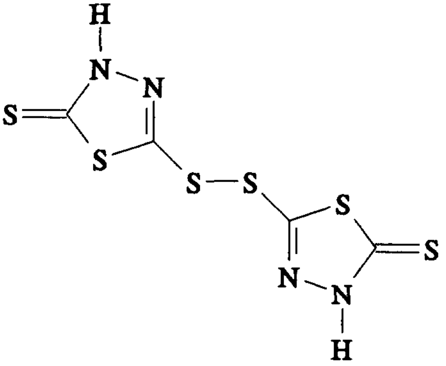
$$2RSH + 2Cu^{2+}(Fe^{3+}) = RSSR + 2Cu^{+}(Fe^{2+}) + 2H^{+}$$

Further oxidative cleavage of disulphides to sulphinates (RSO_2^-), by mercury(I), silver(I) and copper(II) [178], and to sulphonate (RSO_3^-) by gold(III) [179] have also been reported. Among other thioamides, the oxidative desulphurisation of *N*,*N*′-dithiobisamines by copper(II) ions has been reported [180]; the oxidation of mostly non-heterocyclic organo-thiones as well as phosphine-sulphides by metal salts and halogens have also been reviewed [181].

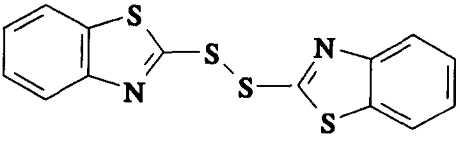
Heterocyclic-thiones undergo reactions similar to those of organo-thiols outlined above. Specific examples involve the oxidation of 4-phenylthiazole-2(3H)-thione to bis-(4-chlorophenacyl)-disulphide (XL) in a moist chlorine atmosphere [182]. Molybdenum pentachloride oxidises 1,3,4-thiadiazole-2,5-dithione to 5,5′-dithioxo-2-2′-di-thiadiazoyl disulphide (XLI) in ethanol [183]. The photochemical oxidation of bztztH has environmental significance in view of its use as a fungicide and pesticide [184]. Ultraviolet radiation of bztztH in dry benzene or toluene in the presence of air produces 2,2′-dibenzothiazolyl disulphide (XLII). In ethanol, methanol or acetonitrile, 2,2′-dibenzothiazolyl-disulphone is obtained as an intermediate with benzothiazole sulphate as the final product. Similar photolytic studies on bzimtH_2 yielded 2,2′-dibenzoimidazolyl-disulphone as intermediate and benzimidazole sulphate as the final product [184].



XL

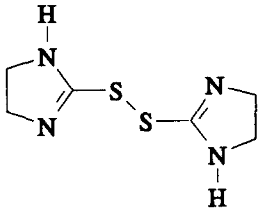


XLI

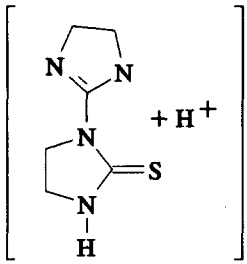


XLII

Structure–activity relationships for a variety of heterocyclic-thione anti-thyroid agents have been equated with their reactions with iodine [185]. For example, the red crystalline powder resulting from the reaction of potassium iodide and iodine with imdtH$_2$ is the hydroiodide-bis(iodine) charge transfer complex of 2,2′-diimidazoyl-disulphide (**XLIII**) [186]. Similar reactions have produced imdtH$_2 \cdot 2(I_2)$ and imdtH$_2 \cdot 3(I_2)$. These charge transfer complexes contain thione···iodine interactions while the salt–molecule complex 1-(1-imidazolin-2-yl)-2-thioxoimidazolidiniumtriiodide-(ethylenethiourea-diiodine), contains the planar, potentially chelating, cation **XLIV** [187].



XLIII



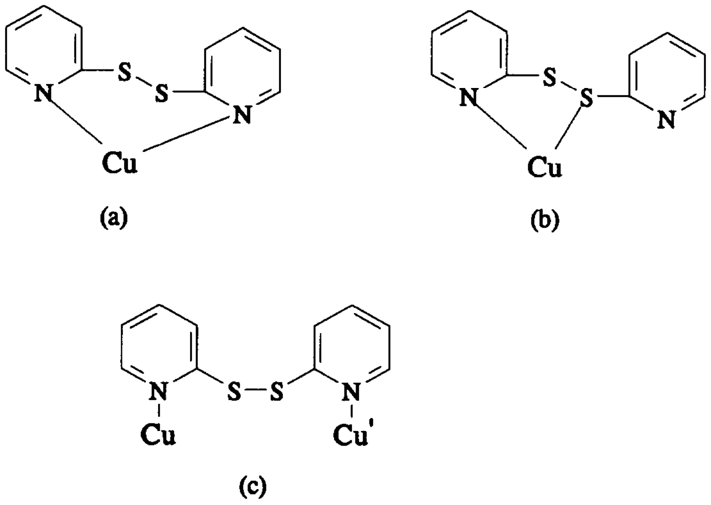
XLIV

The possibility of in situ metal oxidation and coordination of heterocyclic thiones has proved to be of particular interest to coordination chemists, primarily because of the range and inherent coordination potential of the oxidation products involved, but also because of the biochemical implications of copper(I)–disulphide interactions [190].

6.2 *Complexes of oxidised heterocyclic-thiones*

The coordinating ability of the sulphur atoms of organo-disulfide groups was first established for diethyl-disulphide molecules in [{Cl(EtSSEt)Cu}$_n$] [188]. In this structure, the metal has distorted tetrahedral geometry formed from two chlorine atoms in continuous Cl–Cu–Cl chains together with two sulphur atoms, one from each of two disulphide groups. The introduction of terminal pyridyl groups in organo-disulphides generates S,N-donor sites. In [bis{2-(2-pyridyl)ethyl}disulphide copper(I)] perchlorate, the ligand forms six-membered S,N-chelates (mean Cu–S = 2.322, mean Cu–N = 2.029 Å) with distorted tetrahedral geometry and a cationic polymeric chain structure [189].

