STUDIES ON COPPER COMPLEXES CONTAINING AMBIDENTATE LIGANDS

A thesis presented in partial
fulfilment of the requirements for
the degree of Doctor of Philosophy
in Chemistry at Massey University.

Mark Laurence Brader
1988

Errata

The corrections listed here are indicated in the text by an asterisk.

Page 17 Preparation (1) should read: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and 2,2′-bipyridyl (0.31 g, 2 mmol) in water (15 mls) was added dropwise a solution of sodium mercaptoacetate (0.23 g, 2 mmol) in water (5mls).

Page 18 Preparation (4) should read: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and 2,2′-bipyridyl (0.31 g, 2 mmol) in water (15 mls) was added dropwise a solution of mercaptosuccinic acid (0.30 g, 4 mmol) in water (5mls).

Page 30 Table 3.1, F(000) value should read: 956

Page 60 The complex $[Cu(bipy)_2(tu)](ClO_4)_2$ is reported in references [10] and [11] (chapter four).

Page 91 Table 5.3, F(000) value should read: 932

Page 103 Table 5.6, F(000) value should read: 482

Page 136 Table 6.5, F(000) value should read: 1496

ACKNOWLEDGEMENTS

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ABSTRACT

Coordination compounds resulting from the interaction of sulphur- and nitrogen-containing ligands with copper salts have been synthesised and characterised by spectroscopic, magnetic, and crystallographic techniques. These ligand systems are shown to undergo novel copper-promoted reactions in which new ligands are formed. The reaction products of a series of aliphatic thiol-containing carboxylic acids with copper(II) have been characterised. With mercaptoacetate, ligand desulphurisation occurs resulting in the formation of oxalate ions. In contrast, 2- and 3-mercaptopropionic acids are oxidised to their respective disulphides (DTDIP and DTDP) which coordinate to the copper. The resulting copper(II)-disulphide complexes, $[Cu^{II}(bipy)(DTDIP)]\cdot 3H_2O$ and $[Cu^{II}(bipy)(DTDP)]\cdot 2H_2O$, have been characterised by X-ray crystallography (bipy = 2,2′-bipyridyl). The latter complex contains no Cu-S bonding interaction. The former, in contrast to previously reported copper(II)-disulphide structures (which possess weak Cu-S coordination or none at all), displays moderately strong axial Cu-S bonding (Cu-S = 2.678(2) Å).

Methimazole has been shown to undergo a copper-promoted reaction resulting in the new ligand 1,1′-dimethyl-2,2′-diimidazolylsulphide (dmimS) which coordinates to the copper(II) ion forming the complex $[Cu^{II}(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$. This complex has been characterised by X-ray crystallography.

Phenylthiourea has been shown to undergo a copper-promoted desulphurisation reaction resulting in the formation of phenylcyanamide anions which coordinate to the copper(II) ion. The copper coordination chemistry of the phenylcyanamide ligand has been examined, complexes with empirical formulations of $[Cu(bipy)(L)_2]$, $[Cu(phen)(L)_2]$, $[Cu(pip)_2(L)_2]$, and $[Cu(py)_2(L)_2]$ having been prepared and characterised (phen = 1,10-phenanthroline, pip = piperidine, py = pyridine). The crystal structure determinations of

the complexes $[\{Cu^{II}(bipy)(PC)_2\}_2]$, $[\{Cu^{II}(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$, $[\{Cu^{I}(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$, and $[\{Cu^{I}(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ are reported (where PC = $(Ph\text{-}N\text{-}C{\equiv}N)^-$, PPh_3 = triphenylphosphine, dppe = 1,2-bis(diphenylphosphino)ethane, and Ac = acetate). These complexes represent the first examples of copper complexes incorporating phenylcyanamido ligands that have been characterised using X-ray crystallography. These structures show that the phenylcyanamide moiety may coordinate to a metal in a number of different ways. In the 2,2′-bipyridyl complex, the phenylcyanamide anions exhibit two coordination modes: a monodentate ligand which coordinates to the copper through the cyano nitrogen, and a bridging ligand which coordinates to the copper atoms of the dimer via the cyano and amido nitrogens. The 1,10-phenanthroline complex is also dimeric and contains m-Cl-phenylcyanamide anions which bridge the two copper atoms of the dimer via the cyano nitrogen. The copper(I)-phosphine complexes are also dimeric. In the dppe complex, the p-Cl-PC ligand is monodentate to the copper and coordinates through the cyano nitrogen, whereas in the PPh_3 complex, the p-Me-PC ligand bridges the two copper atoms of the dimer via the cyano and amido nitrogen atoms.

CONTENTS

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CHAPTER SEVEN A Summary of Copper Complexation by Phenylcyanamides.

APPENDIX

ABBREVIATIONS AND NOMENCLATURE

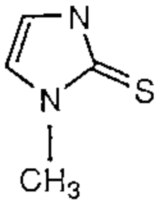
Ac	acetate anion
bipy	2,2′-dipyridine, or bipyridine
cp	cyclopentadienyl ligand, C5H5$^-$
dmimS	1,1′-dimethyl-2,2′-diimidazolylsulphide*, $C_8H_1ON_4S$
DMSO	dimethylsulphoxide, Me_2SO
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
DTDIP	dithiodiisopropionate*
DTDP	dithiodipropionate*
DTDS	dithiodisuccinate*
en	ethylenediamine
Et	ethyl
L	ligand
M	central metal atom in compound
maa	mercaptoacetic acid, $HSCH_2COOH$
2-mpa	2-mercaptopropionic acid, $CH_3CH(SH)COOH$
3-mpa	3-mercaptopropionic acid, $HSCH_2CH_2COOH$
msa	mercaptosuccinic acid*, $HOOCCH_2CH(SH)COOH$
Me	methyl
mimtH	methimazole* (1-methylimidazole-2-thiol), $C_4H_5N_2S$
ox	oxalate ion, $C_2O_4{}^{2-}$
PC	phenylcyanamide anion*, $C_6H_5NCN^-$
Ph	phenyl, C_6H_5
pip	piperidine, $C_5H_{10}NH$
phen	1,10-phenanthroline
py	pyridine
R	alkyl or aryl group
X	halogen or pseudohalogen

Miscellaneous.

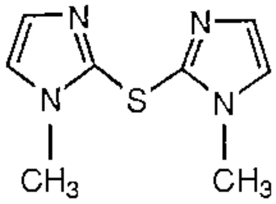
Å	Angstrom unit, 10^{-10} m
BM	Bohr magneton
b.p.	boiling point
br	broad
cm^{-1}	wave number
CT	charge transfer
d	decomposes
e.s.d.	estimated standard deviation
esr	electron spin resonance
ir	infrared
m.p.	melting point
$\mu_{(eff)}$	effective magnetic moment (observed)
ν	stretching frequency
nmr	nuclear magnetic resonance
ORTEP	the computer program used for crystal structure illustrations (see appendix A1).
u.v.	ultraviolet

* Included in ligand illustrations.

LIGAND ILLUSTRATIONS

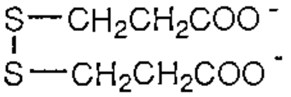


METHIMAZOLE (mimtH)



1,1'-DIMETHYL-2,2'-DIIMIDAZOLYLSULPHIDE

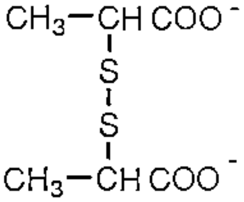
(dmimS)



$$\begin{array}{l} S-CH_2CH_2COO^- \\ | \\ S-CH_2CH_2COO^- \end{array}$$

DITHIODIPROPIONATE

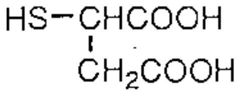
(DTDP)



$$\begin{array}{l} CH_3-CH\,COO^- \\ \quad\quad\;\; | \\ \quad\quad\;\; S \\ \quad\quad\;\; | \\ \quad\quad\;\; S \\ \quad\quad\;\; | \\ CH_3-CH\,COO^- \end{array}$$

DITHIODIISOPROPIONATE

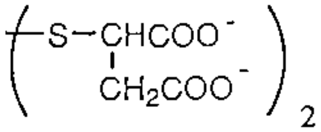
(DTDIP)



$$\begin{array}{l} HS-CHCOOH \\ \quad\quad\; | \\ \quad\quad\; CH_2COOH \end{array}$$

MERCAPTOSUCCINIC ACID

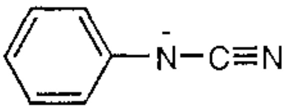
(msa)



$$\left(-S-\begin{array}{l} CHCOO^- \\ | \\ CH_2COO^- \end{array} \right)_2$$

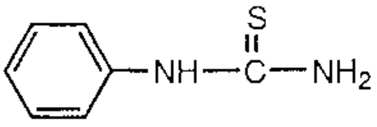
DITHIODISUCCINATE

(DTDS)



PHENYLCYANAMIDE MONOANION

(PC)



PHENYLTHIOUREA

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APPENDIX B1 (Microfiche) Crystallographic diagrams and tables of crystallographic data, atomic coordinates, thermal parameters, bond lengths and angles, and structure factors.

CHAPTER ONE

GENERAL INTRODUCTION

The first row transition metals form a diverse range of coordination complexes in which octahedral, tetrahedral, and square-planar stereochemistries are the most common. Copper is a biologically important transition metal which forms complexes in oxidation states (+1), (+2), (+3) and (+4). Its importance in biological systems generally arises from its redox activity which utilises the interconversion between oxidation states (+1) and (+2) (and in a few cases +3), and the exceptional diversity of its stereochemical behaviour. Copper(III) and copper(IV) are easily reduced and therefore very uncommon. The copper(II) ion displays a greater range of coordination polyhedra than any other transition metal. The reluctance of the copper(II) ion to form complexes with 'regular' stereochemistries is well known. Several hundred crystal structures of copper(II) complexes have been determined by X-ray crystallography in which the coordination number ranges from four to eight. The copper(II) ion possesses a d^9 configuration which gives rise to electronic properties which are relatively sensitive to stereochemistry. The copper(II) system is thus an excellent metal with which to study the coordinating modes of ambidentate ligands, and structural inferences are often based on the results of magnetic, esr and electronic spectral studies.

The copper(I) (d^{10}) oxidation state gives rise to diamagnetic complexes which are usually colourless. Numerous copper(I) complexes have been characterised by X-ray crystallography, the predominant stereochemistry being tetrahedral. However, the stereochemistry of both copper(I) and copper(II) complexes is often highly unpredictable, even with knowledge of the stoichiometry. The structural chemistry presented in this thesis highlights this difficulty and attempts to improve our understanding of the factors which are important in determining the stereochemistry of copper complexes.

One currently emerging aspect which further distinguishes copper from the other transition metals is the ability of Cu^{2+} ions to promote unusual ligand transformations which result in the formation of new ligating molecules. This phenomenon.is associated with the action of the readily interconvertible (+1) and (+2) oxidation states, and the characteristic oxidising and complexing effect that results. The behaviour of copper, particularly towards ligands which contain sulphur, is an aspect of copper chemistry which has received surprisingly little attention. This reactivity is undoubtedly important, and one aim of the work presented in this thesis was to increase our understanding in this area.

In accordance with these aims, the initial chapters of this thesis describe the products encountered as a result of reactions between copper(II) ions and ligands containing thione or thiol sulphur groups. In some cases these reactions have resulted in the copper-promoted desulphurisation of the ligand initially present, producing a new ligating species. The later chapters describe the coordinative behaviour of one such ligand, namely phenylcyanamide, and developes the associated structural chemistry using X-ray crystallography.

The coordination chemistry of the cyanamide group has not received a great deal of attention even though it possesses considerable potential for a very interesting ambidentate behaviour. In response to this potential this thesis has made an attempt to investigate the ambidentate nature of the phenylcyanamide monoanion and characterise a number of different coordination modes. The experimental approach has involved synthesising various series of copper complexes which incorporate different co-ligands and phenylcyanamides. The crystal structures of a number of copper(I) and copper(II) complexes have been determined using X-ray crystallography and are discussed in terms of the stereochemistries of the metal centres and the donor characteristics of the phenylcyanamido group.

CHAPTER TWO

THE REACTIVITY OF METHIMAZOLE WITH COPPER(II)

2.1 INTRODUCTION: COPPER PROMOTED REACTIONS OF LIGANDS CONTAINING SULPHUR AND NITROGEN

Studies on the complexation of copper by ligands containing both nitrogen and sulphur atoms has become a rapidly expanding area. One of the reasons for this has been the increasing interest in the 'blue' or 'type 1' binding site, an essential component of a number of copper electron transfer proteins including azurin, stellacyanin, laccase, plastocyanin, ascorbate oxidase, and ceruloplasmin [1]. The oxidised, Cu(II), form of these 'blue' copper proteins is characterised by two unique spectroscopic features, viz. an extremely intense multi-banded absorption envelope in the 600 nm region, and an esr spectrum having an unusually low hyperfine coupling constant, $A_{//}$. These highly unusual spectroscopic properties are entirely unique to these proteins and have not been reasonably simulated despite considerable attempts to synthesise low molecular weight structural analogues. On the basis of the numerous and extensive spectroscopic and theoretical studies that have been carried out on these proteins, their characteristic features have been attributed to a combination of a highly distorted coordination environment about the copper and the binding of a mercaptide sulphur to the copper. Subsequent structural studies on the metalloproteins have confirmed both of these proposed features and have also shown the importance of imidazole-nitrogen atoms in binding the copper [2-5]. These conclusions have stimulated new interest in the chemistry of copper with sulphur- and nitrogen-containing ligands. This has given rise to a wide variety of copper complexes, some novel copper-promoted ligand rearrangements, and some unusual structural types. It has become increasingly apparent that the chemistry of copper with this category of ligand is surprisingly versatile and often highly unpredictable. As a result the copper promoted reactivity of sulphur ligands, in particular, has become an interesting and rapidly developing field in its own right. One aspect to emerge from this field is the ability of copper(II) ions to desulphurise ligands and form new complexes. One example which illustrates this behaviour has been reported from our laboratory and shows that the cleavage of an exocyclic carbon-sulphur bond readily occurs when copper(II) complexes containing heterocyclic thioamide ligands are dissolved in pyridine. The sulphato complex, $[Cu(py)_4SO_4]\cdot 2H_2O$, was isolated from these reactions [6]. In contrast, the reaction of benzothiazoline-2-thione in chloroform with solid copper(II) perchlorate hexahydrate yields a complex containing an oxidised form of the thioamide, RSSSR, in which an additional sulphur atom has been inserted [7]. The unpredictability of these copper sulphur-ligand systems is again illustrated by a further new type of copper promoted reaction also recently reported from our laboratory [8]. In this reaction the ligand 3-(4,5-dihydro-2-thiazolyl)-2-thiazolidinethione (L^2) is formed via the fusion of two molecules of 2-thiazolidinethione (L^1H), with the concomitant loss of elemental sulphur.

$$CuCl_2\cdot 2H_2O + 2L^1H \dashrightarrow CuL^2Cl_2 + 1/8S_8$$

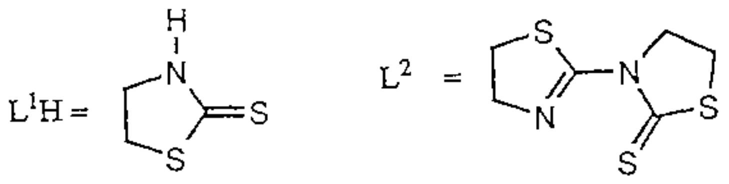

Figure 2.1 The Reactivity of 2-thiazolidinethione (L^1H) with Copper(II)

The use of nitromethane as the solvent is apparently necessary for the occurrence of this reaction, although its exact role is unclear. This reaction is unusual because it is generally accepted that only rarely does ring fusion occur with heterocyclic thiones in the presence of metal ions. To investigate the generality of this reaction, the heterocyclic molecule methimazole (mimtH) was studied as part of the research carried out for this thesis. This molecule may exist in one of the two possible tautomeric forms.

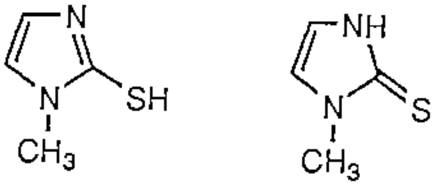

Figure 2.2 The Tautomeric Forms of Methimazole (mimtH).

MimtH is structurally similar to 2-thiazolidinethione (L^1H) and possesses a similar ambidentate coordination chemistry with transition metals. The crystal structures of a number of copper(I) mimtH complexes have been published [9,10], as well as that of the mixed valence compound $[Cu^{(I)}{}_{10}Cu^{(II)}{}_{2}(mimt)_{12}(MeCN)_4](BPh_4)_2\cdot4MeCN$ [11]. In view of the recently established copper promoted reactivity of L^1H, it was considered useful to determine whether mimtH exhibits a similar reactivity pattern. The present work has shown that in fact a different reactivity pattern occurs: the reaction of mimtH with cupric perchlorate hexahydrate in nitromethane yields the new ligand 1,1′-dimethyl-2,2′-diimidazolylsulphide (dmimS).

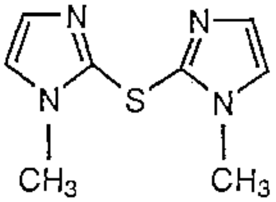

Figure 2.3 1,1′-dimethyl-2,2′-diimidazolylsulphide (dmimS).

2.2 EXPERIMENTAL: THE PREPARATION OF $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$

To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in ethanol (5 mls) was added a solution of mimtH (0.46 g, 4 mmol) in nitromethane (30 mls). The resulting solution initially became an intense purple colour then dark green as the addition was completed. This solution was filtered, and upon standing for three days with slow evaporation, deposited a pale blue crystalline product (0.07 g). These crystals were removed by filtration and upon standing a further week, the solution deposited dark blue needle crystals of $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ (0.28 g, yield = 40%) which were subsequently identified by X-ray crystallography; m.p. = 277-279°C, elemental analyses calculated for $(CuC_{16}H_2ON_8S_2Cl_2O_8).4H_2O$: C, 26.6, H, 3.9, N, 15.5, Cl, 9.8; found: C, 26.9, H, 4.1, N, 15.2, Cl, 11.4%; spectroscopic results: λ_{max} (nujol) = 570 nm (br) d→d; esr (frozen nitromethane, 113 K) $g_{//} = 2.249$, $A_{//} = 195 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.055$.

2.3 RESULTS: THE CHARACTERISATION OF $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$

The crystal structure analysis of the dark blue compound revealed that the ligand dmimS had formed in situ from the reaction between copper(II) perchlorate hexahydrate and methimazole resulting in the complex $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$. The ligand dmimS comprises methyl-imidazoline rings bridged by a single sulphur atom, and coordinates to the copper through the imino nitrogens.

Microanalyses showed that the pale blue crystalline product that initially precipitated, had a very low percentage composition of carbon (approximately 7%) and no nitrogen. Several microanalyses on samples from different reactions were carried out. It became apparent from the pronounced variability of these microanalytical data that this product was in fact a mixture of variable composition. The ir spectrum was very similar, and in some samples identical, to that of an authentic sample of copper(II) sulphate pentahydrate.

During the final stages of this work we became aware that Baldwin et al. [12] had recently reported the formation of the novel ligand 1,1'-dimethyl- 2,2'-diimidazolylsulphide, from a methanolic solution of copper(II)sulphate pentahydrate and mimtH, producing the complex $[Cu(dmimS)_2(H_2O)_2](MeSO_4)_2$. Baldwin et al. also reported a similar reaction in which the dimeric complex, $[\{Cu(dmimS)Cl_2\}_2]$, was formed from the reaction of mimtH with $CuCl_2\cdot 2H_2O$ in methanol [13]. In both of these examples the ligand 1,1'-dimethyl-2,2'-diimidazolylsulphide (dmimS) was formed in situ.

Baldwin's results showed that, in addition to dmimS, the methylsulphate anion also formed from the reaction of mimtH with copper(II) sulphate [12]. It thus appears likely that the pale blue product isolated from the present reaction comprises a mixture of copper(II) sulphate and copper(II) methylsulphate, with the former possibly being a decomposition product of the latter.

The crystal structure of $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ was determined by Dr G. Gainsford (DSIR) using crystals supplied from this work. The crystal data are summarised in table 2.1 and an

ORTEP representation of the $[Cu(dmimS)_2(H_2O)_2]^{2+}$ unit is shown in figure 2.4. Selected bond lengths and angles are given in table 2.2.

The structure consists of crystallographically equivalent copper(II) centres coordinated to two dmimS ligands and two water molecules, with uncoordinated perchlorate counterions participating in an intermolecular hydrogen bonding network with the water molecules. The copper atom is located on a crystallographic centre of symmetry. The coordination environment of the copper atom is tetragonally distorted octahedral, in which dmimS imino nitrogen atoms form a coordination square plane (Cu-N1 = 1.990(3) Å and Cu-N3 = 2.004(3) Å) and the water molecules are coordinated at the axial positions of an octahedron, where Cu-O5 = 2.501(4) Å. This type of coordination geometry is extremely common for copper(II) complexes [14]. The $[Cu(dmimS)_2(H_2O)_2]^{2+}$ cation exhibits no unusual structural features. The bond lengths and angles in the dmimS ligand are not significantly different from those found in the structures of $[Cu(dmimS)_2(H_2O)_2](MeSO_4)_2$ [12] and $[\{Cu(dmimS)Cl_2\}_2]$ [13], and will not be considered in detail.

Table 2.1 Crystallographic Data for $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$.

Formula	$[Cu,C16,H20,N8,S2] \cdot 2(ClO_4) \cdot 4H_2O$
Mol. wt.	722.5
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
a, Å	7.696(2)
b, Å	13.875(3)
c, Å	13.186(2)
β, deg.	95.98(2)
Z	2
V, $Å^3$	1400.3(5)
F(000)	742
D(calc), gcm^{-3}	1.69
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator $\lambda = 0.71069$ Å
Temp., K	143
Reflns. Measd.	$\pm h, +k, +l$
Scan type	$\omega/2\theta$
Max. 2θ, deg.	52
Measd. Reflns.	2685
Unique reflns. ($I > 3_{\sigma(I)}$)	2205
Cryst. dimensions., mm	0.10 x 0.13 x 0.10
Abs. corr. type	Empirical.
Abs. coeff., cm^{-1}	12.0
Trans. Factors	Max. 0.884 Min. 0.478
Wtg scheme	$w = 2.00 / [\sigma_{(F)}^2 + 0.0004F^2]$
R	0.0385
R_w	0.0499

Figure 2.4 The ORTEP representation of the $[Cu(dmimS)_2(H_2O)_2]^{2+}$ cation.

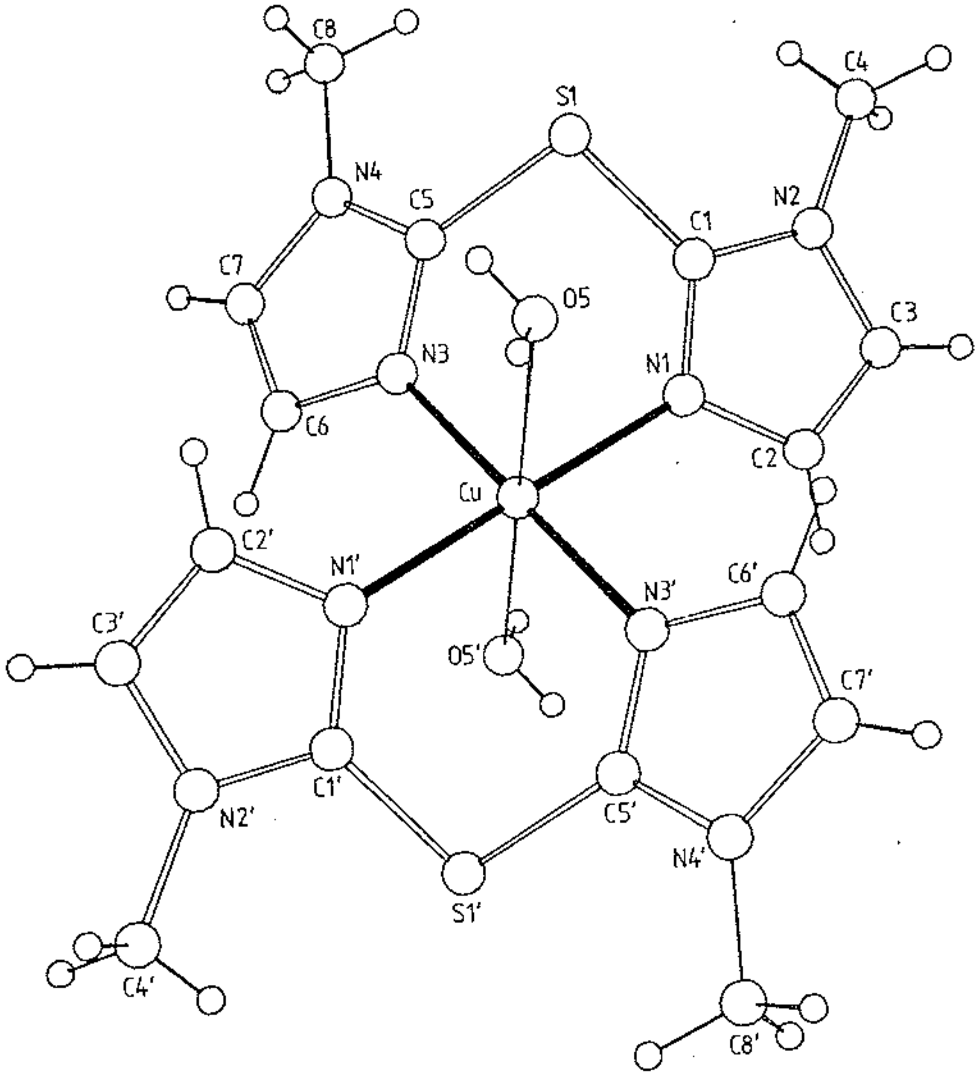

Table 2.2 Bond Lengths (Å) and Angles (deg.) in $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$.

Cu-O5	2.501(4)		
Cu-N1	1.990(3)	N2-C4	1.460(5)
Cu-N3	2.004(3)	N3-C5	1.333(4)
S1-C1	1.755(3)	N3-C6	1.384(4)
S1-C5	1.756(3)	N4-C5	1.352(4)
N1-C1	1.327(4)	N4-C7	1.368(5)
N1-C2	1.383(4)	N4-C8	1.465(5)
N2-C1	1.343(4)	C2-C3	1.348(5)
N2-C3	1.368(4)	C6-C7	1.341(5)

N3--Cu--N1	88.7(1)
C1--N1--Cu	126.3(2)
C2--N1--Cu	128.4(2)
C2--N1--C1	105.2(3)
C3--N2--C1	107.0(3)
C4--N2--C1	127.0(3)
C4--N2--C3	126.0(3)
C5--N3--Cu	126.1(2)
C6--N3--Cu	128.5(2)
C6--N3--C5	105.2(3)
C7--N4--C5	106.4(3)
C8--N4--C5	126.8(3)
C8--N4--C7	126.7(3)
N1--C1--S1	125.8(3)
N2--C1--S1	122.7(2)
N2--C1--N1	111.4(3)
C3--C2--N1	109.4(3)
C2--C3--N2	107.0(3)
N3--C5--S1	125.4(2)
N4--C5--S1	123.3(2)
N4--C5--N3	111.3(3)
C7--C6--N3	109.4(3)
C6--C7--N4	107.7(3)

2.4 SUMMARY

The present reaction is clearly similar to those reported by Baldwin et al.. The copper sulphate and copper methylsulphate coproducts are especially interesting when compared to Baldwin's copper sulphate/mimtH reaction in which the in situ formation of the ligand dmimS and the anion methylsulphate occurred, producing the complex $[Cu(dmimS)_2(H_2O)_2](MeSO_4)_2$. It appears that copper(II) promotes a condensation reaction between two molecules of mimtH in which the elements 'H_2S' are eliminated, either as hydrogen sulphide (from two thiolates), or as elemental sulphur (from two thioamides). However, the mechanism(s) for the formation of dmimS from mimtH certainly remains unclear. In the formation of Baldwin's complex, $[Cu(dmimS)_2(H_2O)_2](MeSO_4)_2$, it was unknown whether the $MeSO_4$ sulphur atom originated from the copper sulphate or the mimtH initially present. The results of the present reaction do establish that the sulphur in the $CuSO_4$ and $Cu(MeSO_4)_2$ must originate from mimtH. The formation of sulphato complexes from the interaction of copper(II) ions with thioamides, or elemental sulphur itself, is not entirely unprecedented. Thus it appears more likely that the formation of dmimS occurs with the initial extrusion of elemental sulphur from two molecules of mimtH. The origin of the methyl group incorporated in the methylsulphate in Baldwin's reaction and the present reaction is unknown - the solvent or the mimtH ligand are the two most likely possibilities.

CHAPTER TWO REFERENCES

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CHAPTER THREE

THE COPPER PROMOTED REACTIVITY OF ALIPHATIC THIOL-CONTAINING CARBOXYLIC ACIDS

3.1 INTRODUCTION: LIGANDS CONTAINING THE SH GROUP

Structural studies indicate that the metal binding sites in the 'blue' copper proteins plastocyanin [1] and azurin [2-4] consist of a copper atom coordinated to one mercaptide (cysteine), one thioether (methionine) and two imidazole (hystidine) ligands in a highly distorted tetrahedral array with an exceptionally long copper-thioether bond. The spectroscopically similar 'blue' copper protein stellacyanin is different because it contains no methionine. In this case disulphide sulphurs have been postulated as being involved in the copper binding [5-7].

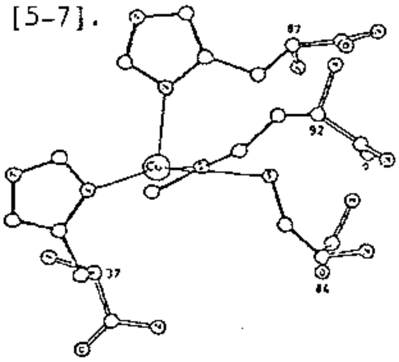


Figure 3.1 The Copper(II) Site of Plastocyanin.

The most immediate problem encountered by chemists attempting to synthesise low molecular weight facsimilies of the 'blue' copper site is the difficulty of stabilising the copper(II)-mercaptide linkage. It has proved extremely difficult to isolate copper(II) mercaptide complexes because of the very rapid reduction of the metal and the irreversible formation of the corresponding disulphide.

$$2Cu(II) + 2RS^- \longrightarrow 2Cu(I) + RSSR$$

The mechanism of this reaction remains poorly understood, but is thought to involve a one electron reductive elimination, producing a copper(I) ion and a mercapto radical [8].

$$\mathrm{Cu(II)\text{-}SR} \rightleftarrows \mathrm{Cu(I)} + \mathrm{RS}\cdot$$

This reaction is supposedly reversible, but is driven to the right because of the formation of the corresponding stable disulphide by radical coupling.

$$2\mathrm{RS}\cdot \longrightarrow \mathrm{RSSR}$$

This redox difficulty is further increased by the fact that only the highly oxidisable aliphatic mercaptans resemble the sulphur of cysteine. Nevertheless this challenge has been tackled by synthetic chemists, and a few copper(II) aromatic [9-13] and aliphatic [14-15]] mercapto complexes have been structurally characterised.

In view of the established unpredictable reactivity of sulphur ligands with copper, and their relevance to the 'blue' copper site, an investigation into mercapto ligands with copper(II) was undertaken as part of this thesis. The aim was to further investigate the reactivity of the mercapto group and establish whether any copper(II)-mercaptide complexes could be isolated. It has been shown that ternary complexes of copper(II) containing a bidentate nitrogen base, such as 2,2'-bipyridyl, and a bidentate oxygen donor ligand, possess unusual stability [16]. It was envisaged that this system could be used to stabilise a copper(II)-mercaptide interaction. The experimental approach was to investigate aliphatic mercapto ligands in which the mercapto interaction with the copper was accompanied by the binding of a carboxylate group. The series of related mercapto-carboxylic acids, mercaptoacetic acid (maa), 2-mercaptopropionic acid (2-mpa), 3-mercaptopropionic acid (3-mpa), and mercaptosuccinic acid (msa) were studied and their respective reaction products characterised.

3.2 EXPERIMENTAL

✱ (1) Mercaptoacetic acid: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) in water (15 mls) was added dropwise a solution of sodium mercaptoacetate (0.23 g, 2 mmol) in water (5 mls). The very intense dark green solution was filtered and upon standing overnight deposited dark blue needle crystals (0.32 g). These were removed from solution by filtration, and upon standing a further week, the solution deposited dark green rhombic crystals (0.10 g). An attempted recrystallisation showed that the blue crystals could also be obtained by dissolving the green crystals in hot water, then cooling the solution. Sodium fusion elemental tests [17] for the presence of sulphur were negative for both the blue and the green compounds, indicating the absence of mercaptoacetate in both cases. An interpretation of the microanalytical data, and the ir spectrum of the blue compound suggested the formulation $Cu(bipy)(ox)\cdot 2H_2O$ (found: C, 41.7; H, 2.55; N, 8.1. requires: C, 41.9; H, 3.5; N, 8.2 %). This hypothesis was confirmed by preparing, from an aqueous solution of an equimolar mixture of sodium oxalate, copper acetate monohydrate, and bipy, dark blue needle-like crystals, whose infrared spectrum was identical to that of the blue compound.

(2) 3-Mercaptopropionic acid: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and bipy (0.31 g, 2 mmol) in water (15 mls) was added dropwise a solution of 3-mercaptopropionic acid (0.36 mls, 4 mmol) in water (5 mls). A small quantity of insoluble brown material formed immediately, which was removed from solution by filtration. Upon standing for a few days, the dark blue solution deposited dark blue needle-like crystals which were subsequently identified by X-ray crystallography as $[Cu(bipy)(DTDP)]\cdot 2H_2O$. These were removed from solution, washed with water, then air dried (0.44 g, yield = 50%), m.p. = 150-152°C. Microanalytical data calculated for [Cu(bipy)(DTDP)] (vacuum dried sample): C, 44.9, H, 3.7, N, 6.5; found: C, 45.0, H, 4.0, N, 6.1 %. The crystal structure determination and discussion of this complex is presented in the following section. Electronic data: esr (frozen 1:1 H_2O/EtOH, 113 K) $g_{//} = 2.28$, $A_{//} = 178 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.07$, $\lambda_{(max)} = 631$ nm (br) (nujol) d→d, $\mu_{(eff)} = 1.85$ BM.

(3) 2-Mercaptopropionic acid: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and bipy (0.31 g, 2 mmol) in water (15 mls) was added dropwise a solution of 2-mercaptopropionic acid (0.36 mls, 4 mmol) in water (5 mls). The resulting dark green solution was filtered and upon standing for a few days deposited dark blue needle crystals which were subsequently identified by x-ray crystallography as $[Cu(bipy)(DTDIP)]\cdot 3H_2O$. These were removed from solution by filtration, washed with water, then air dried (0.31g, yield = 30%), m.p. = 129-131°C. Microanalytical data calculated for $[Cu(bipy)(DTDIP)]\cdot H_2O$ (air dried sample); C, 43.1, H, 4.1, N, 6.3; found: C, 43.5, H, 3.9, N, 6.3 %. Electronic data: esr (frozen 1:1 $EtOH/H_2O$, 113 K) $g_{//} = 2.28$, $A_{//} = 178 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.07$, $\lambda_{(max)} = 664$ nm (br) (nujol) d→d, $\mu_{(eff)} = 1.81$ BM.

✱ (4) Mercaptosuccinic acid: To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) in water (15 mls) was added dropwise a solution of mercaptosuccinic acid (0.30 g, 4 mmol) in water (5 mls). The resulting dark green solution was filtered and upon standing for a few days deposited a dark blue crystalline product. This was removed from solution by filtration, washed with water, then air dried (0.36 g, m.p. = 151-153°C). Microanalytical data calculated for $[Cu_2(bipy)_2(DTDS)]\cdot H_2O$: C, 43.7, H, 3.4, N, 7.3, S, 8.3; found: C, 43.4, H, 3.2, N, 7.3, S, 6.5 %. Electronic data: $\lambda_{(max)} = 647$ nm (br) (nujol), d→d, $\mu_{(eff)} = 1.92$ BM.

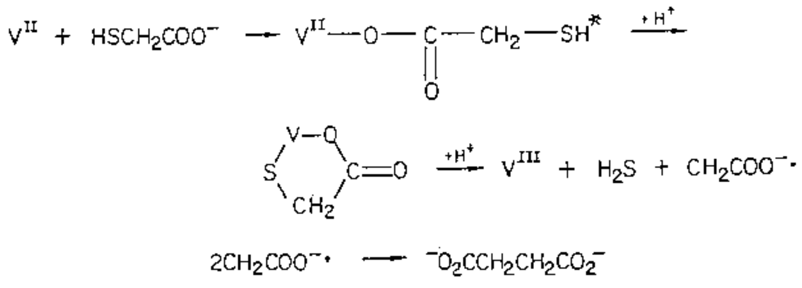
3.3 RESULTS

(1) Mercaptoacetic acid: Two different crystalline complexes were isolated and characterised from the copper(II)/bipy/maa reaction: dark blue needle crystals and dark green rhombic-shaped crystals. The microanalytical data and ir spectrum of the blue complex were consistent with the formulation $[Cu(bipy)(ox)]\cdot 2H_2O$, where ox = oxalate, $C_2O_4{}^{2-}$. A scan of the literature revealed that several ternary copper(II) complexes incorporating 2,2'-bipyridyl and the oxalate ion have been reported. Furthermore, recently it has been reported that they are subject to polymorphism, characterised by marked colour changes, along with changes in the electronic and esr spectrum [18]. O'Brien has reported the preparation and interconversion of a number of these mixed-ligand $Cu(bipy)(ox)\cdot xH_2O$ complexes. The information reported in this paper revealed that the blue and green complexes isolated from the copper(II)/bipy/maa system were in fact differently hydrated forms of the complex $[Cu(bipy)(ox)]\cdot nH_2O$, where n = 2 in the case of the blue form. The crystal structure of the blue modification has been reported [19].

The formation of oxalate ions from the reaction of mercaptoacetate with copper(II) is unexpected and the mechanism is unknown. The reaction did not occur when carried out under vacuum using deoxygenated solvent, which indicated that oxygen was necessary for the occurrence of this reaction. The loss of hydrogen sulphide from the maa may explain the fate of the sulphur in the reaction, as neither elemental sulphur nor sulphate were identified as coproducts. Attempts to detect H_2S were carried out by bubbling oxygen through the reaction mixture and then directing the stream of gas through a saturated solution of lead acetate. These attempts did not produce a black precipitate of lead sulphide and thus failed to identify H_2S.

The desulphurisation of mercaptoacetic acid is not unprecedented. One reaction, which has been reported recently and bears an interesting relevance to the present reaction, is the reductive desulphurisation of mercaptoacetic acid by vanadium(II) [20]. This reaction involves the interaction of V(II) with mercaptoacetic acid, in an inert environment, and results in the formation of a

V(III)-mercaptoacetate complex, succinic acid, and hydrogen sulphide. The authors of this paper propose a mechanism involving the free radical, $\cdot CH_2COO^-$, for the formation of succinic acid as shown in the equation:



The formation of oxalate from mercaptoacetate in the present reaction may also proceed via the formation of this radical species, generated by the redox activity of the Cu(I)/Cu(II) system. In the formation of the succinate ion, the authors proposed the coupling of two $\cdot CH_2COO^-$ radicals (in the absence of oxygen). In the present reaction, oxalate formation may possibly arise from the reaction of this $\cdot CH_2COO^-$ radical with oxygen.

(2) 3-Mercaptopropionic acid: The dark blue crystalline complex isolated from the copper(II)/bipy/3-mpa reaction was identified as a cupric compound from its magnetic moment, esr spectrum and uv-vis electronic spectrum. A sodium fusion test for the presence of sulphur was positive, although an unambiguous identification of the sulphur ligand present could not be made based solely on the microanalytical data. The possibility of a sulphato- or sulphonato-type ligand was excluded on the basis of the absence of $\nu(S=O)$ frequencies in the infrared spectrum. A subsequent X-ray crystallographic structure determination showed that the 3-mpa initially present had in fact been oxidised to its disulphide, dithiodipropionate (DTDP), which coordinates to the copper(II) ions, forming a complex of formulation $[Cu(bipy)(DTDP)]\cdot 2H_2O$.