Heterocyclic-disulphides may also complex directly with copper. Addition of bis(2-pyridyl)disulphide to copper(II) perchlorate hexahydrate in methanol produced [bis{bis(2-pyridyl)disulphide} copper(I)] perchlorate [190]. The crystal structure of this complex contains both discrete $[CuL_2]^+$ and polymeric $[Cu_nL_{2n}]^{n+}$ species, with two types of chelating ligand. Involvement of both of the pyridyl nitrogen atoms generates a seven-membered N,N-chelate (**XLVa**), while the combination of one pyridyl nitrogen with the most distant of the sulphide atoms generates five-membered S,N-chelates (**XLVb**). The discrete $[CuL_2]^+$ complex ion contains one of each type of chelate with distorted tetrahedral geometry at the metal and angles in the range 89.6(3)–117.2(6)°, and a N_3S-donor set (mean Cu–N = 1.988; Cu–S = 2.396(3) Å). In the polymeric complex, each copper(I) atom is coordinated by a pyridyl nitrogen atom from each of two bridging ligands **XLVc** and by a S,N-chelating ligand **XLVb**. Metal geometry is distorted tetrahedral with angles in the range 88.1(3)–137.8(4)°, and a N_3S-donor set (mean Cu–N = 1.36; Cu–S = 1.35(2) Å). Each of the four independent ligands in the structure uses only half of its potential donor atoms.

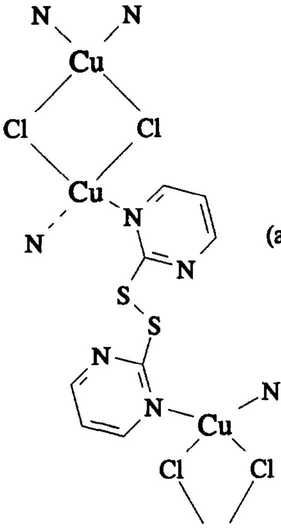


(a) (b)

(c)

XLV

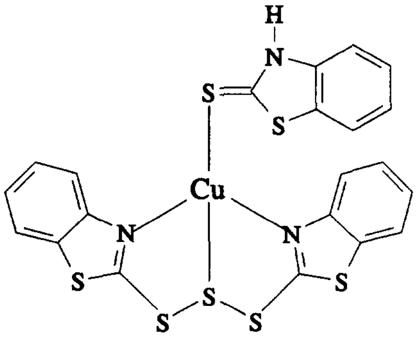
Chloro[bis(2-pyrimidyl)disulphide]copper(I) monohydrate has been prepared in situ by reacting copper(II) chloride dihydrate and pym2tH in 2:1 (metal:ligand) ratio in methanol [191]. The ligands bridge copper(I) atoms in this complex forming polymeric sheets (**XLVI**). Each copper(I) has distorted tetrahedral geometry formed from two chlorine atoms and two nitrogen atoms from two bis(pyrimidyl)-disulphide ligands; angles at the metal are in the range 95.74(4)–142.2(1)°. The chlorine atoms bridge pairs of copper(I) atoms forming a Cu_2Cl_2 rhombus, which is strictly regular, (Cu–Cl = 2.464(1) Å; Cu–Cl–Cu' = 84.26(4)°). The relatively short copper(I)–nitrogen distance (1.966(3) Å), is attributed to d-π^* back-bonding from metal d-orbitals into the low-lying π^*-molecular orbitals of each pyrimidine ring. An unusual feature of the structure is the C–S–S–C torsion angle of 180°, because of crystallographic symmetry, and which contrasts with the free ligand values (83.9 and 85.4°), which are also reported [191]. The unusual torsion angle in the complex is stabilised by a π-system which extends over the whole ligand, although the contribution from the sulphur atoms (S–S = 2.113(1) Å) is small. The N,N'-bridging role clearly enhances the π-character of the ligand in this structure and inhibits the coordinating ability of the sulphur atoms, which is a prominent feature of some organo-disulphide ligands.



(adapted from [191])

XLVI

An unusual complex, $[Cu(bztztH)\{(bztz)_2S_3\}]ClO_4 \cdot 2CHCl_3$, has been prepared from solid copper(II) perchlorate hexahydrate and bztztH in chloroform [192]. Tetrahedral coordination of the metal consists of a monodentate thione S-atom from the parent bztztH ligand (Cu–S = 2.221(4) Å) together with a combination of two nitrogen atoms (Cu–N = 2.04(1), 2.01(1) Å) and the central sulphur atom (Cu–S = 2.486(4) Å) from the trisulphide ligand (**XLVII**). The incorporation of an additional sulphur atom into the original disulphide, $(bztz)_2S_2$, is novel and suggests that additional sulphur atoms could be added under favourable circumstances.



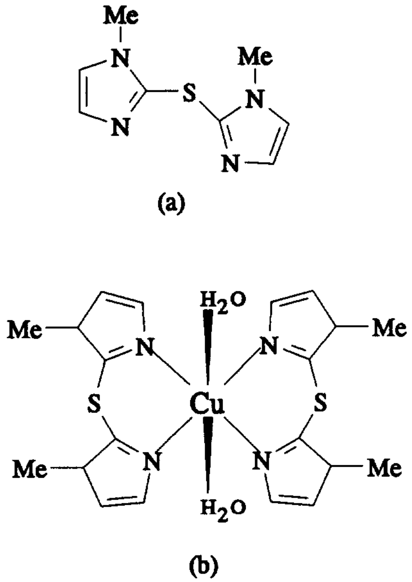
(adapted from [192])

XLVII

Synthetic, spectroscopic and potentiometric studies on the copper(II) complexes of pyridine-, quinoline-, and imidazole-containing disulphides have been reported with the emphasis on copper(II)–sulphur interactions [193]. In the presence of copper(II), the disulphide ligands are more stable in acid than in neutral–alkaline media because of the promotion of hydrolytic cleavage of the disulphide bond in the latter. Both mono- and binuclear complexes have been reported together with square-pyramidal CuN_4S and planar CuN_4 geometry. The authors suggest that stabilisation of copper(II)–sulphur interactions is best achieved when the interaction distance is in the region of 3.0 Å with water and other nucleophiles excluded from the coordination sphere.