(3) 2-Mercaptopropionic acid: The copper(II)/bipy/2-mpa reaction gave rise to a dark blue complex which was identified as a cupric complex by magnetic, esr and electronic spectral measurements. By analogy with the 3-mpa reaction, a product of similar formulation was anticipated for this reaction, <u>i.e.</u> that the formation of the

analogous disulphide, dithiodiisopropionate (DTDIP), had occurred. The microanalytical data supported this reasoning. A subsequent crystal structure determination of this complex confirmed that the ligand DTDIP was coordinated to the copper, the product being $[Cu(bipy)(DTDIP)]\cdot 3H_2O$. Details of the crystal structure determination and discussion of this complex are presented in section 3.6.

(4) Mercaptosuccinic acid: The msa reaction system appeared, superficially at least, very similar to those described for 2-mpa and 3-mpa. By analogy to these systems, the disulphide of msa may have formed and coordinated to the copper. The elemental analyses support this hypothesis, but do not exclude the possibility of the monosulphide of msa as the coordinated ligand (microanalytical data calculated for $[Cu_2(bipy)_2(DTDS)]\cdot H_2O$: C, 43.7, H, 3.4, N, 7.3, S, 8.3; found: C, 43.4, H, 3.2, N, 7.3, S, 6.5 %). The magnetic moment, esr and electronic spectral measurements indicate that the complex does contain copper(II), although, the exact identity of this complex remains unclear. Attempts to grow crystals suitable for X-ray analysis were unsuccessful.

3.4 COPPER-DISULPHIDE COMPLEXATION.

The thiol-disulphide system is biologically important because of the redox activities of copper proteins and the coordinating ability of sulphur [21]. Disulphide sulphur atoms have been postulated as being involved in copper binding in the 'blue' copper protein, stellacyanin. This has stimulated interest in the area of copper-disulphide complexation. Disulphides usually exhibit only weak ligation towards transition metal ions, and in the presence of copper(II) ions are often oxidatively cleaved. Cleavage of the disulphide bond has also been shown to occur with second and third row transition metal ions such as mercury and silver. Kinetic studies [22] have implicated the following mechanism.

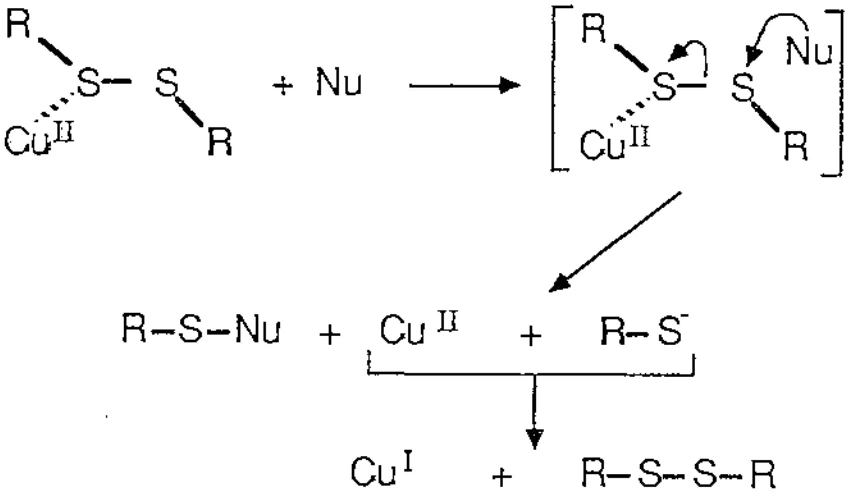
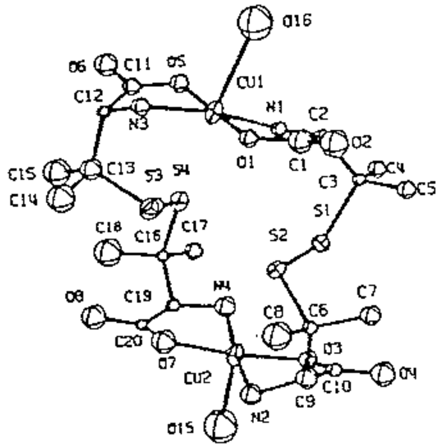


Figure 3.2 The Proposed Mechanism for the Copper(II) Catalysed Scission of a Disulphide Bond.

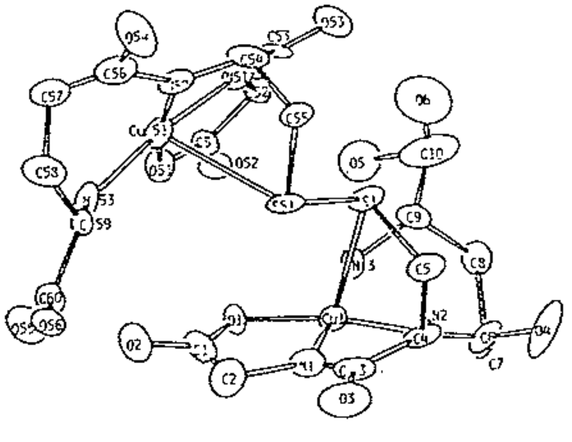
In the first stage of this reaction the S-S bond is polarised by the electrophilic copper(II) ion and thus rendered susceptible to nucleophilic attack. Subsequent nucleophilic attack (by water for example) cleaves the disulphide bond heterolytically as shown. The copper(II) is reduced to copper(I) by the thiol formed, reforming some disulphide. The cuprous ion is stabilised by complexation with that and excess disulphide.

This S-S cleavage reaction has naturally restricted structural studies on copper(II)-disulphide systems whereas copper(I)-disulphide complexes have been more fully characterised. The existing literature on copper(II)-disulphide complexes shows that copper(II)-disulphide complexation, though rare, is possible, although the -S-S- group will not always coordinate to the copper. This tendency is illustrated in figure 3.3 which summarises the previously reported Cu(II)-disulphide structures. The following sections report on the X-ray crystal structure determinations of two new copper(II)-disulphide complexes. These structures show that the geometrical nature of the disulphide ligand is an important factor which influences the outcome of the metal-ligand interaction.

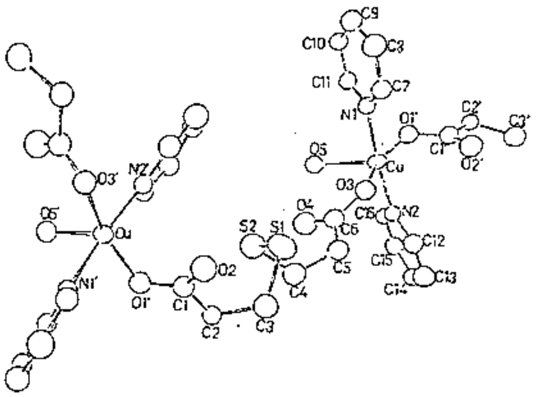
Figure 3.3 Previously reported copper(II)-disulphide structures.



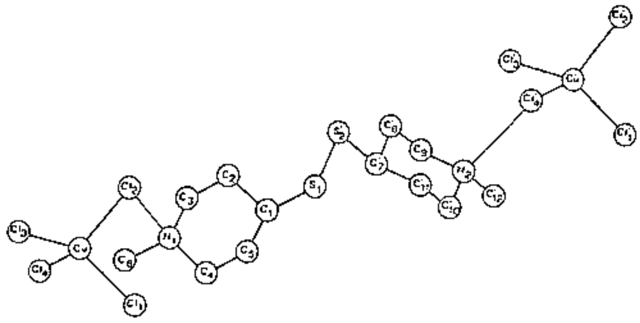
(I) $[Cu(D\text{-}PDS)]_2\cdot 9H_2O$



(II) $[Cu(GSSG)Cu]Na_4\cdot 6H_2O$



(III) $[Cu(py)_2(DTDP)(H_2O)]$
no Cu-S interaction [35].



(IV) $[C_5H_9NH(CH_3)S]_2CuCl_4$
no Cu-S interaction [42].

Metal-Sulphur Bond Distances, Å

				ref.
$[Cu(II)\text{-}D\text{-}PDS]_2\cdot 9H_2O$	Axial	M-S(disulphide)	3.057(10), 3.138(9)	[41]
$[Cu(II)GSSGCu(II)]Na_4\cdot 6H_2O$	Axial	M-S(disulphide)	3.16(1), 3.28(1)	[36]
$[Cu(bipy)(DTDIP)]\cdot 3H_2O$	Axial	M-S(disulphide)	2.678(2)	[this work]

D-PDS = D-penacillamine disulphide.

GSSG = the disulphide of glutathione.

DTDIP = dithiodiisopropionate

DTDP dithiodipropionate

3.5 THE CRYSTAL STRUCTURE DETERMINATION OF $[Cu(bipy)(DTDP)]\cdot 2H_2O$ (catena-2,2′-bipyridine-μ-(3,3′-dithiodipropionato-μ-O,O′,O′′)-copper(II) dihydrate).

CRYSTAL PREPARATION: Deep blue crystals of the complex $[Cu(bipy)(DTDP)]\cdot 2H_2O$ were obtained by the slow evaporation of an aqueous solution as outlined in section 3.2. The parallelepiped-shaped crystals were well formed and completely extinguished polarised light.

DATA COLLECTION: The data set used for this structure analysis was provided by Dr Ward Robinson using Canterbury University's Nicolet R3m diffractometer equipped with Mo radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. The data collection was carried out at 153 K and is summarised in table 3.1

SPACE GROUP DETERMINATION: The space group $P2_1/n$ was assigned unambiguously on the basis of the systematic absences, 0k0 $k = 2n + 1$, h0l $h + l = 2n + 1$.

STRUCTURE SOLUTION AND REFINEMENT: The solution and refinement of this structure was carried out with the assistance of Mr D. Lewandoski whose contribution constituted part of the research requirements for his Bachelor of Science with honours degree.

The software and procedures implemented in this structure solution and refinement are summarised in appendix A1, along with the relevant crystallographic equations and definitions.

The three dimensional Patterson synthesis yielded coordinates of the copper atom consistent with the space group $P2_1/n$. The remaining non-hydrogen atoms were located from subsequent Fourier maps. Several cycles of block diagonal least squares refinement involving the atomic coordinates, individual isotropic temperature factors and scale factor were implemented. Initially unit weights were applied and isotropic refinement resulted in a reliability index, R, which converged to 0.0757. A difference electron density map following this refinement revealed evidence for the anisotropic thermal motion of the heavy atoms. In the next round of calculations the copper and sulphur atoms were assumed to vibrate according to an anisotropic thermal model while the light atoms remained limited to isotropic thermal motion. Two cycles of full matrix least squares refinement reduced the reliability index to 0.0567. The non-water hydrogen atoms were visible in a difference map following this refinement, and were included at their geometrically calculated positions using a C-H bond length of 1.08 Å. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. The hydrogen atoms of the water molecules were located from subesequent difference maps and their positions were fixed in the last three cycles. For the final round of calculations a weighting scheme of the type

$$w = k / [\sigma_{(F)}^2 + gF^2]$$

was applied to the data, where $\sigma_{(F)}$ is the estimated standard deviation of $|F_o|$ and k and g are constants. The values of k and g were redetermined for each cycle of refinement which converged with values of k, g, R and R_w of 1.2342, 0.000619, 0.0376, and 0.0377 respectively for 2248 reflections with $I > 3\sigma_{(I)}$. The largest parameter shifts on the last cycle were less than 0.05 of the estimated standard deviations. A final difference map showed no peak higher than 0.5 eÅ^{-3} whereas the electron density of a typical carbon atom in this structure was approximately 4.0 eÅ^{-3}.

STRUCTURE DESCRIPTION: ORTEP representations of the complex [Cu(bipy)(DTDP)]·$2H_2O$ showing different sections of the ligand bridged polymer are shown in figures 3.4 and 3.5 together with the atomic numbering scheme and unit cell. Interatomic bond distances and angles are presented in table 3.2 and selected planes, torsion angles, and deviations are given in table 3.3

The structure contains no discrete molecules and consists of crystallographically equivalent copper(II) centres linked by DTDP ligands into infinite zigzag chains which extend along the b direction (figure 3.5). There are two uncoordinated water molecules associated with each asymmetric unit. There is no copper-sulphur bonding. The chains are connected into sheets via carboxylate oxygens which asymmetrically bridge adjacent copper atoms from neighbouring chains. The result is the formation of dimeric copper centres in which the Cu...Cu distance is 3.348(3) Å (figure 3.5).

The sheets are connected via a network of hydrogen bonding which involves the two water molecules and carboxylate oxygen atoms.

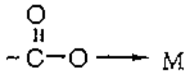
The Copper Coordination Environment: Two bipyridyl nitrogen atoms N1 and N2, and the carboxylate oxygen atoms 01 and 03 coordinate to the copper atom in an approximate square plane. (Cu-N1 = 1.988(3) Å, Cu-N2 = 1.995(4) Å, Cu-01 = 1.934(3) Å, Cu-03 = 1.961(3) Å). Axial bonding is established by the bridging carboxylate oxygen atom 03 which simultaneously occupies an equatorial position in one half of the dimer and an apical position (Cu-03′ = 2.231(4) Å) in the the other half. The coordination is completed by the carboxylate oxygen atom 04 which forms a weak pseudo-axial bond to the copper atom (Cu-04 = 2.826(5) Å) resulting in an irregular six-coordinate geometry. There is also a weak seventh contact between the bridging ligand and the copper atom (Cu-02 = 3.11 Å), but this is probably not a bonding interaction (see below). The geometry can be described as square pyramidal defined by the atoms Cu, N1, N2, 01, 03, and 03′, with an additional weakly coordinated sixth ligand (04) which deviates by approximately 40° from the axial position of an octahedron. The coordination sphere does possess features which suggest that a description in terms of octahedral symmetry is more appropriate. The four atoms, 01, 03, N1, and N2 exhibit poor planarity, but the copper atom is not significantly displaced from the best plane through these basal ligand atoms. In most distorted square pyramidal copper(II) complexes, the copper atom is displaced from the basal plane, typically by about 0.2 Å towards the apical ligand [23]. The absence of this type of distortion suggests that the weakly coordinated 04 atom restricts the copper atom to a position coplanar with the basal ligand atoms. The apical Cu-03′ bond deviates by 12.0° from the normal to the basal plane. These features suggest that the copper coordination environment appears to be more consistent with a tetragonally distorted octahedron, further distorted by the geometrical constraints of the four membered Cu-03-C6-04 chelate ring.

The bond distances within the copper coordination sphere all appear to be normal. The copper to nitrogen distances (Cu-N1 = 1.988(3) Å, Cu-N2 = 1.995(4) Å) are within the range of values usually found for copper(II)-bipyridyl coordination [24-26]. The copper to carboxylate bond distances in this structure are consistent with previously reported copper(II) carboxylate structures (mean Cu-O(carboxyl) = 1.97(24) [27]). A good basis for comparison of these bond lengths is provided in a report by Freeman which summarises the metal to ligand bond lengths in a variety of transition metal complexes containing amino acids, peptides, and imidazole [27]. The two carboxylate groups have very similar orientations (figure 3.5). Although the difference is small, one can be considered to be chelating and the other non-chelating. This difference is reflected in the equatorial bond lengths. The carboxylate group which has the strongest axial interaction (i.e. the chelating carboxylate) also has the weaker equatorial bond. The equatorial Cu-O(carboxyl) distance for the chelated carboxylate is Cu-O3 = 1.961(3) Å whereas that for the unchelated carboxylate is Cu-O1 = 1.934(3) Å).

The electron configuration of the copper(II) ion gives rise to a Jahn-Teller distortion which, in an octahedral environment, is manifested by a lengthening of the axial Cu to ligand bonds [28]. The exact nature and extent of the Jahn-Teller effect depends on the electronic state of the ion with respect to the degeneracy of the Eg orbitals, and energetic considerations of the complex as a function of all possible types and degrees of distortion. For this structure, the Jahn-Teller effect can be assessed by considering the Cu-O3′ axial bond length. In the case of carboxyl-oxygen atoms, the shortest Cu-O bonds reported in a direction perpendicular to the coordination square plane are 2.30 Å long [27]. This implies that the minimum Jahn-Teller distortion expected for complexes of this type corresponds to an increase of about 0.3 Å in the radius of the copper(II) ion in the direction of the apical ligand. The value of 2.231(4) Å for the Cu-O3′ bond length indicates that there is a minimal Jahn-Teller distortion and that this bond length lies near the short end of the range expected for such linkages.

The 2,2′-bipyridyl Ligand: The bond lengths and angles in the bipyridyl ligand agree well with the values usually found in these systems [25-26, 29-30]. The pyridine rings are individually planar but do not lie in the same plane due to a 4.39° twist about the C11-C12 bond.

The DTDP Ligand: The DTDP ligand exhibits no unusual structural features. Both carboxylate groups possess C-O bond lengths consistent with



$$-\overset{O}{\overset{\|}{C}}-O\longrightarrow M$$

units. One of the carboxylate groups of DTDP is chelated to the copper whereas the other is essentially monodentate; one oxygen atom is coordinated, but the other is 3.11 Å from the copper. This distance is too long to be considered a significant interaction, and is thus considered a minor feature of the coordination (c.f. range of values reported for chelating carboxyl groups: Cu-(second carboxyl-oxygen) = 2.59 - 2.94 Å) [27]). The non-equatorial carboxylate oxygen atoms O2 and O4 are also involved in hydrogen bonding to the water molecules. The probable hydrogen bonding contacts are listed in table 3.2 and lie within the range of values usually observed for such interactions [31].

The S-S bond length is 2.032(5) Å, and the S-S torsion angle is 84.5°. According to Hordvik [32], the length of a S-S bond is affected by repulsions between the lone pairs of electrons on adjacent atoms. This repulsion is greatest when the torsion angle CS-SC is 0°, that is, when this part of the molecule is cis and planar. Alternatively, pi-bonding is most pronounced when this angle is 90°, when two p_π-d_π overlaps, at right angles, are possible and this part of the molecule is nonplanar. Jones et al. [33] have presented a detailed summary of Hordvik's conclusions, along with an extensive tabulation of aliphatic-disulphide structural data. These data show that for aliphatic disulphides with torsion angles near 90°, the S-S bond lengths fall in the range 2.00 Å to 2.05 Å, which is consistent with the values observed in the present structure.

Table 3.1 Crystallographic Data for [Cu(bipy)(DTDP)]·$2H_2O$.