In addition to the production of complexes containing disulphide and trisulphide ligands, complexes of bis(1-methylimidazol-2-yl)monosulphide $(meim)_2S$, **XLVIIIa** are also known. This ligand is prepared, and complexed, in situ from meimtH and copper(II) salts. A 1:2 (metal:ligand) ratio of copper(II) sulphate pentahydrate and meimtH in methanol produced $[Cu\{(meim)_2S\}_2(H_2O)_2]MeSO_4$ [194] and 1:1 ratios of hydrated copper(II) perchlorate and nitrate in ethanol with meimtH in nitromethane produced $[Cu\{(meim)_2S\}_2(H_2O)_2]X$ ($X = ClO_4, NO_3$) [195]. Both reactions produced dark-blue crystals from deep-green solutions. The complex cations are effectively isostructural; that which contains the methylsulphate anion is centrosymmetric. The metal has tetragonally distorted octahedral geometry with a N_4O_2 donor set formed from two, N,N-chelating, trans-related $(meim)_2S$ ligands (Cu–N = 1.990(3)–2.005(6) Å) as well as pairs of axial water molecules (Cu–O = 2.47(1)–2.501(4) Å) (**XLVIIIb**). Electronic and ESR spectra are consistent with this structure. A further reaction, involving copper(II) chloride dihydrate and meimtH (1:1 molar ratio in methanol) produced deep-green crystals of bis(μ-chloro)-bis[chloro-bis{1-methylimidazol-2-yl)-monosulphide}-copper(II)] [196]. The metal atoms in this dimeric complex have tetrahedrally distorted square-pyramidal, five-coordinate geometry, consisting of pairs of bridging chlorine, ($Cu–Cl_{br} = 2.295(1)$ and 2.265(1) Å), terminal chlorine ($Cu–Cl_t = 2.265(1)$ Å), and N,N-chelating $(meim)_2S$ (Cu–N = 1.992(1) and 2.013(1) Å) (**XLIX**). The asymmetric, central Cu_2Cl_2 core is centrosymmetric with Cu–Cu = 3.74 Å and $Cu–Cl_{br}–Cu = 94.6(1)°$. The basal plane of the polyhedron consists of the terminal chlorine, one of the two bridging chlorines and the two nitrogen atoms.

The production of $(meim)_2S$ from two molecules of meimtH formally requires the loss of two molecules of hydrogen and one of sulphur. Ainscough et al. suggest that the course of this reaction proceeds initially by the formation of tetrahedral $[Cu(meimtH)_4]^{2+}$; this ion contains thione-S coordinated metal. In the next stage of the reaction meimtH is oxidised to the disulphide by copper(II) with concomitant reduction of the metal. The complex cation $[Cu\{(meim)_2S\}_2(H_2O)_2]^+$ is then formed from reoxidised copper(I) and the desulphurised ligand with the abstracted ligand sulphur probably converted to sulphate [195]. These reactions are summarised in Scheme 1.

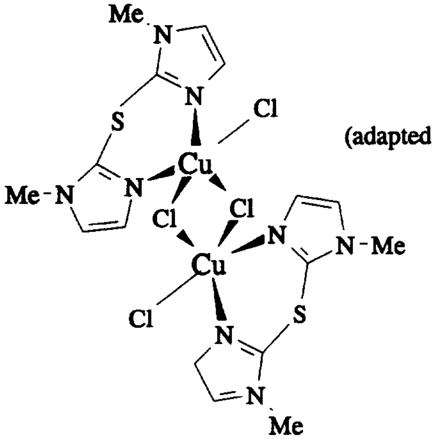


(a)

(b)

(adapted from [195])

XLVIII



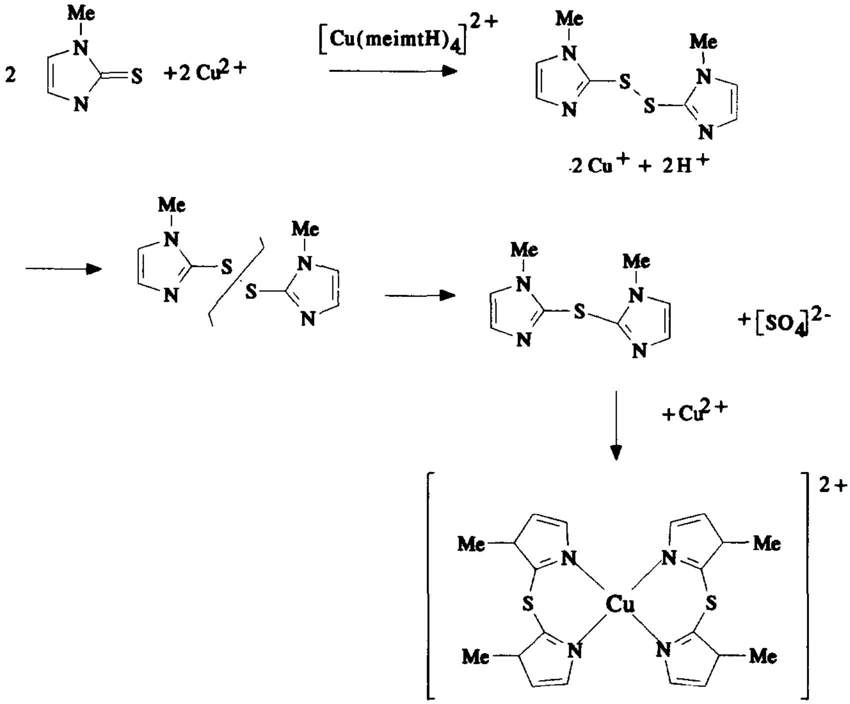
(adapted from [196])

XLIX

The conversion of thioamido sulphur to sulphate is supported by the behaviour of copper(I) complexes of thiazolidine-2-thione and imidazolidine-2-thione derivatives (RSH) in pyridine [197].

$$[Cu(RSH)_2Cl] + 4py \rightarrow [Cu(py)_4SO_4] + R_2S + 2HCl$$

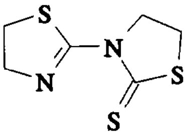
The above conversion is not restricted to heterocyclic-thiones. Organo-thiolate ligands, phosphorus sulphides as well as copper(II) sulphide and oxide are similarly converted. By using copper(I) chloride dissolved in pyridine, the source of oxidisable sulphur has been extended to other disulphides and elemental sulphur. The scope of



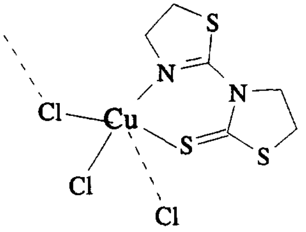
Scheme 1.

the above reactions suggest the involvement of common copper species, which have yet to be established. In addition, sulphate production in the above reactions is reminiscent of the behaviour of chemolithotrophic bacteria, which utilise a variety of sulphur-containing compounds as energy sources. Ainscough et al. suggest that transition metal-mediated enzymic reactions may be more strongly implicated as a result of the above observations [197].

Another example of the in situ production and coordination of an oxidised ligand involves the preparation of 3-(2-thiazolin-2-yl)thiazolidine-2-thione (tztzdt, **La**) from the parent ligand, tzdtH, and copper(II) salts; copper(II)–tztdtH complexes have also been used in the preparation [198]. Green crystalline polymeric $[\{Cu(tztzdt)Cl_2\}_n]$ is produced by the slow addition of copper(II) chloride dihydrate in ethanol to tzdtH in nitromethane or by dissolving $[Cu(tzdtH)_3Cl_2]$ in nitromethane. The structure consists of $(Cu(tztzdt)Cl_2)$ units linked into extended chains by copper–chlorine–copper bridges ($Cu\cdots Cl'_{br} = 2.727(10)$ Å). The copper(II) atom has distorted square-pyramidal geometry with S,N-chelating tztzdt (Cu–S = 2.294(10); Cu–N = 2.00(3) Å; N–Cu–S = 89.1(8)°), terminal chlorine (Cu–Cl = 2.275(9), 2.299(9) Å; Cl–Cu–Cl = 92.4(4)°), with the bridging chlorine provided by an adjacent $(Cu(tztzdt)Cl_2)$ unit (**Lb**). Electronic and ESR spectra are also consistent with copper(II). Brown crystalline [Cu(tztzdt)Br] was produced by dissolving the copper(II) complex [Cu(tzdtH)$_3$Br$_2$] in nitromethane. The metal in [Cu(tztzdt)Br] has distorted trigonal planar geometry formed from a combination of S,N-chelating tztzdt (Cu–S = 2.193(1); Cu–N = 1.980(1) Å; N–Cu–S = 98.9(1)°) and terminal bromine (Cu–Br = 2.280(1) Å). With copper(II) perchlorate hexahydrate as the copper(II) source, oxidative cleavage of tzdtH occurs and the ketonic analogue of the thione (tztzdo, **LIa**) is produced. Typically, the addition of tzdtH in nitromethane to the metal salt in ethanol produces the diamagnetic copper(I) complex [Cu(tztzdt)$_2$]ClO$_4$. However, allowing this complex to remain in solution produced bright-green crystals of [Cu(tztzdo)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$. In this centrosymmetric complex, the metal has tetragonally distorted octahedral geometry formed from two equatorial, N,O-chelating, tztzdo ligands (Cu–N = 1.99(1), Cu–O = 2.01(1) Å), and two axially bound water molecules (Cu–O = 2.36(1) Å) (**LIb**).

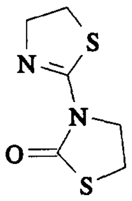


L (a)

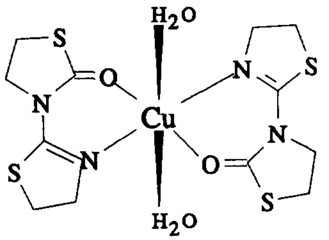


(b)

(adapted from [198])



LI (a)

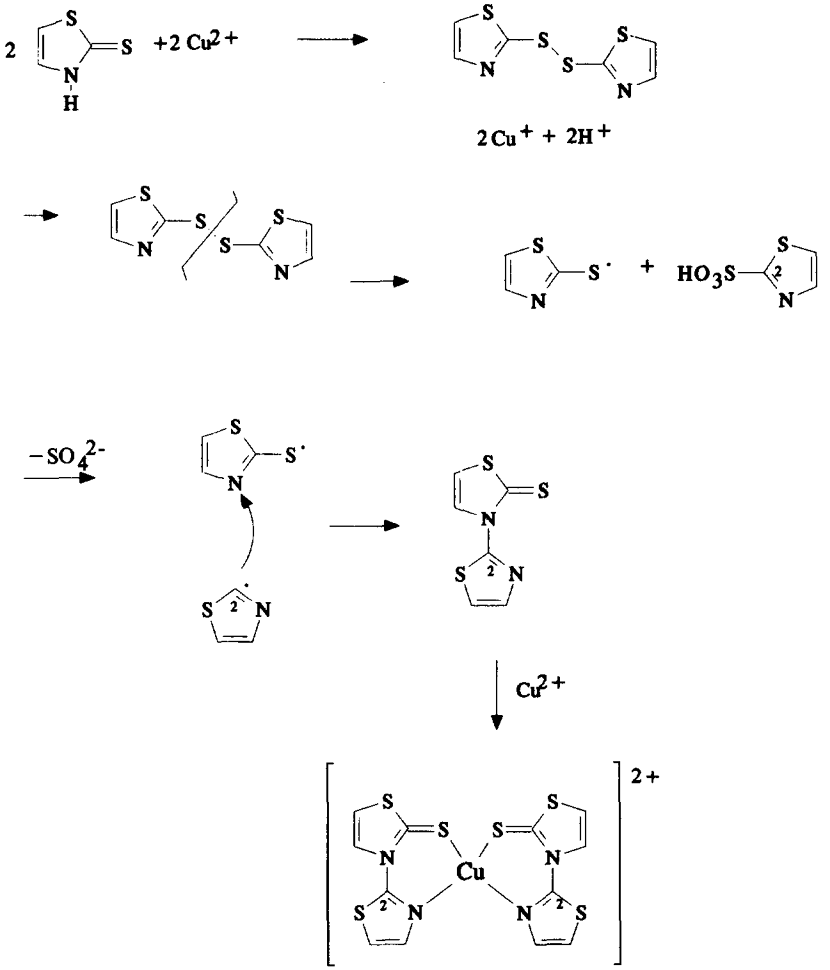


(adapted from [198])