Formula.	(Cu,C16,H16,N2,O4,S2)·$2H_2O$
Mol. wt.	463.5
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
a, Å	9.686(4)
b, Å	9.409(3)
c, Å	21.231(4)
β, deg.	102.0(2)
Z	4
V, $Å^3$	1893(1)
* F(000)	948.0
D(calc), gcm^{-3}	1.62
D(obsd), gcm^{-3}	1.61
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator $\lambda = 0.71069$ Å
Temp., K	153
Reflns. Measd.	h,k,±l
Scan type.	ω/2θ
Scan range, deg.	1.4
Scan speed, deg/min.	5.86
Max. 2θ, deg.	45
Measd. Reflns.	3356
Unique reflns.($I > 3\sigma_{(F)}$)	2248
Cryst. dimensions, mm	0.7 x 0.1 x 0.08
Wtg scheme	$1.2342 / [\sigma_{(F)}^2 + 0.000619F^2]$
Abs. coeff., cm^{-1}	13.36
Trans. factors	Max. 0.777 Min. 0.762
R	0.0376
R_w	0.0377

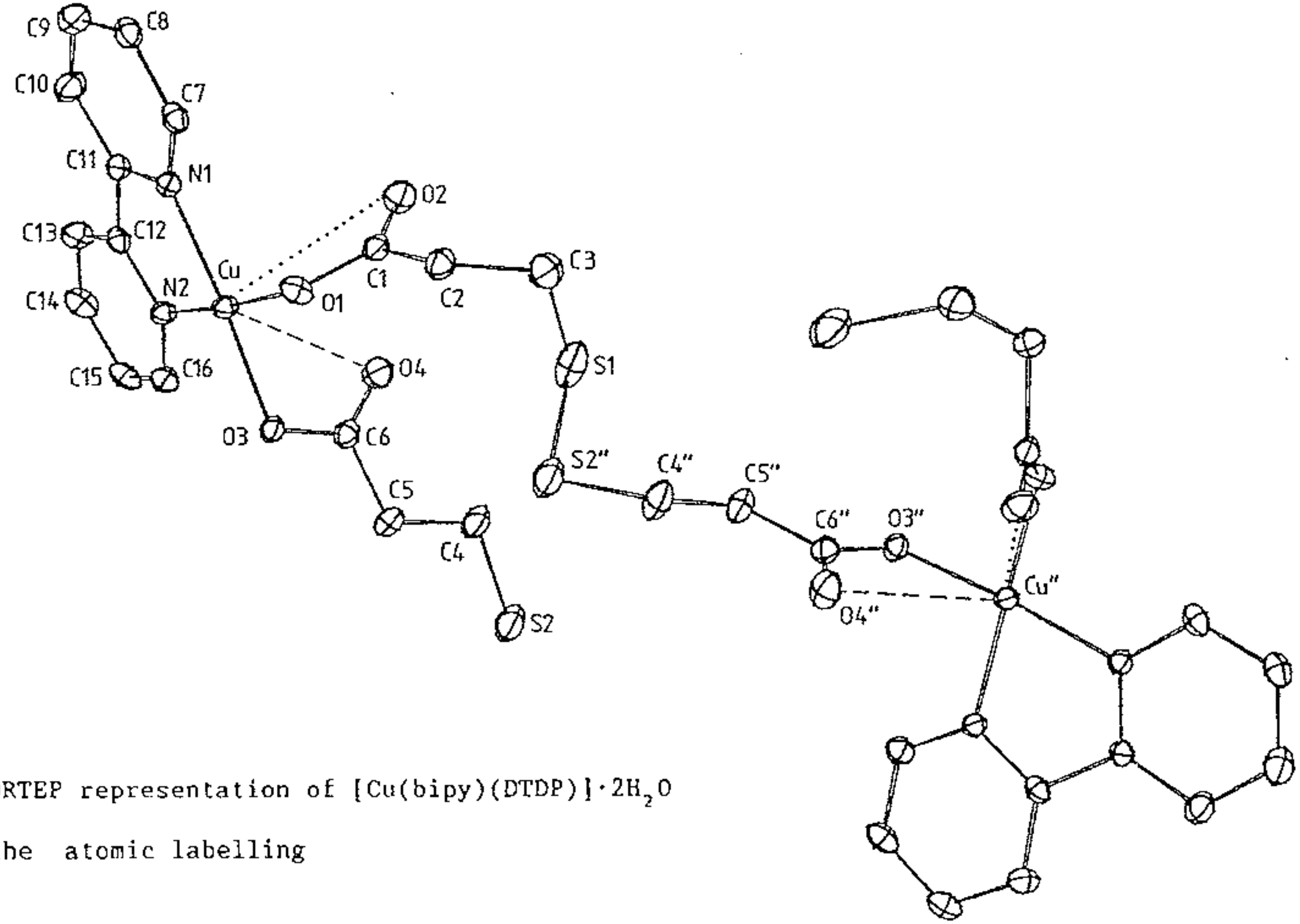


Figure 3.4 The ORTEP representation of [Cu(bipy)(DTDP)]$\cdot 2H_2O$ showing the atomic labelling

Figure 3.5 The ORTEP representation of [Cu(bipy)(DTDP)]·$2H_2O$ showing the coordination sphere and stereoscopic unit cell.

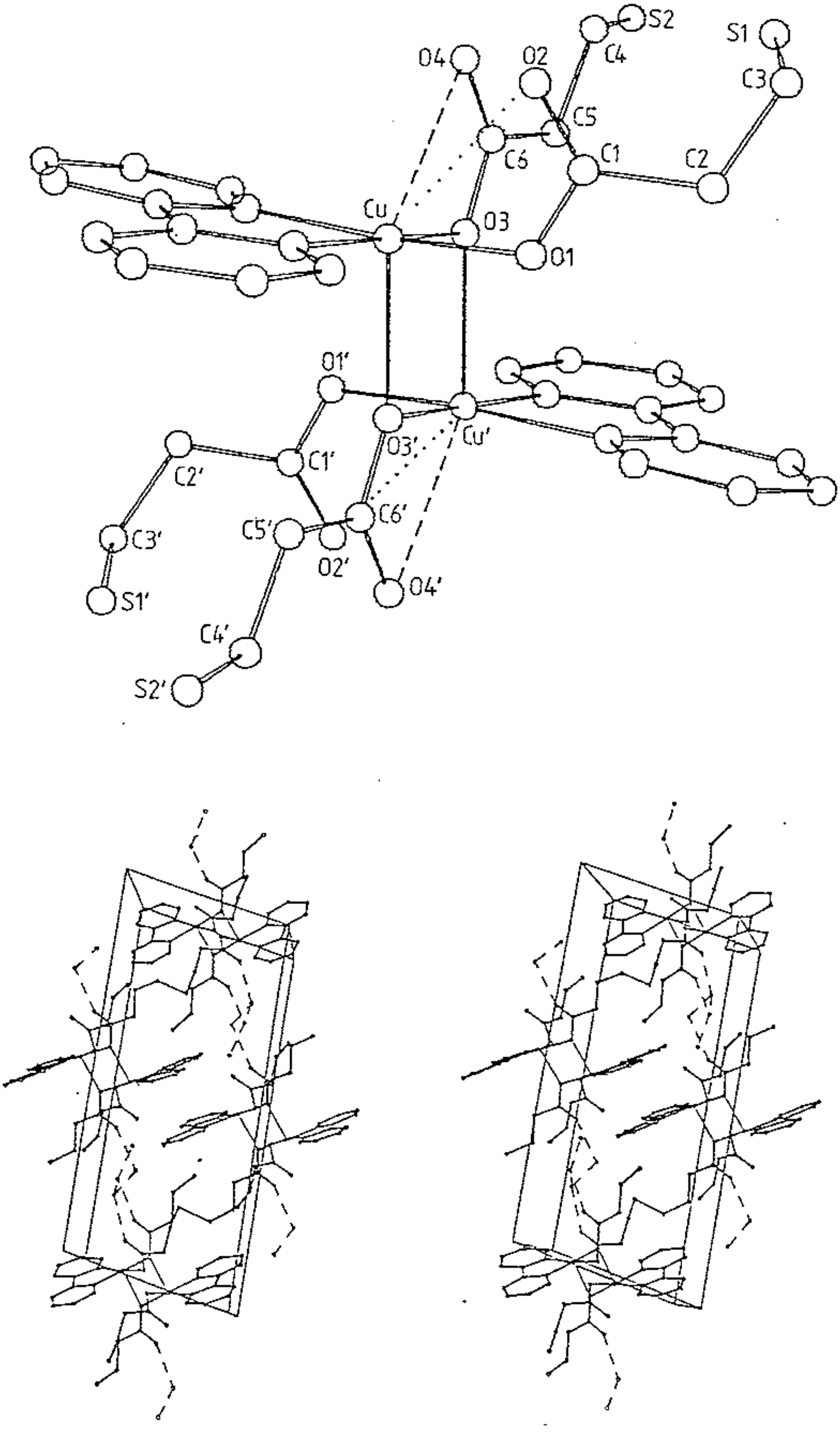


Table 3.2 Bond Distances(Å) and Angles(deg.) in $[Cu(bipy)(DTDP)]\cdot 2H_2O$.

Cu...Cu′	3.348(3)	C4-C5	1.506(6)
Cu-O1	1.934(3)	C5-C6	1.513(6)
Cu-O3	1.961(3)	C6-O3	1.294(5)
Cu-O3′	2.231(4)	C6-O4	1.225(5)
Cu-O4	2.826(5)	C7-C8	1.374(6)
Cu-N1	1.988(3)	C8-C9	1.387(6)
Cu-N2	1.995(4)	C9-C10	1.375(7)
S1-S2′′	2.032(5)	C10-C11	1.389(6)
S2-C4	1.814(5)	C11-N1	1.343(5)
N1-C7	1.346(6)	C11-C12	1.473(6)
N2-C12	1.360(5)	C12-C13	1.386(6)
C1-O1	1.286(5)	C13-C14	1.381(6)
C1-O2	1.230(5)	C14-C15	1.397(6)
C1-C2	1.519(6)	C15-C16	1.380(6)
C2-C3	1.510(7)	C16-N2	1.335(6)
C3-S1	1.808(5)		

O1--Cu--N1	96.0(1)	C6--O3--Cu′	144.7(3)
O1--Cu--N2	173.8(1)	C6--O4--Cu	73.0(3)
O1--Cu--O3	89.1(1)	O1--C1--O2	125.1(4)
O1--Cu--O3′	91.3(1)	O1--C1--C2	113.6(4)
O1--Cu--O4	92.0(1)	O2--C1--C2	121.2(4)
O3--Cu--N1	174.8(1)	C1--C2--C3	113.8(4)
O3--Cu--N2	94.1(1)	C2--C3--S1	114.1(4)
O3--Cu--O3′	77.5(1)	S2--C4--C5	114.3(4)
O3--Cu--O4	51.3(1)	C4--C5--C6	113.6(4)
N1--Cu--N2	80.9(1)	C5--C6--O3	115.0(4)
N1--Cu--O4	129.2(1)	C5--C6--O4	122.6(4)
N1--Cu--O3′	101.4(1)	O3--C6--O4	122.4(4)
N2--Cu--O4	85.9(1)	N1--C7--C8	121.9(4)
N2--Cu--O3′	94.6(1)	C7--C8--C9	119.1(4)
O4--Cu--O3′	128.5(1)	C8--C9--C10	119.3(4)
C3--S1--S2′	103.6(3)	C9--C10--C11	118.9(5)
C11--N1--Cu	115.6(3)	C10--C11--C12	123.8(4)
Cu--N1--C7	125.3(3)	C10--C11--N1	121.7(4)
C11--N1--C7	118.9(4)	N1--C11--C12	114.5(4)
C16--N2--C12	119.1(4)	C11--C12--C13	124.5(4)
C16--N2--Cu	126.4(3)	C11--C12--N2	114.1(4)
Cu--N2--C12	114.9(3)	N2--C12--C13	121.5(4)
C1--O1--Cu	121.1(3)	C12--C13--C14	119.5(4)
C6--O3--Cu	112.9(3)	C13--C14--C15	118.8(4)
Cu--O3--Cu′	102.5(3)	C14--C15--C16	118.7(4)
		C15--C16--N2	122.8(4)

Probable Hydrogen Bonding Contacts and Angles in $[Cu(bipy)(DTDP)]\cdot 2H_2O$.

O5...O4	2.720	O4--O5--O6(I)	102.2
O5...O6	2.768	O4--O5--O6	95.4
O5...O6(I)	2.781	O6--O5--O6(I)	154.3
O6...O2(II)	2.722	O5--O6--O5(II)	120.6
O6...O5(II)	2.781	O5--O6--O2(II)	124.7
		O5(II)--O6--O2(II)	90.7

The Postscripts Refer To The Following Positions.

(I) (0.5-X,Y-0.5,0.5-Z) (II) (0.5-X,0.5+Y,0.5-Z)

Table 3.3 Selected least-squares planes and deviations (Å) in $[Cu(bipy)(DTDP)]\cdot 2H_2O$.

Atoms in the Plane: Cu, N1, N2, O1, O3

Equation: $(0.6116)X + (-0.1894)Y + (-0.7681)Z - (-9.0409) = 0$

χ^2: 3429

Deviations:	Cu	-0.03	N2	0.06
	N1	-0.05	O1	0.06
	O3	-0.05	O2	2.15
	O4	2.15		

Atoms in the Plane: N1, N2, O1, O3

Equation: $(0.6118)X + (-0.1893)Y + (-0.7680)Z - (9.0323) = 0$

χ^2: 995.3

Deviations:	Cu	-0.04	N1	-0.06
	N2	0.06	O1	0.05
	O3	-0.06	O2	2.15
	O4	2.14		

Atoms in the Plane: N1, C7, C8, C9, C10, C11

Equation: $(0.6288)X + (-0.2473)Y + (-0.7372)Z - (-8.8975) = 0$

χ^2: 8.84

Deviations:	N1	-0.01	C7	0.00
	C8	0.00	C9	0.00
	C10	0.00	C11	0.01
	Cu	-0.09	O1	0.06
	O2	2.20	O3	-0.23
	O4	1.96		

Atoms in the Plane: N2, C12, C13, C14, C15, C16

Equation: $(0.5727)X + (-0.2597)Y + (-0.7775)Z - (-9.4872) = 0$

χ^2: 7.25

Deviations:	N2	0.01	C12	0.00
	C13	0.00	C14	0.00
	C15	0.00	C16	-0.01
	Cu	0.07	N1	0.05
	O1	0.32	O2	2.42
	O3	0.05	O4	2.22

3.6 THE CRYSTAL STRUCTURE DETERMINATION OF [Cu(bipy)(DTDIP)]·$3H_2O$ (catena-2,2′-bipyridine-μ-(2,2′-dithiodipropionato-O,O′,S)-copper(II) trihydrate).

CRYSTAL PREPARATION: Deep blue prism-shaped crystals of the complex [Cu(bipy)(DTDIP)]·$3H_2O$ were obtained by the slow evaporation of an aqueous solution as described in section 3.2. The crystals were small but well formed and completely extinguished polarised light.

DATA COLLECTION: A single crystal of dimensions 0.26 x 0.24 x 0.18 mm was mounted on Canterbury University's Nicolet R3m four-circle diffractometer equipped with Mo radiation (λ = 0.71069 Å) and a graphite monochromator. The data collection was carried out at 153 K and is summarised in table 3.4.

SPACE GROUP DETERMINATION: An examination of the intensity statistics revealed no systematic absences. The choice of the triclinic space group P1 was confirmed by the successful refinement of the structure.

STRUCTURE SOLUTION AND REFINEMENT: The software and procedures implemented in this structure solution and refinement are summarised in appendix A1, along with the relevant crystallographic equations and definitions. The three dimensional Patterson synthesis yielded coordinates of the copper atom which were consistent with a subsequent direct methods structure solution. The remaining non-hydrogen atoms were located from subsequent Fourier maps. Several cycles of block diagonal least squares refinement involving the atomic coordinates, individual isotropic temperature factors and scale factor were implemented. Initially unit weights were applied and isotropic refinement resulted in a reliability index, R, which converged to 0.0966.

A difference electron density map following this refinement revealed evidence for the anisotropic thermal motion of the heavy atoms. In the next round of calculations the copper and sulphur atoms were assumed to vibrate according to an anisotropic thermal model while the light atoms remained limited to isotropic thermal motion. Two cycles of full matrix least squares refinement reduced the reliability index to 0.0826. An inspection of a difference map calculated at this stage revealed a number of peaks, three of which were within close proximity to the disulphide ligand and had heights approximately 1 e$Å^{-3}$. The distances and angles associated with these peaks indicated that they were consistent with a second conformation of the disulphide ligand resulting from a twofold disorder of the atoms C2, O2, and C3. The isotropic thermal parameters associated with the atoms originally assigned as C2, O2, and C3 were found to be marginally higher than the mean values of the other carbon and nitrogen atoms in the structure, indicating that the site occupancy factors originally assigned to these atoms were probably incorrect. In order to refine the site occupancy factors of the disulphide atoms involved in the disorder, the atoms concerned were included in a cycle of least squares with the isotropic thermal parameters fixed at 0.04. This refinement resulted in site occupancy values close to 0.75 for the original portion of the disulphide ligand and values close to 0.25 for the remaining three positions. Reinspection of the difference map revealed that the remaining three highest peaks were located close to the oxygen atoms of the three water molecules. The original positions of the three disordered disulphide atoms and the three water molecules were assigned site occupancy factors of 0.75 and the remaining corresponding positions were assigned values of 0.25. The inclusion of these atoms in a further two cycles of least squares refinement lowered the reliability index to 0.0766.

The non-water hydrogen atoms were observed in the difference map obtained from this refinement, and were included at their geometrically calculated positions using a C-H bond length of 1.08 Å. Anisotropic thermal parameters were introduced for all non-hydrogen atoms, except those atoms with site occupancy factors of 0.25, and three further cycles of least squares refinement converged at reliability indices, R and R_w, of 0.0553 and 0.0566 respectively for 1935 reflections with $I > 3\sigma_{(I)}$. The largest parameter shifts on the last cycle were less than 0.05 of the estimated standard deviations.

For the last few cycles of refinement a weighting scheme of the type

$$w = k / [\sigma_{(F)}^2 + gF^2]$$

was applied to the data, where $\sigma_{(F)}$ is the estimated standard deviation of |Fo| and k and g are constants. The values of k and g were redetermined for each cycle of refinement. This resulted in a reasonable distribution of variance with respect to $|F_o|$ and sinθ with final values of 2.9332 and 0.000296 for k and g respectively. A final difference map showed no peak higher than 0.6 $eÅ^{-3}$ whereas the electron density of a typical carbon atom in this structure was approximately 4.0 $eÅ^{-3}$. Efforts to locate unambiguously the hydrogen atoms of the water molecules were unsuccessful.

STRUCTURE DESCRIPTION: ORTEP representations of the polymeric complex $[Cu(bipy)(DTDIP)]\cdot3H_2O$ and its packing are shown in figures 3.6 and 3.7. Interatomic bond distances and angles are given in table 3.5 along with selected torsion angles, planes, and deviations in table 3.6.

The structure contains no discrete molecules and consists of crystallographically equivalent copper(II) centres linked by DTDIP ligands into infinite chains which extend along the a direction. There are three uncoordinated water molecules per copper which participate in a hydrogen bonding network that connects DTDIP ligands in adjacent chains. A portion of the disulphide ligand and the water molecules are disordered over two positions. The disorder associated with the DTDIP ligand is shown in figure 3.7.

The Copper Coordination Environment: The cis arrangement of bipyridyl-nitrogen atoms and carboxylate-oxygen atoms O1 and O3 coordinate to the copper atom in an approximate square plane, where Cu-N1 = 1.998(6) Å, Cu-N2 = 2.008(6) Å, Cu-O1 = 1.925(5) Å, and Cu-O3 = 1.981(5) Å. The distorted square pyramidal coordination geometry is completed by the apically bound disulphide sulphur atom S1, (Cu-S1 = 2.678(2) Å). The planarity of the four basal donor atoms is poor, but the copper is clearly displaced towards the sulphur (0.1 Å) from the best plane though these atoms. The poor planarity of the basal atoms may originate from steric interactions between the bipyridyl 3,3′-hydrogen atoms and the disulphide ligand forcing the bipyridyl ligand to twist out of the equatorial plane. This type of distortion is a bulk effect which has been recognised in other copper(II)-bipyridyl complexes [23]. The Cu-S1 bond deviates by 13.9° from the normal to the basal plane. This distortion may arise as a consequence of the geometrical constraints imposed by the five-membered chelate ring (atoms Cu, O1, C1, C2, and S1).

The copper to nitrogen distances are normal for copper(II)-bipyridyl coordination [24-26]. The copper to carboxylate distances are not equivalent, viz. Cu-O1 = 1.925(5) Å and Cu-O3 = 1.981(5) Å. The latter falls within the range of values expected for equatorially bound, monodentate carboxylate groups (1.97(24) Å [27]), whereas the former is somewhat shorter.

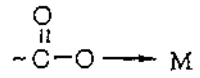
The particularly short apical Cu-S(disulphide) bond distance is the most significant feature of the overall coordination environment. Disulphide complexation with first row transition metals is rare, and to our knowledge, with copper(II) only two examples have been previously characterised crystallographically. These complexes and their respective Cu-S distances are listed in table 3.7 which also lists a number of previously reported M-S(thioether or disulphide) distances. For Cu-S(thioether) interactions, the equatorial Cu-S bond lengths are normally within the range 2.30-2.41 Å [43]. In the case of Cu-O interactions, apical distances are typically 0.3-0.5 Å longer than the corresponding equatorial ones [27]. On this basis, the Cu(II)-S(disulphide) distance should probably lie in the range 2.6-2.9 Å. The observed Cu-S1 distance of 2.678(2) Å lies at the short end of this range and clearly represents a moderately strong copper-sulphur interaction. This value is also in the range calculated by summing the Pauling covalent radii (Cu = 1.30 Å, S = 1.04 Å [34]), and allowing for a 0.3-0.5 Å apical lengthening.

The coordination environment exhibited by [Cu(bipy)(DTDIP)]$\cdot 3H_2O$ provides an interesting contrast with the crystal structures of [Cu(bipy)(DTDP)]$\cdot 2H_2O$ (this work) and that of [Cu(DTDP)]$\cdot$2Py$\cdot 2H_2O$ [35], both of which contain the chain isomer of DTDIP, DTDP. These latter complexes are ligand bridged polymers, but neither displays Cu-S coordination. The most comparable previously reported structure is that of the binuclear copper(II) glutathione complex [Cu(II)GSSGCu(II)]$\cdot Na_4 \cdot 6H_2O$ [36]. The copper centres in this complex are shown in figure 3.3. The two five coordinate CuN_3OS centres are connected through a disulphide bridge formed between the two cysteinyl side chains. The coordination geometry around each copper atom is approximately square pyramidal with apical copper-sulphur(disulphide) distances of Cu-S1 = 3.11(1) Å and Cu-S51 = 3.28(1) Å. The disulphide sulphur atoms participate in five membered chelate rings involving the copper, and although the two copper coordination geometries in this complex are really quite similar to that in the present structure, the long Cu-S distances are indicative of significantly weaker metal-ligand interactions. The origin of this weakening is probably attributable to the fact that the multidentate GSSG ligand is considerably less flexible than DTDIP due to the geometrical constraints imposed by its chelation to the copper atom.

The 2,2′-Bipyridyl Ligand: The bond lengths and angles in the 2,2′-bipyridyl ligand agree well with the values usually found in these systems [25-26, 28-29]. The pyridine rings are individually planar and virtually coplanar with each other, but for a 1.30° twist about the C11-C12 bond.

The DTDIP Ligand: The DTDIP atoms O2, C2, and C3, are involved in a twofold disorder over the positions O2a, C2a, and C3a respectively, as shown in figure 3.7. The site occupancies are 0.75 for the former and 0.25 for the latter. In addition, the three water molecules are similarly disordered, each occupying positions O5, O5a, O6, O6a, O7, and O7a. Each of the two orientations corresponds to a different hydrogen bonding network within the crystal lattice. The molecular orientation which includes the atoms with occupancies of 0.25 is necessarily poorly defined and will not be considered in detail. The hydrogen bonding scheme associated with atoms O5, O6, and O7 is shown in figure 3.7 along with the O..O distances and angles in table 3.5. The O..O distances are within the range reported for typical hydrogen bonding interactions [31].

The carboxylate groups of the DTDIP ligand are monodentate to the copper and possess C-O bond distances consistent with



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O\longrightarrow M$$

units. The C-S bond lengths of 1.856(9) Å and 1.811(11) Å are comparable with other reported disulphides [37]. The conformation of the five membered chelate ring which includes Cu, S1, C1, C2, and O1 is denoted by the endocyclic torsion angles given in table 3.6. The bond lengths and angles in the half of the disulphide ligand which is involved in the chelate ring show no unusual differences in comparison with the remainder. This indicates that there is not a great deal of strain introduced by the sulphur coordination.

Jones et al. [33] have produced a detailed summary of bond distances, bond angles, and torsion angles for molecules containing aliphatic C-S-S-C fragments.

The S-S bond length in $[Cu(bipy)(DTDIP)]\cdot 3H_2O$ is 2.043(3) Å which lies in the range reported for aliphatic disulphides (2.00-2.084 Å). As discussed in section 3.5 Jones et al. have proposed that there is a relationship between the S-S bond length and the τ[S-S] torsion angle. The τ[S-S] torsion angle of 90.07° in the present complex clearly places the DTDIP ligand in the category of disulphides with torsion angles near 90°, and as such the S-S bond length of 2.043(3) Å is consistent with the interpretation proposed by Jones. The interaction of the sulphur atom with the copper evidently does not shift sufficient electron density away from the sulphur atom (or sufficient electron density into the σ^* system of the S-S group) to produce an observable S1-S2 bond lengthening.

Table 3.4 Crystallographic Data for $[Cu(Bipy)(DTDIP)]\cdot 3H_2O$.

Formula	$(Cu,C16,H16,N2,O4,S2)\cdot 3H_2O$
Mol. wt.	481.5
Cryst. syst.	Triclinic
Space group	P1
a, Å	8.598(5)
b, Å	10.378(6)
c, Å	11.205(6)
α, deg.	96.43(5)
β, deg.	94.34(4)
γ, deg.	91.16(5)
Z	2
V, $Å^3$	990(1)
F(000)	494
$D_{(calc)}$, gcm^{-3}	1.62
$D_{(obsd)}$, gcm^{-3}	1.60
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator, $\lambda = 0.71069$ Å
Temp., K	153
Reflns. Measd.	h, ±k, ±l
Scan type	$\omega/2\theta$
Scan range, deg.	2.0
Scan speed, deg/min.	5.86
Max. 2θ, deg.	45
Measd. Reflns.	2674
Unique reflns.($I > 3\sigma_{(I)}$)	1935
Cryst. dimensions (dist. from centroid, mm)	±(100), 0.09
	±(010), 0.13
	±(001), 0.12
	±(011), 0.09
Abs. Corrn. Type.	Empirical
Wtg scheme.	$2.9332 / [\ \sigma_{(F)}^2 + 0.000296F^2\ ]$
Abs. coeff., cm^{-1}	12.82
Trans. Factors	Max. 0.794 Min. 0.771
R	0.0553
R_w	0.0566

Figure 3.6 The ORTEP representation of [Cu(bipy)(DTDIP)]·$3H_2O$ showing the atomic labelling and stereoscopic unit cell.

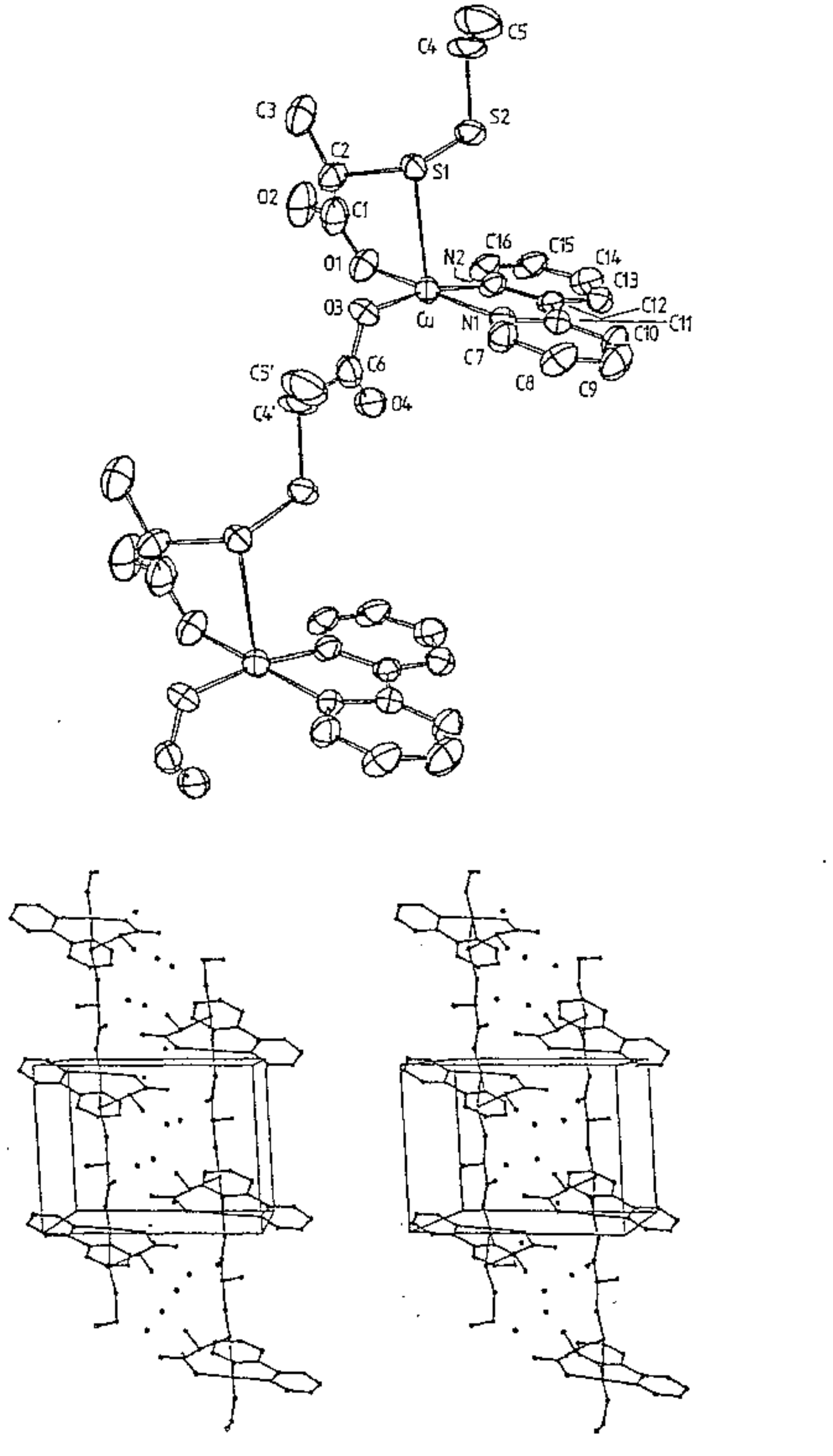


Figure 3.7 The ORTEP representation of $[Cu(bipy)(DTDIP)]\cdot 3H_2O$ showing the disorder of the DTDIP ligand and the hydrogen bonding network.

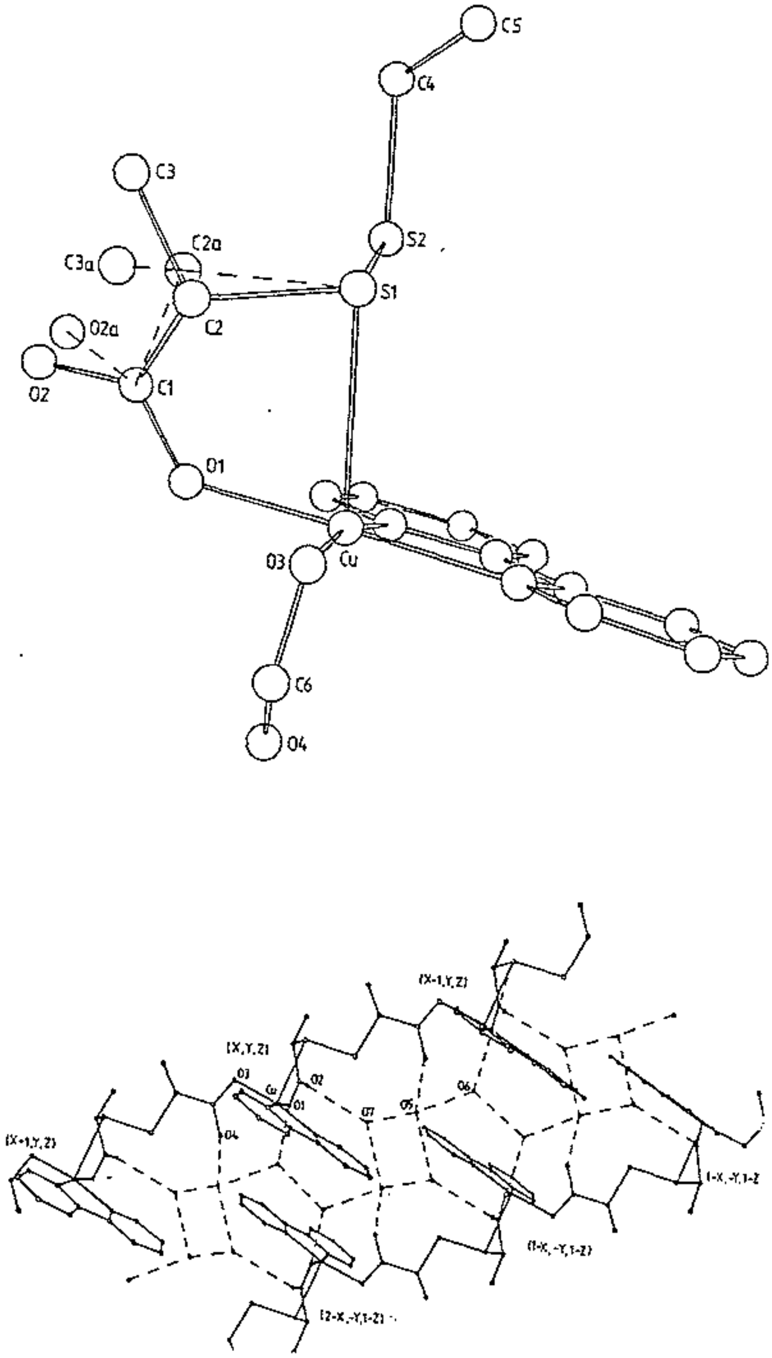


Table 3.5 Bond Lengths(Å) and Angles(deg.) in
[{Cu(bipy)(DTDIP)]·3H$_2$O.

Cu-O1	1.925(5)	C2-S1	1.811(11)
Cu-O3	1.981(5)	C2a-S1	1.954(10)
Cu-N1	1.998(6)	C2a-C3a	1.552(10)
Cu-N2	2.008(6)	C4-C5	1.427(13)
Cu-S1	2.678(2)	C4-C6	1.591(11)
S1-S2	2.043(3)	C6-O3	1.271(10)
S2-C4	1.856(9)	C6-O4	1.233(10)
N1-C7	1.350(9)	C7-C8	1.345(11)
N1-C11	1.338(9)	C8-C9	1.359(12)
N2-C16	1.336(9)	C9-C10	1.389(11)
N2-C12	1.349(9)	C10-C11	1.378(10)
C1-O1	1.253(11)	C11-C12	1.491(10)
C1-O2	1.213(11)	C12-C13	1.378(10)
C1-O2a	1.358(9)	C13-C14	1.391(11)
C1-C2	1.635(15)	C14-C15	1.354(12)
C1-C2a	1.374(11)	C15-C16	1.376(11)
C2-C3	1.466(16)		

O1--Cu--O3	94.4(2)	C3--C2--S1	113.4(8)
O1--Cu--S1	80.6(2)	C1--C2a--C3a	107.8(4)
O1--Cu--N1	172.2(2)	C1--C2a--S1	113.5(4)
O1--Cu--N2	91.6(2)	C3a--C2a--S1	107.3(1)
O3--Cu--S1	86.5(2)	C2--S1--S2	111.2(4)
O3--Cu--N1	92.6(2)	C2--S1--Cu	86.6(4)
O3--Cu--N2	169.2(2)	S2--S1--Cu	96.8(1)
S1--Cu--N1	103.3(6)	C2a--S1--S2	92.8(1)
S1--Cu--N2	103.4(2)	C2a--S1--Cu	89.0(1)
N1--Cu--N2	81.0(2)	S1--S2--C4	102.5(3)
C11--N1--Cu	115.5(5)	S2--C4--C5	114.8(7)
C7--N1--Cu	125.2(5)	S2--C4--C6	101.4(6)
C11--N1--C7	119.2(7)	C5--C4--C6	114.2(8)
C16--N2--Cu	127.5(6)	C4--C6--O3	114.8(8)
C12--N2--Cu	114.6(5)	C4--C6--O4	120.6(8)
C16--N2--C12	117.8(7)	O3--C6--O4	124.5(7)
O1--C1--O2	124.5(1.0)	N1--C7--C8	121.2(8)
O1--C1--C2	114.3(8)	C7--C8--C9	120.5(8)
O1--C1--O2a	123.2(8)	C8--C9-C10	119.4(8)
O1--C1--C2a	127.3(8)	C9--C10--C11	117.8(8)
O2--C1--C2a	114.5(9)	C10--C11--N1	121.9(7)
O2--C1--C2	119.7(1.0)	C10--C11--C12	123.8(7)
O2a--C1--C2a	102.1(7)	C12--C11--N1	114.3(7)
O2a--C1--O2	24.8(4)	C11--C12--C13	123.2(7)
C2--C1--O2a	120.4(8)	C11--C12--N2	114.5(7)
C2--C1--C2a	21.5(4)	N2--C12--C13	122.3(7)
Cu--O1--C1	127.6(6)	C12--C13--C14	118.4(8)
Cu--O3--C6	105.0(5)	C13--C14--C15	119.4(8)
C1--C2--C3	112.9(1.0)	C14--C15--C16	119.2(7)
C1--C2--S1	108.6(7)	C15--C16--N2	122.8(8)

Probable Hydrogen Bonding Contacts and Angles for
[Cu(bipy)(DTDIP)]·3H$_2$O.

O5...O7	2.715	O7--O5--O6	114.6
O5...O7(I)	2.722	O7--O5--O7(I)	92.0
O5...O6	2.808	O7--O5--O4(II)	130.1
O5...O4(II)	2.809	O7(I)--O5--O6	95.8
O6...O1(II)	2.820	O7(I)--O5--O4(II)	132.7
O6...O6(III)	2.652	O6--O5--O4(II)	85.8
O7...O2	2.880	O6(III)--O6--O5	110.1
		O6(III)--O6--O1(II)	111.4
		O5--O6--O1(II)	103.5
		O5--O7--O5(I)	88.0
		O5--O7--O2	118.9
		O5(I)--O7--O2	134.8

The postscripts refer to the following positions.

(I) (1-X,-Y,1-Z) (II) (X-1,Y,Z) (III) (-X,-Y,1-Z)

Table 3.6 Selected least-squares planes, deviations (Å), and torsion angles in [Cu(bipy)(DTDIP)]$\cdot$3H_2O.

Atoms in the Plane: O1, O3, N1, N2

Equation: $(-0.7779)X + (0.6134)Y + (-0.1361)Z - (-4.8490) = 0$

χ^2: 355.0

Deviations:

O1	0.05	O3	-0.05
N1	0.05	N2	-0.06
Cu	0.10	C1	0.98
C6	-1.30	S1	2.70

Atoms in the Plane: Cu, O1, O3, N1, N2

Equation: $(-0.7782)X + (0.6129)Y + (-0.1369)Z - (-4.8340) = 0$

χ^2: 7938

Deviations:

Cu	0.08	N1	0.04
N2	-0.07	O3	-0.07
O1	0.03	C1	0.95
C6	-1.32	S1	2.68

Atoms in the Plane: N1, C7, C8, C9, C10, C11

Equation: $(-0.8191)X + (0.5471)Y + (-0.1725)Z - (-5.2747) = 0$

χ^2: 4.23

Deviations:

N1	-0.01	C7	0.01
C8	-0.01	C9	0.00
C10	0.00	C11	0.00
Cu	-0.04	O1	-0.14
O3	-0.34	S1	2.51

Atoms in the Plane: N2, C12, C13, C14, C15, C16

Equation: $(-0.8107)X + (0.5635)Y + (-0.1591)Z - (-5.2095) = 0$

χ^2: 0.74

Deviations:

N2	0.00	C12	0.00
C13	0.00	C14	0.00
C15	0.00	C16	0.00
Cu	0.03	O1	-0.05
O3	-0.24	S1	2.59

Torsion Angles in the DTDIP Chelate Ring.

t[Cu-S1]	28.5	t[S1-C2]	43.1
t[C2-C1]	-50.4	t[C1-O1]	-19.9
t[Cu-O1]	-8.7		

3.7 SUMMARY

This series of mercapto-carboxylic acids have given rise to in situ ligand transformations with copper(II) and 2,2′-bipyridyl. Stable mercaptide complexes were not isolated nor identified from any of these reaction systems. Instead, the products formed further emphasise the unpredictable behaviour of sulphur-containing ligands with copper. The formation of oxalate ions from mercaptoacetate is highly unusual and clearly represents a different reactivity pattern relative to the other mercapto-carboxylic acids. The complexes identified from the 2-mpa and 3-mpa reactions show that these mercapto-carboxylic acids are oxidised to their corresponding disulphides. The mechanism for thiol oxidation suggests that this reaction occurs with the concomitant reduction of copper(II) to copper(I). The subsequent oxidation of copper(I) to copper(II) by O_2 probably accounts for the reformation of cupric ions and the resulting cupric complexes. On the basis of the observations and data for the msa system, msa may undergo an analogous reaction which would give rise to a complex of empirical formulation, $[Cu_2(bipy)_2(DTDS)]\cdot xH_2O$. The insolubility of these complexes prevented further solution studies. The unpredictable behaviour of these thiol-carboxylic acids, with copper(II), is summarised in figure 3.8 as follows.

thiol-carboxylic acid.	copper complex.
maa, $HS\text{-}CH_2\text{-}COOH$	$[Cu(bipy)(C_2O_4)]\cdot 2H_2O$
2-mpa, $CH_3\text{-}CH(SH)\text{-}COOH$	$[Cu(bipy)(DTDIP)]\cdot 3H_2O$
3-mpa, $HS\text{-}CH_2\text{-}CH_2\text{-}COOH$	$[Cu(bipy)(DTDP)]\cdot 2H_2O$

Figure 3.8 Summary of the products formed from the thiol-carboxylic acids.