LI (b)

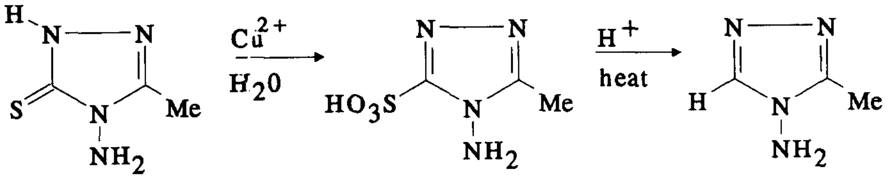
The production of tztzdt from tzdtH, like that of (meim)$_2$S from meimtH, also requires oxidative desulphuration of the parent thione. Ainscough et al. suggest that the reaction between tztdtH and copper(II) initially produces the corresponding disulphide, with concomitant reduction of the metal, followed by intramolecular nucleophilic attack of the imino nitrogen of one ring onto the trigonal (C(2)) carbon of the other ring giving L together with the elimination of sulphur, probably as the sulphate. These reactions are summarised in Scheme 2.

A final example of copper(II)-promoted desulphurisation involves 4-amino-3-methyl-1,4-dihydro-1,2,4-triazole-5-thione (ammetrztH, **LIIa**) [199]. This ligand



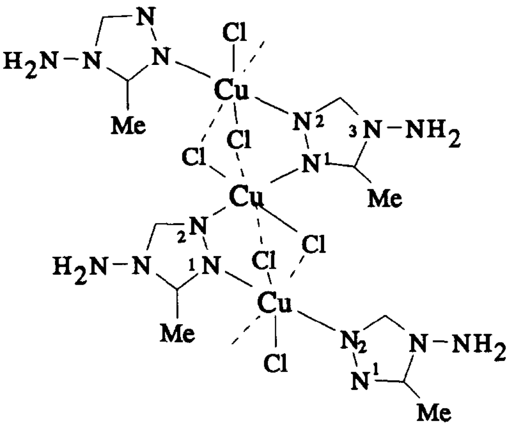
Scheme 2.

forms two complexes with copper(II) chloride dihydrate, the first of which, [$CuCl_2$(ammetrztH)], involves S,N-chelation by the thione (see **LIV**). The second reaction involves desulphurisation of ammetrztH, giving the parent triazole ammetrz (**LIIc**) and the complex [{$CuCl_2$(ammetrz)}$_n$]. The chlorine atoms and the vicinal nitrogen atoms of the heterocyclic ligand are both involved in bridging metal atoms in this polymeric structure (**LIII**). The copper(II) atoms adopt tetragonally distorted (4+2) octahedral coordination with trans heterocyclic nitrogen (Cu–N = 2.012(8), 2.001(7) Å) and trans chlorine, atoms (Cu–Cl = 2.301(3), 2.300(3) Å) forming the basal plane. The coordination is completed by pairs of bridging chlorine atoms provided by neighbouring planar [$CuCl_2(ammetrztH)_2$] units (Cu–Cl = 2.882(3), 2.919(3) Å). Two routes have been proposed for ligand desulphurisation in this reaction. The first involves the formation of the corresponding disulphide followed by conversion to either a sulphinic or a sulphonic acid derivative (**LIIb**) with, presumably, eventual removal of sulphur as sulphate. Alternatively, direct formation of the sulphonic acid is proposed by using a large excess of copper(II) followed by acid-catalysed conversion to the parent triazole (**LIIc**).



(a) (b) (c)

LII

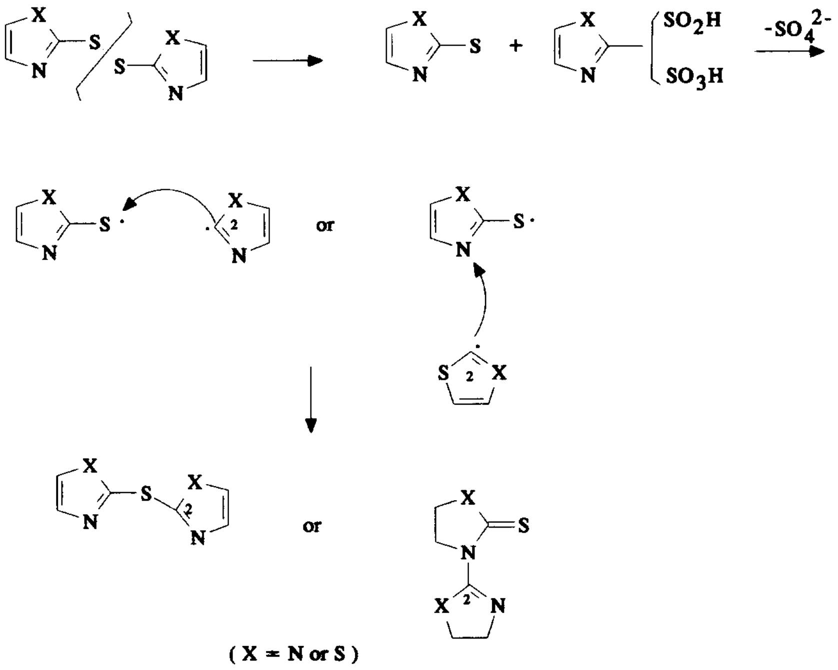


LIII (adapted from [199])