The results of the crystallographic studies show that copper(II)-disulphide complexation can be acheived when the -S-S- linkage is close enough to the donor groups to which it is bonded to bring it into the vicinity of the copper atom. In contrast to the

DTDP ligand, the short length of the DTDIP chain between the coordinated carboxylate group and the disulphide linkage means that the disulphide sulphur atoms are necessarily in the vicinity of the copper, and that coordination is more likely to occur. The axial copper(II)-S(disulphide) bond distance found for [Cu(bipy)(DTDIP)]·3H_2O is the shortest Cu-S(disulphide) bond yet reported, and indicates that moderately strong copper(II)-disulphide coordination is possible. This result is an important addition to the existing structurally characterised copper(II)-disulphide complexes, which display only weak (if any) axial copper(II)-S(disulphide) interactions (3.06-3.28 Å).

Table 3.7 Metal-Sulphur Bond Distances.

			distance, Å	ref.
(a) Ni(II)($C_{16}H_{22}N_4S_2$)Cl(ClO_4)	Equatorial	M-S(disulphide)	2.472(5)	[38]
(b) Cu(II)($C_6H_{16}N_2O_2S$)Cl_2	Equatorial	M-S(thioether)	2.410(1)	[39]
(c) Cu(I)($C_4H_{10}S_2$)Cl		M-S(disulphide)	2.34(1), 2.40(1)	[40]
(d) [Cu(II)-D-PDS]$_2$·9H_2O	Axial	M-S(disulphide)	3.057(10), 3.138(9)	[41]
(e) [Cu(II)GSSGCu(II)]Na_4·6H_2O	Axial	M-S(disulphide)	3.16(1), 3.28(1)	[36]
(f) [Cu(bipy)(DTDIP)]·3H_2O	Axial	M-S(disulphide)	2.678(2)	[this work]

D-PDS = D-penacillamine disulphide.

GSSG = the disulphide of glutathione.

DTDP = dithiodiisopropionate

CHAPTER THREE REFERENCES

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CHAPTER FOUR

THE COPPER PROMOTED REACTIVITY OF PHENYLTHIOUREA

4.1 INTRODUCTION: THE COORDINATION CHEMISTRY OF COPPER WITH THIOUREAS

Interest in the structural chemistry of copper(I) with soft donor ligands has arisen because of the extensive array of stoichiometries and stereochemistries apparent in these systems. A case in point is the complexation of copper(I) by the thione sulphur-ligand, thiourea. Thioureas have a particular affinity with copper(I) and this is reflected by the very thorough documentation this chemistry has received [1]. A wide range of copper(I)-thiourea complexes, including many crystal structure determinations, have been reported. The stereochemistry of copper(I) in these systems has emerged as being varied and quite unpredictable even with knowledge of the stoichiometry. For example three-coordinate complexes are common, such as $Cu[SCN_2(CH_3)_4]_3^+BF_4^-$ and $Cu[SCN_2H_2(CH_2)_2]_3^+(SO_4^{2-})_{\frac{1}{2}}$ [2]. Polynuclear complexes are also very common, examples including $Cu_4(tu)_6(NO_3)_4$, $Cu_4(tu)_9(NO_3)_4$ [3] and $Cu_4(tu)_{10}(SiF_6)_2$ [4] (tu= thiourea), each of which contains approximately tetrahedral copper(I) centres. The emergence of unusual stoichiometries and unpredictable coordination geometries has provided the main impetus for the interest centred on these complexes. The donor properties of the planar thiourea molecule have also attracted considerable attention.

Oxidation-reduction systems involving copper are very important. These systems are relevant to copper-containing enzymes whose biological function is related to the accessibility of the copper(I)/copper(II) oxidation states and the ligating species present at these sites [5]. The industrial electro-refinement of copper uses thiourea, although the mechanisms of the chemical and electrochemical reactions taking place during this process remain poorly understood. The copper-thiourea system has also been utilised to study the relationship between the complexing capacity and the redox potential of the metal [6]. The reducing properties of thioureas in both aqueous and non-aqueous solution have been well established. Thioureas are easily oxidised; the products formed depend on the oxidant and the reaction conditions [7]. The interaction of thiourea with copper(II) usually results in the formation of a copper(I) compound. The oxidation-reduction process that takes place involves the immediate bonding of thiourea to copper(II), producing a short lived intermediate. Potentiometric studies have shown that the oxidation product of thiourea in these systems is the diformamidine disulphide cation $[(NH_2)_2CS\text{-}SC(NH_2)_2]^{2+}$ [8]. These cations have an extremely weak coordinating ability, so the copper(I) ions are quickly preferentially complexed by any excess thiourea. The mechanisms and the exact nature of the intermediates in these reactions are not well understood. The observation of transient coloured intermediates has been noted in systems containing copper(II) and thiourea or substituted thioureas. Attempts to isolate these species have been reported [9]. There are relatively few well characterised copper(II)-thiourea complexes, although several have been characterised by X-ray crystallography [10-13]. In these complexes the co-ligand(s) plays an important role in stabilising the copper in oxidation state +2. It has become evident that the reducing behaviour of thioureas towards the copper(II) ion can be sufficiently inhibited by the presence of π-acceptor ligands, allowing stable copper(II)-thiourea complexes to be isolated. These ligands are generally bi- or multidentates possessing vacant π^* orbitals which are able to participate in metal to ligand π bonding. This π bonding, in conjunction with the strong chelation of these ligands, produces some electron delocalisation in the chelate ring. This situation evidently produces the stabilisation necessary to prevent copper reduction. Examples of these ligands include 2,2'-bipyridyl, 1,10-phenanthroline, bis(salicylaldehyde)ethylenediimine, bis(acetylacetone)trimethylenediimine, and 2,6-pyridinedicarboxylate anion [10]. The intrinsic difficulties associated with stabilising copper(II)-thiourea compounds have restricted the number of X-ray structural characterisations of these systems. These difficulties are widely acknowledged and there is clearly potential for further development in this area. The synthetic work described in this section was therefore initiated order to investigate the complexation of copper by phenylthiourea. However, these attempts resulted in the isolation and characterisation of an unexpected copper(II) complex formed as a result of the desulphurisation of phenylthiourea.

4.2 EXPERIMENTAL

(i) The Preparation of Phenylthiourea.

α-phenylthiourea was prepared by the method reported by Frank and Smith as follows [14].

$$NH_4SCN + Ph\text{-}COCl \longrightarrow Ph\text{-}CONCS + NH_4Cl$$
$$Ph\text{-}CONCS + Ph\text{-}NH_2 \longrightarrow Ph\text{-}CONHCSNH\text{-}Ph$$
$$Ph\text{-}CONHCSNH\text{-}Ph \longrightarrow Ph\text{-}NHCSNH_2$$

In a 500 ml three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a 100 ml dropping funnel ware placed 17 g (0.22 mol) of ammonium thiocyanate and 100 ml of dry acetone*. Through the dropping funnel 28.2 g (0.2 mol) of benzoyl chloride was added with stirring. After the addition was complete the mixture was refluxed for 5 minutes. A solution of 18.6 g (0.2 mol) of aniline in 50 ml of dry acetone was then added at such a rate that the solution refluxed gently. The mixture was poured carefully with stirring into 1 litre of water, and the resulting yellow precipitate (α-benzoyl-β-phenylthiourea) was separated by filtration. The crystals were heated for 5 minutes in a boiling solution of 30 g of sodium hydroxide in 270 ml of water. After the removal of a small amount of insoluble material by filtration, the solution was acidified with concentrated hydrochloric acid and then made slightly basic with ammonium hydroxide. Upon standing, the solution deposited the crystalline product. Recrystallisation from ethanol yielded 22 g (75%) of white plates, m.p. 152-153°C, (lit., 152.5-153°C).

The substituted phenylthioureas (p-chloro, m-chloro, o-chloro, p-bromo, p-fluoro) were prepared by the same method, using the corresponding substituted anilines: p-chloro (60%) m.p. 158-160°C (lit., 164°C), m-chloro (60%) m.p. 137-139°C (lit., 140°C), o-chloro (80%) m.p. 144-146°C (lit., 146°C), p-bromo (70%) m.p. 123-125°C (lit., 125°C), p-fluoro (60%) m.p. 161-163°C (lit., 164°C) [15,16].

*The acetone was dried over anhydrous calcium sulphate and distilled just before use.

(ii) The Preparation of $[\{Cu(bipy)(PC)_2\}_2]$ from Phenylthiourea.

To a solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) and 2,2′-bipyridyl (0.16 g, 1 mmol) in ethanol (30 mls) was added a solution of phenylthiourea (0.30 g, 2 mmol) in ethanol (10 mls). The intensely dark green solution was filtered, and upon standing for a few days, deposited a yellow crystalline solid (0.02 g) which was identified as elemental sulphur on the basis of its infrared spectrum and melting point 111-112°C (lit., 113°). The sulphur was removed by filtration from solution which, upon standing for a further few days, deposited a dark red crystalline compound, 0.27 g (yield = 60%), m.p. = 197-199°C. The empirical formula was subsequently determined as $Cu(bipy)(C_7H_5N_2)_2$, where $C_7H_5N_2$ = phenylcyanamide(1-).

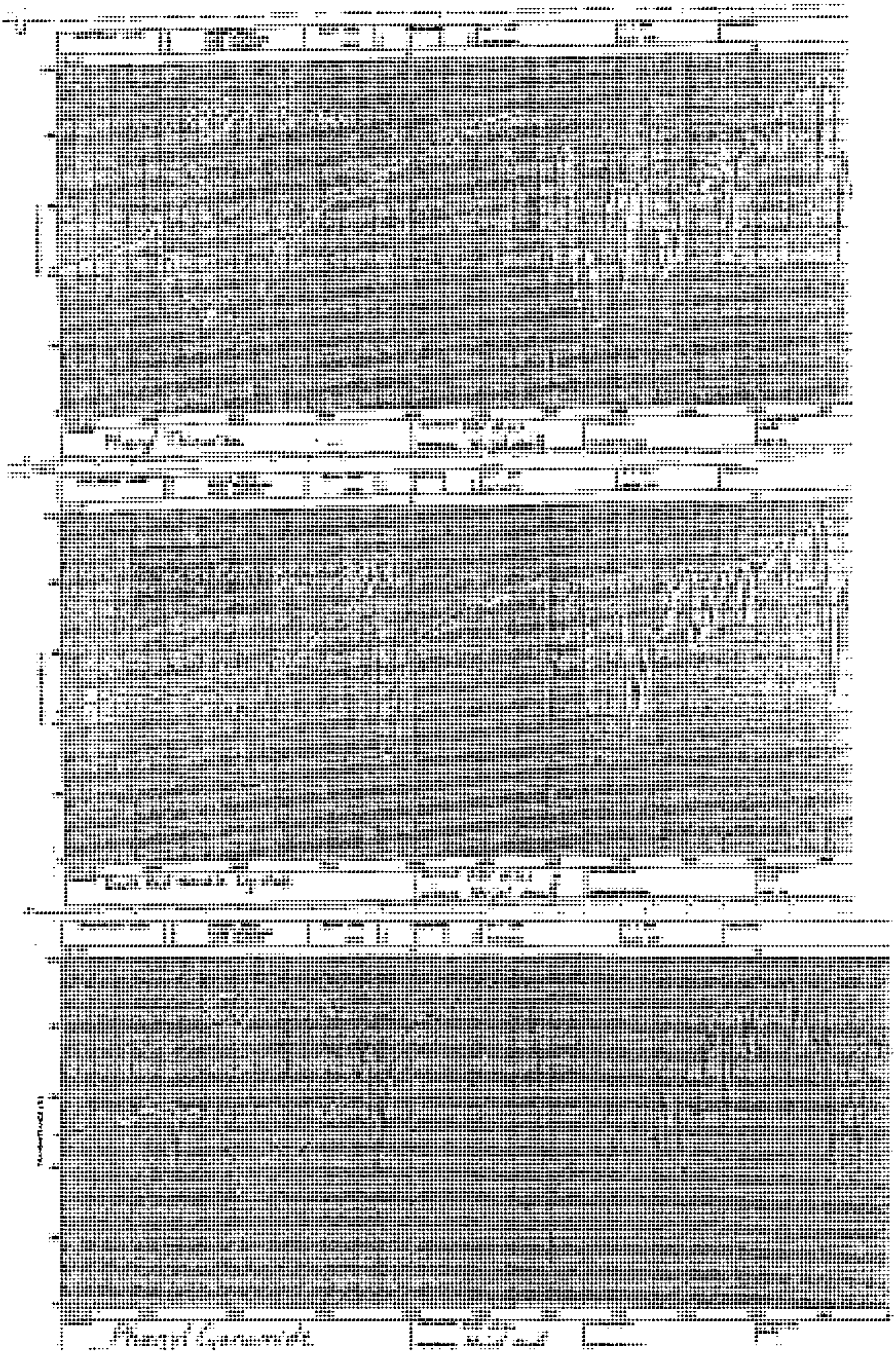
4.3 RESULTS: THE CHARACTERISATION OF $[\{Cu(bipy)(PC)_2\}_2]$.

The reaction between copper(II) acetate monohydrate, 2,2′-bipyridyl, and phenylthiourea in ethanol gave rise to a dark red crystalline copper(II) complex which clearly did not contain phenylthiourea. The infrared spectrum of this dark red compound is shown in figure 4.1 along with those of phenylthiourea and phenylcyanamide. A comparison of these spectra clearly shows that the phenylthiourea initially present has undergone an extensive chemical transformation, and that the new ligand is phenylcyanamide. The phenylthiourea $\nu(NH)$ ir frequency (3430 cm^{-1}) is absent from the ir spectrum of the dark red compound, whereas the latter exhibits additional very intense bands in the region 2100 cm^{-1}, characteristic of $\nu(CN)$ frequencies. The infrared spectrum of the dark red compound shows no evidence of the acetate ion ($\nu(C{=}O)$ approx. 1600 cm^{-1}), which suggests that a new anionic species is present. The magnetic moment and esr spectrum showed that this compound is paramagnetic, the value of 1.98 BM for μ_{eff} being normal for copper(II) complexes [17]. Esr measurements yielded the following data (frozen ethanol, 113 K) $g_{//} = 2.28$, $A_{//} = 181 \times 10^{-4}$ cm^{-1} , $g_{\perp} = 2.07$.

On the basis of these results, and the microanalytical data, the empirical formula of this compound was established as $[Cu(bipy)(C_7H_5N_2)_2]$ (microanalytical data: C, 63.3, H, 4.1, N, 18.4; calculated for $CuC_{24}H_{18}N_6$: C, 63.5, H, 4.0, N, 18.5%).

This dark red compound was also subsequently prepared from a reaction using phenylcyanamide itself as a starting reagent (section 5.2). The crystal structure determination of this complex indicated a dimeric structure of formulation $[\{Cu(bipy)(PC)_2\}_2]$ (section 5.5). A number of halogen-substituted phenylthioureas were also prepared, which gave rise to analogous halogen-substituted phenylcyanamide complexes. The identities of these complexes were confirmed by comparing their ir spectra with those of the compounds prepared from the corresponding phenylcyanamides (section 5.5).

Figure 4.1 The infrared spectra of phenylthiourea, [{Cu(bipy)(PC)$_2$}$_2$], and phenylcyanamide.



4.4 DISCUSSION

This reaction can be described as a room temperature desulphurisation of phenylthiourea which is promoted by the presence of copper(II) ions. The elements 'H_2S' are eliminated from one molecule of phenylthiourea forming the phenylcyanamide(1-) anion, which coordinates to the copper atom. Elemental sulphur has been identified as a reaction coproduct. The overall reaction can be represented by the following equation:

$$2Cu^{2+} + bipy + 2Ph\text{-}NH\text{-}C(S)\text{-}NH_2N \dashrightarrow [\{Cu(bipy)(PC)_2\}_2] + 1/4S_8 + 4H^+$$

where $PC = (Ph\text{-}N\text{-}C{\equiv}N)^-$

Figure 4.2 The reactivity of phenylthiourea with copper(II).

This desulphurisation reaction of phenylthiourea is believed to be attributed to the redox activity of the Cu^{2+} ions as presented in the equation:

$$PhNHC(S)NH_2 + 2Cu^{2+} \dashrightarrow Ph\text{-}NH\text{-}C{\equiv}N + 1/8S_8 + 2Cu^+ + 2H^+$$

The Cu^+ is oxidised in the presence of air and the monodeprotonated form of phenylcyanamide forms a coordination complex to the resulting Cu^{2+} ions. This reaction is intriguing because, from similar reaction conditions, the complex $[Cu(bipy)_2(tu)](ClO_4)_2$ has been isolated and structurally characterised by X-ray crystallography. The factors important for the occurrence of the present reaction are unclear. The formation of phenylcyanamide from phenylthiourea is not unprecedented, however. One laboratory preparation of phenylcyanamide is carried out by the addition of phenylthiourea to a boiling solution of lead acetate in concentrated potassium hydroxide [18]. This desulphurisation occurs via the precipitation of lead sulphide, but in contrast to the present reaction, involves extremes of temperature and pH. Phenylcyanamide has also been obtained from phenylthiourea by oxidation of the latter using the superoxide ion [19]. In living cells, the oxidative desulphurisation of thioamides such as ethionamide (2-ethylisonicotinthionamide) is known [20]. The most likely initial oxidation product of phenylthiourea with copper(II) is the N-phenylformamidine disulphide cation $[(PhNH)(NH_2)CS-SC(NH_2)(NHPh)]^{2+}$. Disulphide salts of this type have been shown to decompose spontaneously in neutral or weakly acidic medium with the precipitation of sulphur [21]. These reactions take place very quickly and as a consequence the redox and complexation processes that occur are not well understood. These difficulties extend to the present reaction and thus it seems likely that the mechanism of this reaction is not easily definable.

At the same time as we were studying this reaction, Weiss et al. reported a reaction involving thiourea which closely parallels the present reaction [22]. Weiss et al. reported the formation of a complex which incorporates the ligand hydrogencyanamide(1-), formed by an unusual copper(II) promoted desulphurisation reaction of thiourea. The redox process postulated for this reaction is shown by the following equation.

$$(H_2N)_2C{=}S + 2Cu^{2+} \dashrightarrow H_2N{-}C{\equiv}N + 1/8S_8 + 2Cu^+ + 2H^+$$

The Cu^+ formed is reoxidised in the presence of air. The coordination complex then formed has been identified by X-ray crystallography, and exists as dimeric cations of formula $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-}HNCN)_2]^{2+}$ with uncoordinated perchlorate anions and water of crystallisation ($C_9H_{21}N_3$ = a tridentate cyclic amine) (figure 5.1). This reaction also proceeds with the elimination of elemental sulphur and is essentially analogous to the present reaction. The resultant copper(II) complex is novel and highlights the paucity of structural data available on coordination complexes which incorporate cyanamide ligands. The following section reports on the crystal structure of $[\{Cu(bipy)(PC)_2\}_2]$, and extends the chemistry presented in this section to a more extensive investigation of phenylcyanamide complex formation.

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CHAPTER FIVE

PHENYLCYANAMIDES AND THEIR COORDINATION CHEMISTRY WITH COPPER(II).

5.1 INTRODUCTION: CYANAMIDES AS DONOR MOLECULES

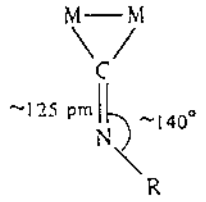
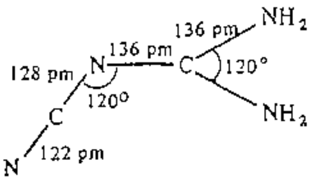
The complexation of ligands such as cyanide (CN^-), cyanate (NCO^-) and thiocyanate (NCS^-) ions, which all contain CN bonds, to transition metal ions, is a widely studied area of chemistry. These anionic ligands are generally regarded as pseudohalides by analogy with the halide electronic structure. Of these anions, cyanide is particularly important because it has a special affinity for, and forms complexes with, virtually all the transition metals. The range of properties and bonding types among the cyanides is wide and interest naturally extends to the behaviour of other organic compounds containing the cyano functionality. Examples of these compounds are listed along with some basic structural information in table 5.1.

The aim of this section of work is to examine more closely the phenylcyanamide ligand, Ph-NH-C≡N, and its coordination chemistry with copper as an ambidentate monoanion. Cyanamide itself, $H_2N-C\equiv N$, is a colourless crystalline compound, which melts at 40°C and readily polymerises, and can be thought of as the dehydration product of urea ($(NH_2)_2CO$). Cyanamides do not exhibit tautomerism with a carbodiimide form, and disubstituted cyanamides (I) are, of course, distinct from the corresponding N,N′-disubstituted carbodiimides (II).

$$\underset{(I)}{RR'-N-C\equiv N} \qquad \underset{(II)}{R-N=C=N-R'}$$

Although diazomethane (H_2CNN) is an isomer of cyanamide, it is not chemically similar.