A combination of Schemes 1 and 2 gives an indication of the oxidative desulphurisation processes which result from the interactions of heterocyclic thiones with copper(II) salts. Most authors suggest that the first major product is the disulphide with the involvement of thione-donating ligands in tetrahedral $[Cu(RSH)_4]^{2+}$ intermediates [194]; similar processes have been established for the copper(II)-promoted oxidation of thiourea [181]. In addition, kinetic studies on mostly pyrimidine-thione derivatives with a range of oxidising agents suggest that rapid combination of thiyl (RS•) radicals forms the final stage of disulphide formation [200]. Two possibilities result from desulphurisation of the disulphide, either a monosulphide such as

$(meim)_2S$ (**XLVIII**) (Scheme 1), or a heteroyl-substituted heterocyclic thione such as tztzdt (**La**) (Scheme 2). Desulphurisation involves scission of the disulphide bond coupled with conversion of the abstracted sulphur to sulphate through sulphinic or sulphonic acid formation (Scheme 3). The final, recombination stage involves nucleophilic attack by the carbon atom (C(2)) of the desulphurised heterocycle at either the sulphur, or the nitrogen, of the thioamido group (Scheme 3); the latter has been proposed for tztzdt [198].

The factors which control the composition of the final complex are not at all clear. With either a disulphide, a monosulphide, a heteroyl-substituted thione, or the parent heterocycle resulting from any given reaction, all of which are capable of coordinating to either copper(II) or copper(I), there are, in principle, eight possible complexes arising from any given reaction. What is currently evident is that the products from any given combination of reactants are limited, namely: $(pyS)_2$ from py2tH complexed with copper(I) [190], $(pymS)_2$ from pym2tH also complexed with copper(I) [191], $(meim)_2S$ from meimtH complexed with copper(II) [194–196], ammetrz from ammetrztH complexed with copper(II) [199], and, exceptionally, tztzdt from tzdtH complexed with both copper(I) and copper(II) [198]. The limitations may be a result of practical factors such as the solvents used, the molar ratios of the reactants and their order of addition, or they may be due to fundamental properties of the ligands, such as their chemical composition and structure or inherent redox



Scheme 3.

behaviour, as well as the donor behaviour of the counter ion. Current indications suggest that complexes of oxidised ligands are favoured by oxidising solvents such as nitromethane or oxidisable solvents such as methanol; slow addition of the ligand to the copper(II) salt assists ligand oxidation; parity of reactants assists the production of copper(I) complexes and an excess of the metal salt assists the production of copper(II) complexes. The use of inert or oxidising atmospheres may also affect the outcome. As with other synthetic strategies in this field (see Sect. 4) control of the various factors in order to produce a specific complex is still somewhat elusive.

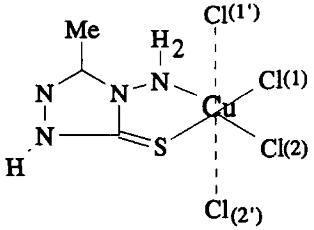
6.3 Redox-stabilised copper(II)-thione complexes

Most reactions involving heterocyclic-thiones and copper(II) salts have produced copper(I)-thione complexes, especially when the thione is in excess, as well as concomitant generation of the oxidised ligand. In spite of the complicated nature of such reactions, there are some reported instances where copper(II) complexes of the original thione ligand have been directly prepared.

N,N′-Dimethyl and diethyl-substituted imdtH$_2$ produced [Cu(LH)$_2$X$_2$] (X = Cl, Br) by fusion of the reactants and extraction with heated chloroform; it has also been suggested that *N*-alkyl ligand substitution inhibits copper(II)-thione redox reactions [201]. Copper(II) chloride dihydrate and tzdtH in absolute ethanol produced [Cu(tzdtH)$_2$Cl$_2$] [202]. Cryogenic magnetic measurements and ESR data at 143 and 293 K indicated magnetically non-dilute behaviour of the copper(II) atoms; metal–ligand attachments were established by ν(Cu–S) at 390 cm^{-1} and ν(Cu–Cl) at 326 and 232 cm^{-1}. Copper(II) complexes of thiohydantoin with a range of counter ions have [Cu(thdtH)$_n$X$_2$] ($n = 1,2$) stoichiometries [203]; a combination of room-temperature magnetic measurements ($\mu_B = 1.43$) and ESR data established the presence of copper(II). Mononuclear and dinuclear complexes of 1-phenyl-4,6-dimethyl-pyrimidine-2-thione (LH) have been reported with stoichiometries ranging from [Cu(LH)X$_2$] (X = Cl, NO$_3$), to [Cu$_2$(LH)$_7$X$_4$] (X = ClO$_4$, BF$_4$, NO$_3$) [204]. Spectroscopic data suggested distorted octahedral metal geometry while polarographic studies in DMF indicated [Cu(LH)$_2$]$^{2+}$, [Cu(LH)$_3$]$^{2+}$ and [Cu$_2$(LH)$_7$]$^{4+}$ species for the perchlorate complexes. Cryogenic magnetic measurements and ESR data have been used to establish the oxidation state of the metal for a series of redox-stabilised copper(II) complexes involving imdtH$_2$, H$_4$pymtH and tridentate anionic Schiffs bases [205]. Copper(II)–thioamide contacts have been stabilised by the addition of thdtH, imdtH$_2$ and thiourea derivatives to copper(II)–bis-(1,2-diaminoethane) (en), complexes. The [Cu(en)$_2$(LH)$_2$X$_2$] (LH = thdtH, imdtH$_2$; X = Cl, Br, NO$_3$), complexes have normal room-temperature magnetic moments and tetragonally distorted geometry [206].

Magnetic and spectroscopic data have been the major indicators of the presence of copper(II) in the above complexes while structural evidence for copper(II)-thioamide contacts is rather scarce. Consequently, the structure of [Cu(ammetrztH)Cl$_2$]

(**LIV**) [199] has provided welcome evidence of a copper(II)–thioamide interaction. The metal has distorted octahedral (4+2) coordination in this structure with the tetrahedrally distorted basal plane formed from the terminal chlorine atoms and S,N-chelating ammetrztH (**LIV**). Ligand coordination is unusual and involves the thione sulphur and imino nitrogen atoms (Cu–N = 2.069(5), Cu–S = 2.288(7), Cu–Cl = 2.256(1) and 2.276(2) Å). The short copper(II)–imino nitrogen distance probably helps to stabilise the copper(II)–sulphur thione interaction in this complex. Two long axial contacts, from the terminal chlorine atoms of neighbouring planar units (Cu–Cl′ = 2.913(2), 3.259(2) Å) complete the coordination.

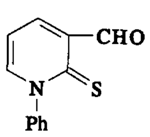


LIV

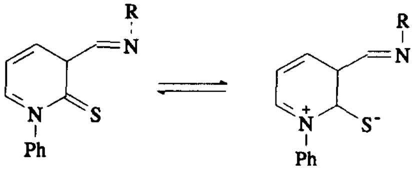
Copper(II)–thiolate interactions have been used to simulate copper–cysteine environments, which generate the charge-transfer spectra typical of copper "blue" proteins in their oxidised form [7]. The inherent redox instability of the copper(II)–alkane–thiolate system with respect to copper(I) disulphide production, especially where the ligand geometry favours copper(I), has inhibited the succesful production of satisfactory models. However, the residual π-character in heterocyclic thione (C = S) groups has been used to moderate copper(II)–alkane thiolate redox instability [207,208]. Imines derived from 1-phenyl-3-formyl-2(1)H-pyridine-thione (**LV**), which exist as thione–thionate tautomers (**LVI**), provide copper(II)–thionate systems with reasonable redox stability through the formation of S,N- (**LVII**) and S_2N_2-donating ligands (**LVIII**).

The reaction shown in **LVII** has been succesfully extended to the copper(II) complexes of triazole, thiazole, imidazole and pyrazole formyl-substituted thione derivatives [209].

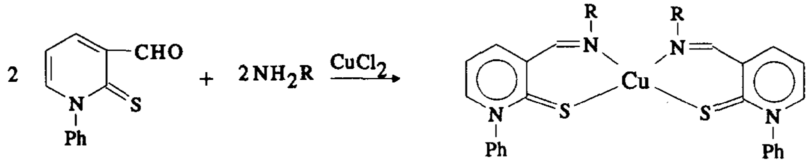
The spectral properties of the S_2N_2-donor complexes **LVIII** indicate progressive distortion of the metal coordination geometry from square-planar to flattened tetrahedral as the number (*n*) of carbon atoms in the alkane bridging chain increases. In contrast, the spectral properties of the S,N-donor complexes **LVII** are similar to one another, (R = *n*-butyl, *sec*-butyl, *p*-toluidine); they all indicate significantly distorted square-planar geometry. The crystal structure of the 1,3-diaminopropane derivative (*n* = 3 in **LVIII**) confirmed N_2S_2 coordination of the metal (Cu–S = 2.259(2), 2.288(2); Cu–N = 1.989(5), 1.980(5) Å), and indicated a slightly tetrahedrally distorted planar geometry with angles at the metal in the range 86.0(1)–102.9(2)°. Electrochemical studies showed the complex to have a reversible Cu(II)/Cu(I) couple in acetonitrile



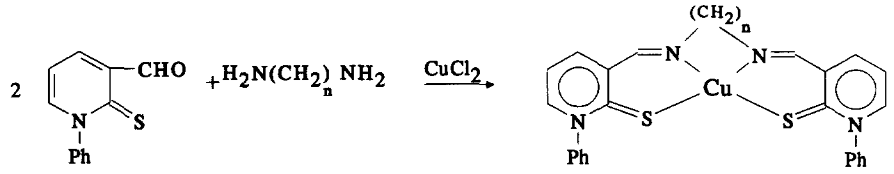
LV



LVI



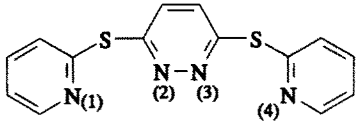
LVII



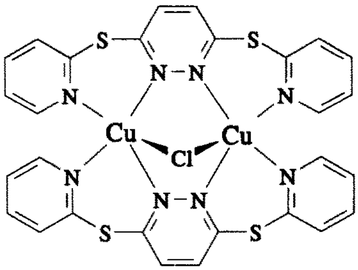
LVIII

($E'_o = +0.01$ V vs. SCE), followed by a Cu(I)/Cu(0) peak at -0.25 V with rapid demetallation of the complex. A further, anodic peak ($E_p = +1.15$ V vs. SCE) is consistent with copper(II)–copper(III) oxidation. Results are also reported for related complexes in acetonitrile and DMF. This work has been extended by the preparation of a series of alkane–thiolate Schiff's bases prepared from (IR)-3-hydroxymethylene-bornane-2-thione with several 2-aminothia-alkyl-1-methyl-benzimidazoles [210]. The resultant ligands are S_2N_2-coordinating to copper(II). Electronic and ESR spectral data are also indicative of a progressive distortion towards pseudo-tetrahedral geometry for the metal as the ligand chain length increases. Electrochemical studies of the complexes are also reported.

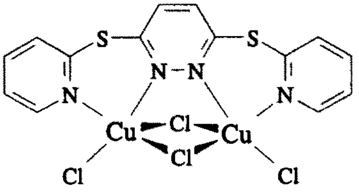
The spontaneity of the reduction of copper(II) species to copper(I) is clearly influenced by the ligand environment and stereochemistry at the metal centre [211]. In addition to the stabilisation of copper(II) complexes by means of S,N-donating heterocyclic-thione derivatives (**LVII**, **LVIII**), there are instances where the thione character of the original ligand has been relegated to a thioethereal (methionine) role. A typical example involves a ligand formed from py2tH and 3,6-dichloropyridazine in absolute ethanol; other heterocyclic-thiones have also been used [212]. The resultant ligand, 3,6-bis(2-pyridylthio)-pyridazine (ptp, **LVIVa**) [212], is nitrogen-



(a)



(b) (adapted from [215])



(c) (adapted from [213])

LVIV

donating and open-chain polydentate in character. Mononuclear and binuclear complexes of ptp have been reported.