Table 5.1 Some Compounds Containing the CN Group.

Name	Conventional formula	r (C–N)/pm	Remarks
Cyanogen	$N{\equiv}C{-}C{\equiv}N$	115	Linear; r (C–C) 138 pm (short)
Paracyanogen	$(CN)_x$	—	Involatile polymer, see text
Hydrogen cyanide	$H{-}C{\equiv}N$	115.6	Linear; r (C–H) 106.5 pm
Cyanide ion	$(C{\equiv}N)^-$	116	r_{eff} 192 pm when "freely rotating" in MCN
Cyanides (nitriles)	$M{-}C{\equiv}N$ $(R{-}C{\equiv}N)$	115.8	Linear; r (C–C) 146.0 pm (for MeCN)
Isocyanides	$R{-}N{\equiv}C$	116.7	Linear, r (H_3C-N) 142.6 pm (for MeNC). Coordinated isocyanides are slightly bent. e.g. $[M(\leftarrow C{=}N{-}C_6H_5)_6]$ angle CNC 173°, r (C=N) 117.6 pm; bridging modes also known, e.g.: 
Cyanogen halides (halogen cyanides)	$X{-}C{\equiv}N$	116	Linear
Cyanamide	$H_2N{-}C{\equiv}N$	115	Linear NCN; r (C-NH_2) 131 pm
Dicyandiamide	$N{\equiv}C{-}N{=}C(NH_2)_2$	122-136	
Cyanuric compounds	$\{-C(X){=}N-\}_3$	134	Cyclic trimers; X = halogen, OH, NH_2
Cyanate ion	$(O{-}C{\equiv}N)^-$	~121	Linear
Isocyanates	$R{-}N{=}C{=}O$	120	Linear NCO; ∠RNC ~ 126°
Fulminate ion	$\rangle(C{=}N{-}O)^-$	109	Linear; another form of AgCNO has r(C–N) 112 pm
Thiocyanate ion	$(S{-}C{\equiv}N)^-$	115	Linear
Thiocyanates	$R{-}S{-}C{\equiv}N$ $(M{-}S{-}C{\equiv}N)$	116	Linear NCS; ∠RSC 100° in MeSCN; ∠MSC variable (80–107°)
Isothiocyanates	$R{-}N{=}C{=}S$	122	Linear NCS; ∠HNC 135° in HNCS; ∠MNC variable (111–180°)
Selenocyanate ion	$(Se{-}C{\equiv}N)^-$	~112	Linear NCSe

Extracted from 'Chemistry of the Elements', N. N. Greenwood and A. Earnshaw, Pergamon Press (1984).

Cyanamides are highly reactive molecules. They are used as starting materials in a wide variety of organic syntheses. Calcium cyanamide (CaNCN) is the basic chemical of the cyanamide industry and is obtained by the nitrogenation of CaC_2. In addition to its role as a direct application fertiliser, calcium cyanamide is the basic material for the industrial synthesis of a great range of substances including polymers, medicinals, thiourea, cyanamide, dicyandiamide (cyano-guanidine) (III) and melamine plastics.

$$N{\equiv}C{-}N{=}C(NH_2)_2$$

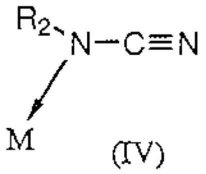
(III)

Acidification of CaNCN yields free cyanamide, H_2NCN, which can react further to give different products depending on the pH : at pH less than 2, or greater than 12, urea is formed, but at pH 7-9 dimerisation to dicyandiamide occurs. Perhaps the most important reactions of cyanamides are those involving polymerisation. This polymerisation is promoted by the presence of metal salts and involves the addition of the cyanamide ion to the nitrile group of an undissociated molecule. Cyanamide itself slowly dimerises on standing to form dicyandiamide.

The question of multiple bonding in organic and inorganic chemistry has, over the years, been an area of intense interest. As such, the challenge of describing the structure of cyanamide both in the solid and gaseous phase has been the subject of numerous investigations involving many physical and spectroscopic techniques. Initially, the impetus for this work arose in order to address the question of whether the cyanamide molecule itself exists in the amide form (H_2NCN), or the carbodiimide form (HNCNH). The possibility of the individual existence of these two tautomers became a fascinating question which remained inadequately explained until the 1950s. Raman spectral analyses by Kahovec and Kohlrausch in 1937 and 1944 concluded that cyanamide exists almost entirely as the amide form [1,2]. In 1942, Imanishi and Tachi interpreted the results of an ultra-violet spectroscopic study of cyanamide vapour as indicating the presence of almost 100% imide form [3]. Other evidence of a purely chemical nature further complicated the issue by suggesting that the compound exists as a mixture of the two forms [4,5]. This earlier confusion in the literature was eventually resolved. In 1952, the crystal structure of cyanamide was published [6,7]. Dipole moment measurements [8], refractivity investigations [9] and nmr studies [10] have since been accepted as indicating that cyanamide must exist in practically 100% amide form. There is currently very little evidence for the existence of the carbodiimide form in the gas phase.

Attention then shifted to the question of the planarity of the molecule. Raman and infrared spectroscopic studies, of liquid H_2NCN and D_2NCN in chloroform and acetonitrile, with a molecular orbital approach, supported the assumption of a planar molecule [11]. Following this, the conflicting results of a number of vibrational and spectroscopic investigations were published creating a considerable amount of controversy regarding the exact geometry of the NH_2CN group. More recent studies on the microwave spectra of NH_2CN, NHDCN, ND_2CN, $^{15}NH_2CN$, $NH_2C^{15}N$, $^{15}ND_2CN$ and $ND_2C^{15}N$ [12], including an analysis of the nuclear quadrupole coupling in cyanamide, have produced more definite structural results and conclude that cyanamide possesses a non-planar equilibrium configuration [13].

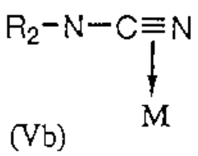
The great deal of interest generated over the question of the structure and geometry of cyanamide itself has left the mono- and di-substituted derivatives relatively ignored as a class of donor ligands. Cyanamides represent a potentially versatile ligand type which possesses two functional groups linked directly together. As monodentate ligands, cyanamides may coordinate to a metal atom through either the cyano group or the lone pair of electrons on the amido nitrogen (IV). Coordination through the cyano group may involve the sigma (Va) or the pi electrons resulting in a μ-type bond (Vb).



(IV)

$R_2{-}N{-}C{\equiv}N \longrightarrow M$

(Va)



$R_2{-}N{-}C{\equiv}N \downarrow M$

(Vb)

As bidentate ligands they may coordinate to two different metal atoms. Cyanamide itself may coordinate as the dianion NCN^{2-}, the monoanion $HNCN^{-}$, or in the neutral form H_2NCN. Examples of each of these cases have been reported [14-18], although X-ray crystallographic data are sparse. Cyanamide and its derivatives clearly give rise to an extensive coordination chemistry with transition metals, although their ligating properties and the structural aspects of their coordination complexes have received exceedingly little attention. The metal-cyanamide compounds that have been characterised by X-ray crystallography are summarised as follows: salt-like metal-cyanamides (K^+, Na^+, Sr^{2+}) [19-21]; complexes of $[SbCl_6]^-$ in which protonated bulky cyanamides act as uncoordinated counterions [22-24]; a complex of $[SbCl_5]$ which contains a neutral uncoordinated cyanamide [25]; two Mo complexes which contain neutral coordinated dimethylcyanamide [26,27]; two complexes of d-metals (Cu(II) and Ni(0)) which contain coordinated cyanamides [18,28].

The organometallic and coordination chemistry of dicyanamide (VI) is more thoroughly documented than that of cyanamide itself.

$$N(CN)_2^-$$

(VI)

A number of complex types incorporating this ligand with a wide range of transition metals have been described [29-32]. Ni(II)- and Fe(II)-dicyanamide react with diamines such as 2,2′-bipyridyl and 1,10-phenanthroline to form tris diamine complexes $[M(diamine)_3](N(CN)_2)_2$. Octahedral azido-bis(diamine) complexes $[M(N(CN)_2)_2(diamine)_2]$ are obtained for M = Co, Ni, or Cu and diamine = bipy, phen or en [33]. X-ray crystallographic studies are again limited [34-37].

Jain and Rivest [15] synthesised a series of coordination compounds of cyanamide and diethylcyanamide with group(IV) halides, MX_4 (where M = Ti, Sn or Zr and X = Cl or Br). With cyanamide, complexes of the type $MX_4 \cdot (L)_n$ (where n = 3 or 6) were formed. The infrared spectra showed that definite changes in the $\nu(CN)$ region occurred on coordination, which were interpreted as evidence for monodentate coordination through the lone pair of electrons of the cyano group. The insolubility of these adducts seriously limited the number of physical measurements to infrared spectroscopy only. Conclusions were restricted only to suggestions about the possible geometry of these complexes.

Unlike the mono-substituted compounds, the N,N′-disubstituted cyanamides do not ionise. Studies on the interaction of diorganocyanamides with triphenyltin halides have been reported [38]. Triphenyltin chloride and triphenyltin iodide were allowed to react separately with dibenzylcyanamide and benzyltritylcyanamide, forming complexes of the type $RR'NCN\cdot(C_6H_5)_3SnX$. Their Mossbauer spectra indicated probable trigonal bipyramidal structures.

The preparation of metal carbonyl complexes with substituted cyanamide ligands has generated some interest. The metals Mo, Ni, and Ir have been investigated. The crystal structure determinations of $[cp_2Mo_2(CO)_4(NCNMe_2)]$ [26] and $[(C_5H_{10}NCN)Ni(CO)]$ ($C_5H_{10}NCN$ = piperidine cyanamide) [28] have resulted, and clearly illustrate the interesting bonding possibilities that exist for coordinated cyanamide ligands (figure 5.1 (a) and (b)). In each of these structures the cyanamide ligand coordinates to one metal atom through the sigma electrons of the cyano group, and to another metal atom through the pi electrons of the C-N triple bond. Although the cyanamide ligands are coordinated in a similar fashion, the bond lengths indicate that there is a marked difference in the respective R_2NCN electronic structures. Chisholm <u>et al.</u> [26] point out that the electronic structure of the dialkyl-cyanamide ligand can be formulated as a resonance hybrid of (VII) and (VIII) <u>viz.</u>,

$$\underset{\text{(VII)}}{R_2{-}N{-}C{\equiv}N} \longleftrightarrow \underset{\text{(VIII)}}{R_2{-}\overset{+}{N}{=}C{=}\overset{-}{N}}$$

in which (VII) predominates. In the Ni complex, the bond lengths in the piperidine cyanamide ligand show that this ligand is closely represented by structure (VII). The bond lengths in the dimethylcyanamide ligand of the Mo complex show that structure (VIII) makes a significantly greater contribution. The coordination mode described for these two complexes also occurs in the complex $[Mo_2(OCH_2\text{-t-Bu})_6(\mu\text{-NCNMe}_2)]$, whose structure has been determined by X-ray crystallography [27] (figure 5.1 (d)). However, there are some very distinct differences in the respective bond lengths of the Me_2NCN ligands. In $[Mo_2(OCH\text{-t-Bu})_6(\mu\text{-NCNMe}_2)]$ there is a much longer $Me_2NC\text{-}N$ distance 1.333(4) Å, (cf. 1.236(9) Å for $[cp_2Mo_2(CO)_4(\mu\text{-NCNMe}_2)]$, and 1.351 Å for free Me_2NCN) [39]. The factors important in causing these differences remain unclear.

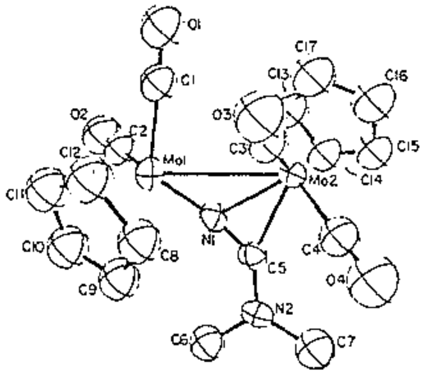
The only crystal structure determination of a transition metal complex which incorporates a coordinated cyanamide monoanion was reported recently by Weiss et al. (1985) [18]. In this study, the structure of $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-HNCN})_2](ClO_4)\cdot 2H_2O$ (figure 5.1 (c)) was found to consist of two copper(II) centres connected via two bridging hydrogen cyanamido(1-) ligands. The remaining coordination sites of each copper atom were occupied by the macrocyclic triamine N,N′,N′′-trimethyl-1,4,7-triazacyclononane. Studies on the spectroscopic and structural aspects of HNCN(1-) and of deprotonated monosubstituted cyanamides (RNCN(1-)) in general have received limited attention. These species are isoelectronic with the pseudohalide anions, which raises the possibilty of preparing cyanamido analogues of structurally characterised copper-pseudohalide complexes.

In 1971, Hollebone and Nyholm reported the preparation of a number of halogen-substituted phenylcarbodiimide complexes of copper(II) [40]. The aim of their work was to examine the physical and spectroscopic properties of these complexes as part of a series of transition metal pseudohalide complexes. The Copper(II)-phenylcarbodiimide complexes were formulated as $[Ph_4As]_2[Cu(L)_4]$ on the basis of microanalytical data. No spectroscopic data was published to support the assertion that the ligand exists in the carbodiimide form rather than the cyanamide form. It seems unlikely that the carbodiimide structure would be favoured and this assignment of structure is considered rather specious in view of the lack of accompanying structural evidence.

In the past, conclusions concerning the coordination environments of cyanamide complexes have relied heavily on infrared spectroscopic data. The effect of coordination on the ν(CN) and the ν(N-H) frequencies has been widely quoted as a means of deciding whether the cyanamide ligand is bound through the cyano or the amido end of the molecule [17]. This approach has supposedly been adequate for those compounds which possess N-H groups. These are not present in N,N-disubstituted cyanamides and deprotonated monosubstituted cyanamides which, in view of the various potential coordination modes, makes a structural assignment on the basis of the ν(CN) frequency alone rather tentative.

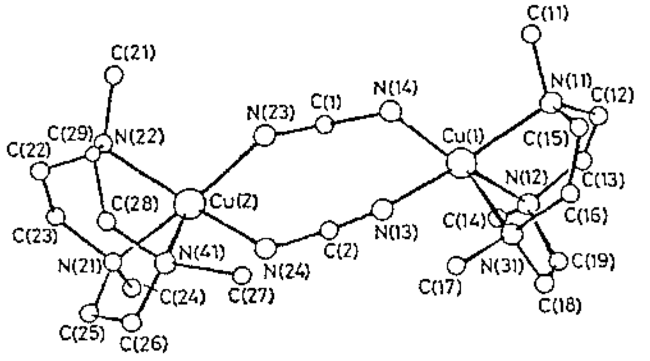
The coordination chemistry that has been carried out clearly shows the ability of cyanamide ligands to form complexes of unpredictable formulation and structure with a wide range of metals. Only in a few cases are the structural conclusions supported by X-ray crystallographic studies. A more thorough and systematic approach to the coordination chemistry of cyanamide ligands is therefore clearly desirable. This section of work aimed to contribute towards this area by reporting on the synthetic and structural chemistry of a number of new copper complexes which incorporate phenylcyanamido(1-) ligands. In this chapter, details of a number of mixed-ligand copper(II) complexes incorporating coordinated phenylcyanamide anions and the nitrogen donor ligands, bipy, py, phen, and pip, are described. The crystal structure determinations of $[\{Cu(bipy)(PC)_2\}_2]$ and $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ are also presented.

Figure 5.1 Some structurally characterised cyanamide complexes.



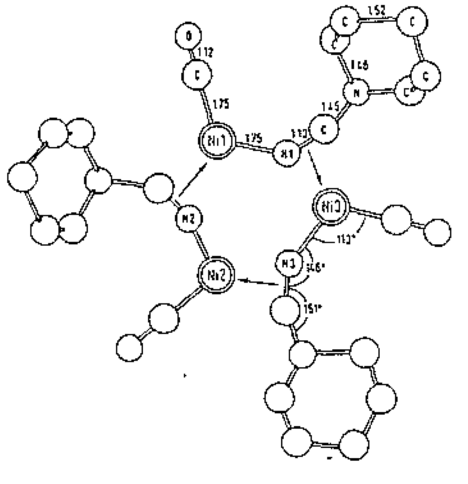
An ORTEP drawing of the molecular structure of $Cp_2Mo_2(CO)_4(NCNMe_2)$. Atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of the electron density.

(a) $Cp_2Mo_2(CO)_4(NCNMe_2)$ ref. [26]

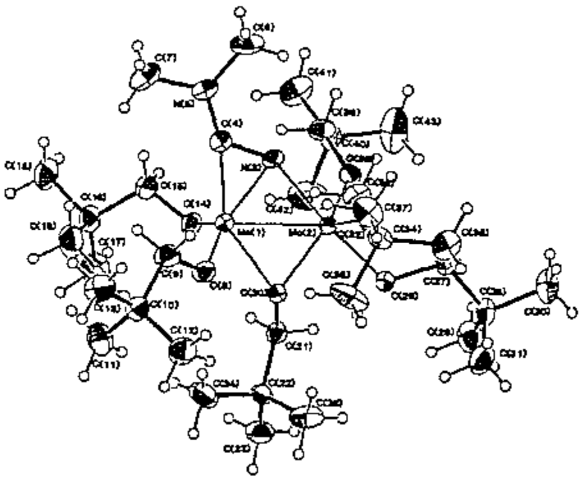


A perspective view of the binuclear cation (H atoms are omitted). Selected bond distances (Å) and angles (°) are: Cu(1)–N(14) 2.017(6), Cu(1)–N(13) 1.964(5), Cu(1)–N(11) 2.082(5), Cu(1)–N(12) 2.066(5), Cu(1)–N(31) 2.221(6), C(1)–N(14) 1.27(1), C(1)–N(23) 1.15(1), C(2)–N(13) 1.15(1), C(2)–N(24) 1.29(1), Cu(2)–N(24) 1.977(6), Cu(2)–N(23) 1.962(5); Cu(2)–N(23)–C(1) 146.6(8), N(23)–C(1)–N(14) 178.3(6), C(1)–N(14)–Cu(1) 120.9(5), N(14)–Cu(1)–N(13) 89.6(3), Cu(1)–N(13)–C(2) 144.6(8), N(13)–C(2)–N(24) 175.4(8), C(2)–N(24)–Cu(2) 124.5(5), N(11)–Cu(1)–N(12) 84.8(3), N(11)–Cu(1)–N(14) 92.5(3), N(11)–Cu(1)–N(13) 170(1), N(12)–Cu(1)–N(13) 91.8(3).

(c) $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-HNCN})_2]^{2+}$ ref. [18]



(b) $[(C_5H_{10}NCN)Ni(CO)]$ ref. [28]



ORTEP view of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$ molecule. Pertinent distances (Å) and angles (deg) are Mo–Mo = 2.449 (1), Mo–O (terminal OR) = 1.92 (2) (averaged), Mo(1)–O(20) = 2.146 (2), Mo(1)–N(3) = 1.908 (3), Mo(1)–C(4) = 2.014 (4), Mo(2)–O(20) = 1.999 (2), Mo(2)–N(3) = 2.134 (2), N(3)–C(4) = 1.333 (4), C(4)–N(5) = 1.324 (4); ∠Mo(1)–C(4)–N(5) = 167.0 (3), ∠(3)–C(4)–N(5) = 127.1 (3), ∠C–N(5)–C = 120 (1) (averaged).

(d) $[Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)]$ ref. [27]

5.2 EXPERIMENTAL

(i) The Preparation of Phenylcyanamide.