In mononuclear $[Cu(ptp)_2(H_2O)](ClO_4)_2 \cdot 3.3H_2O$, the copper(II) atom has distorted square-pyramidal geometry with the basal plane formed from two trans related ptp ligands. Ligand coordination involves a combination of one pyridyl, N(1), and one pyridazine, N(2), nitrogen atoms (Cu–N = 2.016(8), 1.993(9) Å); the apical site is occupied by a water molecule (Cu–O = 2.016(8) Å). The complex has a redox potential of +0.57 V vs. SCE and is spontaneously reduced to the copper(I) complex $[Cu_2(ptp)_2](ClO_4)_2$ on refluxing in methanol or acetonitrile [212,214]. Alternatively, the binuclear complex can be prepared directly from ptp and $[Cu(CH_3CN)_4](ClO_4)$ in acetonitrile [214]. The structure of the dinuclear cation $[Cu_2(ptp)_2]^{2+}$ consists of two pseudo-tetrahedrally coordinated copper(I) centres which are separated by 3.422(1) Å and bridged by two pyridazine nitrogen atoms with terminal pyridine-nitrogen atoms completing the coordination (Cu–N = 2.008(3)–2.024(3) Å). Angles at the metal range from 93.4(1) to 120.8(1)° [214].

Two diazine-chloro bridged dimers have also been reported. Mixing ptp in boiling ethanol with copper(II) chloride dihydrate in water produced $[Cu_2(ptp)Cl_4] \cdot C_2H_5OH$ [213]. This structure (**LVIVc**) involves triply bridged, distorted square-pyramidal copper(II) centres (Cu–Cu = 3.198 Å), consisting of two diazine-nitrogen atoms (Cu–N = 2.075(6), 2.009(6) Å), two asymmetric bridging chlorines (mean Cu–Cl = 2.652(2), 2.269(2) Å; mean $Cu–Cl_{br}–Cu = 80.7°$) and terminal chlorine (mean Cu–Cl = 2.227(2) Å). The reduced room-temperature magnetic moments indicate antiferromagnetically coupled copper(II) centres. The diazine-chloro-bridged copper(II) dimer $[Cu_2(ptp)_2Cl](ClO_4)_3 \cdot CH_3CN$ has been prepared by dissolving $[Cu(ptp)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ in acetonitrile followed by rapid addition to an acetonitrile solution of copper(II) chloride dihydrate [215]. The structure of the binuclear cation **LVIVb** consists of two copper(II) atoms (Cu–Cu = 3.269(2) Å) with distorted square-pyramidal geometry formed from two bridging diazine-nitrogen atoms, two terminal pyridine-nitrogen atoms (Cu–N = 2.002(6)–2.018(6) Å), and an apical bridging chlorine atom (mean $Cu{-}Cl_{br} = 2.439(3)$ Å; $Cu{-}Cl_{br}{-}Cu = 84.2°$). Cryogenic magnetic measurements show strong antiferromagnetic exchange between the metal atoms ($-2J = 479\ cm^{-1}$).

The reported intramolecular copper–sulphur distances, 3.183(2) and 3.210(3) Å [215], are similar to the copper–methionine (sulphur) distance reported in plastocyanin and azurin (Cu–S = 2.90 Å) [216].

7. FINAL COMMENTS

The coordination characteristics of neutral heterocyclic thioamides and related molecules are primarily dependent on the relative positions of the HN—C—S atoms in the heterocycle. When all the atoms occupy heterocyclic positions, as in the 1,3-thiazoles and related molecules, the heterocyclic nitrogen is invariably the major donor. When the thioamido group is exocyclic, as in the thioamido-pyridines, then either the nitrogen or the sulphur thioamido atoms, usually in combination with a hetero-atom from the attached heterocycle, are invariably involved in coordination. When the thioamido sulphur atom is exocyclic, as in the thione derivatives, then thione-sulphur donation invariably occurs. Among heterocyclic-thionates, both the nitrogen and sulphur thioamido atoms are available with consequent enrichment of the coordination chemistry, especially among polynuclear complexes.

The structural chemistry and coordination of the metal are also ligand-dependent. Monovalent copper adopts either trigonal or tetrahedral environments, invariably distorted, in mononuclear, dinuclear and polynuclear complexes which are based primarily on terminal or bridging S-donating heterocyclic-thiones. S,N-Chelation and bridging of copper(I) also occurs, especially with thioamido-pyridines and heterocyclic-thionates, respectively. Divalent copper adopts either tetragonally distorted (4 + 2), or square-based pyramidal coordination in mononuclear, binuclear and occasionally polynuclear complexes. These complexes invariably involve nitrogen-donating thiazoles and related ligands in terminal and bridging modes. Copper(III) is rare, adopts square-planar coordination, and is produced by quinazoline-2,3-dithionate and probably by other vicinal dithionates.

All of the groups of ligands included in this survey reduce copper(II) to a varied extent. The extensive redox chemistry exhibited by the heterocyclic thiones is probably assisted by the location of the hydrogen atom on the thioamido nitrogen atom, which facilitates its removal. Redox behaviour among thioamido pyridines is variable, although again more readily achieved when the hydrogen is attached to the thioamido nitrogen atom. In direct contrast to the above examples, the thiamin-thiachrome copper(II)-catalysed oxidation is manifestly more complicated. Furthermore, the in situ generation and coordination of oxidised ligands has produced much novel copper chemistry, which may be extended to other metals with closely related oxidation states.

Electrochemical techniques will probably be a prominent feature of future developments both in determining the redox properties of the ligands and in the preparation and characterisation of their complexes. Attempts to increase the range of polynuclear complexes, probably by using heterocyclic-thionates, to stabilise copper(II)–thione reactions and to mimic copper protein environments, all appear likely to continue.

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