The preparation of phenylcyanamide was carried out according to the method of Kurzer [41], as follows. To a boiling suspension of phenylthiourea (11.8 g, 0.1 mol) in water (150 ml) at 100°C, a boiling solution of potassium hydroxide (56 g,1 mol in 150 ml of water) was added, immediately followed by a hot saturated solution of lead acetate (38 g, 0.1 mol). The reaction mixture was boiled for 6 minutes and then cooled to 0°C, and the lead sulphide removed by filtration under reduced pressure. On acidification of the colourless filtrate with glacial acetic acid (60 ml) at 0-5°C (addition of ice), a white crystalline precipitate of phenylcyanamide (7.6 g, 65%) separated, forming large lustrous needles which were recrystallised from benzene-light petroleum. The substituted phenylcyanamides were prepared by an analogous method using the corresponding substituted phenylthioureas and were all obtained as white crystalline products with well defined melting points. It was found that the experimentally determined melting points varied greatly from the literature values, where available, although this observation was probably due to encountering differently solvated formulations, and/or different crystal forms. The phenylcyanamides were stored in the dark and remained unchanged for long periods of time. The microanalyses of these phenylcyanamide ligands and their copper complexes provided some difficulty for the analysts at Otago University. Initially they found consistently low carbon and nitrogen figures, but this was largely rectified by their use of sealed sample capsules during the analytical procedure. The free-ligand data are summarised in table 5.0.

(ii) The Preparation of Ag(+) Phenylcyanamide Salts.

These were prepared according to the method of Hollebone [40] as flocculent white precipitates by mixing equivalent quantities of silver perchlorate with the protonated ligand in methanol to give salts of formulation Ag^+L^-.

Table 5.0 Data for the Phenylcyanamide Ligands.

Ligand	m.p., °C	ν(CN), cm^{-1}	Analyses(%) C	H	N	X
PC	173-175	2251, 2215	71.3 (71.2)	5.3 (5.1)	24.0 (23.7)	
p-Cl-PC	184-186	2243	56.6 (55.1)	3.6 (3.3)	18.4 (18.4)	22.3 (23.3)
m-Cl-PC	68-70	2243	52.2 (55.1)	3.8 (3.3)	17.2 (18.4)	22.0 (23.3)
o-Cl-PC	85-88	2242	55.1 (55.1)	3.4 (3.3)	18.4 (18.4)	23.1 (23.3)
p-Br-PC	107-109	2239	42.5 (42.7)	2.6 (2.5)	14.4 (14.2)	40.1 (40.6)
p-F-PC	116-118	2241	61.7 (61.8)	3.7 (3.7)	20.5 (20.6)	13.7 (14.0)

Calculated figures in brackets.

Ag(+) salt	ν(CN), cm^{-1}
PC	2111, 2087
m-Cl-PC	2103
p-Br-PC	2088
o-Cl-PC	2104(br)
p-F-PC	2104, 2087

(iii) The Preparation of Copper(II) Complexes with Phenylcyanamides.

(a) 2,2′-Bipyridyl Complexes, $[\{Cu(bipy)L_2\}_2]$.
L = phenylcyanamide, p-chloro-, m-chloro-, o-chloro-, p-bromo- and p-fluorophenylcyanamide.

To a solution of copper acetate monohydrate (0.20 g, 1 mmol) and 2,2′-bipyridyl (0.16 g, 1 mmol) in ethanol (30 ml) a solution of L (2 mmol) in ethanol (10 ml) was added slowly with stirring. The resulting intensely dark red solution was filtered to remove all trace of insoluble material. Upon standing overnight, slow evaporation produced a quantity of the dark red crystalline product. This was washed with ethanol then vacuum dried; yields 40-60%.

(b) 1,10-Phenanthroline Complexes, $[Cu(phen)L_2]$.
L = phenylcyanamide, p-chloro-, o-chloro-, p-bromo- and p-fluorophenylcyanamide.

These compounds were prepared using an analogous method to that described for the $[\{Cu(bipy)L_2\}_2]$ compounds. Stoichiometric quantities of copper acetate monohydrate, 1,10-phenanthroline, and L were combined in ethanol, producing solutions from which intensly dark red crystalline complexes were obtained; yields 40-60%.

(c) The Preparation of $[Cu(phen)(m\text{-}Cl\text{-}PC)_2]$.

A solution of sodium ethoxide was prepared by dissolving sodium metal (0.05 g, 2 mmol) in ethanol (5 ml). This was added to a solution of m-chlorophenylcyanamide (0.31 g, 2 mmol) in ethanol (10 ml) which was then added slowly with stirring to a solution of copper acetate monohydrate (0.20 g, 1 mmol) and 1,10-phenanthroline

(0.20 g, 1 mmol) in ethanol (30 ml). The resulting intensely dark red solution was then filtered to remove all trace of insoluble material. Upon standing overnight; slow evaporation produced 0.38 g (70%) of the dark red crystalline product. This was washed with ethanol then vacuum dried.

(d) The Preparation of $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$.

To a solution of copper acetate monohydrate (0.20 g, 1 mmol) and phen (0.20 g, 1 mmol) in ethanol (30 ml) a solution of m-chlorophenylcyanamide (0.15 g, 1 mmol) in ethanol (10 ml) was added slowly with stirring, resulting in an intensely dark green solution. Upon standing overnight, large dark green plate-like crystals of the product appeared (0.28 g, 60%). These were washed with ethanol then air dried.

(e) Pyridine Complexes, $[Cu(Py)_2L_2\ ]\cdot ½H_2O$.

L = p-chloro-, m-chloro-, p-bromo-, and p-fluorophenylcyanamide.

To a warmed solution of copper acetate monohydrate (0.20 g, 1 mmol) and pyridine (1 ml) in ethanol (30 ml), a solution of L (2 mmol) in ethanol (10 ml) was added slowly with stirring. The resulting intensely dark red solution was filtered and upon cooling, the dark red microcrystalline product appeared. This was washed with ethanol then air dried; yields 40-50%.

(f) Piperidine Complexes, $[Cu(Pip)_2(L)_2]$.

L = phenylcyanamide, p-chloro-, and p-Bromophenylcyanamide.

These complexes were prepared using a method directly analogous to that described for the $[Cu(Py)_2(L)_2]$ complexes; yields 40-50%.

(g) $[Cu(II)L_2]$ Complexes.

Attempts to prepare compounds of formulation $Cu(II)L_2$ were carried out with the phenylcyanamides prepared in (i) using the method outlined below. This produced dark red amorphous powders whose microanalyses in most cases were not consistent with the formulation CuL_2, or solvated modifications thereof. Attempts to improve the analyses by further purification of these compounds were unsuccessful. It appears from the analyses that these compounds contain impurities and or there is some difficulty with their microanalysis. In view of these results, these compounds are only tentatively formulated as $Cu(II)L_2$. An account of the preparation and of the data for the two compounds whose analyses did produce reasonable agreement between the observed and calculated figures is presented below (i.e. where L = m-Cl-PC and p-Br-PC).

A solution of deprotonated ligand, L (2 mmol), was prepared by dissolving sodium metal (0.05 g, 2 mmol) in ethanol (5 ml). To a warmed solution of copper acetate monohydrate (0.20 g, 1mmol) in water (50 ml), the solution of L was added slowly with stirring resulting in the immediate formation of a dark red precipitate, which was washed with ethanol then vacuum dried (yields 61% and 73% for p-Cl-PC and p-Br-PC respectively).

Analyses(%)

L	m.p.	C	H	N	X	$\mu_{(eff)}$	$\lambda_{(max),nm}$
p-Br-PC	d	36.6 (36.9)	1.7 (1.8)	12.4 (12.3)	35.3 (35.1)	2.02	805(173) 478(1210)
m-Cl-PC	d	46.0 (45.8)	2.2 (2.2)	15.5 (15.3)	19.5 (19.4)	1.83	744(244) 479(1182)

* calculated microanalytical figures in brackets
* $\mu_{(eff)}$ in units of BM
* electronic solution spectra: solvent = DMSO, extinction coefficient bracketted in units of $lmol^{-1}cm^{-1}$
*d decomposes > 250°C.

5.3 RESULTS: THE CHARACTERISATION OF THE COPPER(II) COMPLEXES

The microanalytical and physicochemical data for the copper(II) complexes are presented in table 5.2. Four series of complexes as well as the complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ have been prepared and characterised. Complexes tentatively formulated as $Cu^{II}L_2$ have also been prepared.

The measured room temperature magnetic moments lie in the range 1.80-2.0 BM, which are consistent with the values usually observed for magnetically dilute copper(II) complexes [42]. Conductivity measurements using DMSO solvent indicated that all these complexes are non-electrolytes, i.e. the anionic ligands remain coordinated in solution. The solution electronic spectra show two absorption maxima. In all cases, the band in the range 650-790 nm is assigned as a predominantly d→d transition and the second band, in the region 460-500 nm, to a charge transfer transition. On the basis of the results of previous authors [43], the former is consistent with the '4 + 1' coordination geometry as shown by X-ray crystallography for $[\{Cu(bipy)(PC)_2\}_2]$ and $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ (sections 5.5 and 5.6). The latter is tentatively assigned as a L→M charge transfer from the filled σ or π orbitals on the cyano nitrogen, to the $d_{\sigma*}$ orbitals on the copper. The observed values compare with bands in the region of 410-445 nm for a number of copper(II)-phenolato complexes which have been assigned as L→M, $p_{\pi}\rightarrow d_{\sigma*}$, transitions [44]. The infrared $\nu(CN)$ frequencies are listed for each compound and generally fall in the range 2100-2180 cm^{-1}. The ir spectrum of $[\{Cu(bipy)(PC)_2\}_2]$ is presented in figure 4.1. The profiles of the ir spectra in the $\nu(CN)$ region appear to be reasonably consistent within each series of compounds. This suggests that there is one structural type common to each series. By comparison with the $\nu(CN)$ frequencies of the phenylcyanamide Ag(+) salts (section 5.2), the $\nu(CN)$ are shifted to higher wavenumbers, by up to 90 cm^{-1}, upon coordination. This observation is consistent with previous studies which show that for ligands containing CN triple bonds, the formation of the nitrogen-to-metal bond results in an increase in the ir frequency of the CN bond [65]. These results suggest that, in the complexes prepared, the cyano nitrogens of the phenylcyanamido ligands are coordinated to the copper. However, the inherent difficulties associated with interpreting infrared data (section 5.4) prevents more detailed conclusions from being drawn concerning the exact coordination mode(s) of the ligands present in these complexes. In response to these difficulties, the X-ray crystal structure determination of the complex $[\{Cu(bipy)(PC)_2\}]$ has been undertaken and is presented in section 5.5.

The complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ was initially prepared according to the method used for the $[Cu(phen)L_2]$ complexes, where L = PC, p-Cl-, o-Cl-, p-Br-, and p-F-PC. In contrast to the latter series, this complex involves only one m-Cl-phenylcyanamide ligand per copper, the charge being balanced by the inclusion of an acetate anion. The presence of the acetate ion was deduced by the appearance of a strong band at 1591 cm^{-1} consistent with the $\nu(C{=}O)$ frequency of coordinated acetate [45]. A broad band centred on 3330 cm^{-1} was also observed, consistent with the $\nu(O\text{-}H)$ frequency of lattice water [45]. This complex is unique and its formation evidently results from a delicate balance between the affinities of the acetate and m-Cl-phenylcyanamide anions with copper. The exceptional outcome of this particular reaction may be related to an anticipated decreased acidity of the amide proton of m-Cl-phenylcyanamide relative to the ortho-, para-substituted molecules. The resonance forms of the phenylcyanamide anion involve negative charges at the ortho and para positions. These resonance forms would be stabilised by the inductive effect of halogen substituents at these positions, resulting in the amide proton becoming more readily dissociable. This interpretation appears to be consistent with the observation that the complex $[Cu(phen)(m\text{-}Cl\text{-}PC)_2]$ could be prepared by initially deprotonating the m-Cl-phenylcyanamide ligand using sodium ethoxide solution. An investigation into the structural character of this mixed anion complex was considered important because of the interesting range of ligating possibilities. The acetate ligand itself may be mono- or bidentate, bridging or non-bridging. In addition to the largely unknown coordinating capabilities of the phenylcyanamide group, these factors necessitated an X-ray crystallographic analysis to obtain an unambiguous structural characterisation (section 5.6).

TABLE 5.2 PHYSICOCHEMICAL DATA FOR THE COPPER(II)-PHENYLCYANAMIDO COMPLEXES

EMP. FORMULA	$\mu_{(eff)}$,BM	$\lambda_{(max)}$,nm	ν(CN),cm^{-1}	COLOUR	M.P., °C	MICROANALYTICAL DATA (%)							
						(found)				(calculated)			
						C	H	N	X	C	H	N	X
$[Cu(bipy)(L)_2]$													
L													
PC	1.98	496 (1900) 658 (400)	2175, 2147, 2103	dark red	197-199	63.3	4.3	18.5		(63.5)	(4.0)	(18.5)	
p-Cl-PC	1.96	498 (2476) 662 (462)	2179, 2159, 2111	dark red	194-196	54.9	3.0	16.0		(55.1)	(3.0)	(16.1)	(13.6)
m-Cl-PC	1.95	488 (2314) 674 (370)	2169, 2141, 2107	dark red	180-182	55.1	3.1	16.1	13.5	(55.1)	(3.0)	(16.1)	(13.6)
o-Cl-PC	1.93	476 (1272) 678 (382)	2187, 2139, 2119	dark red	204-206	54.9	3.1	15.8	13.5	(55.1)	(3.0)	(16.1)	(13.6)
p-Br-PC	1.94	489 (1930) 663 (447)	2171, 2151, 2111	dark red	200-202	47.2	2.5	13.7	26.3	(47.1)	(2.6)	(13.7)	(26.1)
p-F-PC	1.95	486 (1821) 658 (398)	2173, 2137, 2111	dark red	195-197	58.9	3.4	16.9	7.5	(58.8)	(3.3)	(17.2)	(7.8)
$[Cu(phen)(L)_2]$													
L													
PC	1.82	498 (1364) 670 (641)	2175, 2141, 2103	dark red	204-206	64.7	3.7	17.4		(65.3)	(3.8)	(17.6)	
p-Cl-PC	1.95	493 (1898) 662 (511)	2179, 2147, 2095	dark red	208-210	57.0	2.8	15.1	12.9	(57.1)	(2.9)	(15.4)	(13.0)
m-Cl-PC	1.89	481 (1560) 686 (400)	2155, 2107	dark red	191-193	57.2	3.0	15.2	13.1	(57.1)	(2.9)	(15.4)	(13.0)
o-Cl-PC	1.91	477 (988) 692 (353)	2185, 2119, 2103	dark red	207-209	56.9	2.9	15.3	13.0	(57.1)	(2.9)	(15.4)	(13.0)
p-Br-PC	2.11	494 (1774) 669 (576)	2165, 2123, 2111	dark red	170-172	48.8	2.5	12.9	25.2	(49.1)	(2.5)	(13.2)	(25.1)
p-F-PC	1.93	493 (1194) 669 (585)	2175, 2149, 2087	dark red	203-205	60.7	3.1	16.2	7.3	(60.8)	(3.1)	(16.4)	(7.4)
$[Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)]\cdot H_2O$													
L													
m-Cl-PC	1.89	462 (820) 677 (167)	2107	dark green	181-184	55.5	3.8	12.1	7.9	(55.5)	(3.3)	(12.3)	(7.8)
$[Cu(pip)_2(L)_2]$				$[Cu(pip)_2(L)_2]$		$[Cu(pip)_2(L)_2]$							
L				L		L							
PC	1.85	474 (931) 659 (403)	2175, 2143	orange-red	117-119	61.3	7.1	18.1		(61.6)	(6.8)	(18.0)	
p-Cl-PC	1.78	476 (940) 655 (403)	2161, 2145	orange-red	129-131	53.3	5.7	14.9	13.0	(53.5)	(5.6)	(15.6)	(13.2)
p-Br-PC	1.97	476 (1030) 671 (430)	2179, 2143	orange-red	138-140	45.6	4.8	13.2	25.3	(46.1)	(4.8)	(13.4)	(25.6)
$[Cu(py)_2(L)_2]\cdot\frac{1}{2}H_2O$													
L													
PC	1.89	494 (861) 752 (240)	2171, 2142	purple	125-127	62.0	4.4	17.4		(62.0)	(4.5)	(18.1)	
p-Cl-PC	1.93	485 (807) 732 (265)	2167, 2143	purple	129-131	54.4	3.5	15.2	13.5	(54.0)	(3.6)	(15.8)	(13.3)
m-Cl-PC	1.96	481 (1656) 775 (233)	2173, 2071	purple	109-111	54.4	3.4	16.1	13.4	(54.0)	(3.6)	(15.8)	(13.3)
P-Br-PC	2.07	496 (807) 757 (234)	2159, 2107	purple	d	46.8	3.0	13.0	25.2	(46.3)	(3.1)	(13.5)	(25.7)
p-F-PC	1.93	492 (865) 736 (227)	2155, 2109	purple	134-136	57.7	3.7	16.4	7.5	(57.5)	(3.8)	(16.8)	(7.6)

Notes. Solution electronic spectra - solvent DMSO. Molar extinction coefficient bracketted in units of lmol^{-1}cm^{-1}.

5.4 INFRARED SPECTROSCOPY OF SYSTEMS CONTAINING TRIPLE BONDS

The vibrations of triple bonds have long been recognised as providing excellent group frequencies in infrared spectroscopy. The principles that underlie the behaviour of the CN stretching frequency both in coordinated and uncoordinated molecules have been extensively dealt with in the literature [45]. Inorganic cyanides absorb over a wide frequency range (NaCN 2080 cm^{-1}, AuCN 2239 cm^{-1}) as do the coordination compounds (2150-1985 cm^{-1}). Any survey of the literature will quickly reveal the readiness at which authors discuss these variations in terms of changes in the ionic/covalent character of the metal-ligand bonds. An important point to be aware of is that although the nature of the metal-ligand bond is obviously an important factor, the interpretation of the direction of frequency shifts is not straightforward; as an example consider a cyanamide molecule RR'NCN: an increase in the covalent character of the metal-N(terminal) bond will certainly be accompanied by a change in the C-N force constant and in the vibrational frequency. However, the fact that the metal-N bond has a positive force constant and will resist movement of the nitrogen atom, will also have a large effect. The cases of the nitrile oxides studied by Califano [46] are good examples of this difficulty. Experience thus shows that the mass and coupling effects may not always be safely ignored and that the frequency shifts cannot necessarily be interpreted solely in terms of changes in the electron distribution within the bonds.

The coordinated cyanide ion exhibits three characteristic bands in the infrared spectrum: a very intense band in the range 1900-2250 cm^{-1} which is associated with the C-N stretching vibration, and two other bands in the range 100 cm^{-1} to 600 cm^{-1}. These are assigned to the M-C stretching vibrations as well as to the MCN and CMC deformation vibrations. In principle, the NCN absorption of the cyanamide group should be useful in providing data on the ionic/covalent character of the N-C bond, and any double bond character this may aquire through back donation into the vacant d-orbitals. However in practice, the occurrence of other bands in the same frequency region produce coupling effects which complicate the interpretation. These difficulties highlight the advantages of an X-ray crystallographic investigation to determine unambiguously the coordination mode(s) of the phenylcyanamide complexes prepared in this study.

5.5 THE CRYSTAL STRUCTURE DETERMINATION OF $[\{Cu(bipy)(PC)_2\}_2]$ (bis[2,2'-bipyridine-μ-(phenylcyanamido-N,N')phenylcyanamido-N-copper(II)]).

CRYSTAL PREPARATION: Dark red crystals of the complex $[\{Cu(bipy)(PC)_2\}_2]$ were obtained by the slow evaporation of an ethanol solution. The crystals were of a regular plate-like shape and completely extinguished polarised light.

DATA COLLECTION: A single crystal of dimensions 0.06 x 0.03 x 0.34 mm was mounted on Canterbury University's Nicolet R3m four-circle diffractometer equipped with Mo radiation (λ = 0.71069 Å) and a graphite monochromator. The data collection was carried out at 153 K as described in appendix A1 and is summarised in table 5.3.

SPACE GROUP DETERMINATION: The space group $P2_1/c$ was assigned unambiguously on the basis of the systematic absences, $l = 2n + 1$ for h0l and $k = 2n + 1$ for 0k0.

STRUCTURE SOLUTION AND REFINEMENT: Structure solution and refinement were performed according to the description in appendix A1.

The three dimensional Patterson synthesis yielded coordinates of the copper atom consistent with the space group $P2_1/c$. The same coordinates were also given by a subsequent direct methods structure solution. The remaining non-hydrogen atoms were located from subsequent Fourier maps. Several cycles of block diagonal least squares refinement of the atomic coordinates, individual isotropic temperature factors and scale factor were implemented. Initially unit weights were applied, and isotropic refinement resulted in a reliability index, R, which converged to 0.129.

An inspection of a difference electron density map, calculated at this stage, revealed the presence of two peaks (heights approximately 2-3 eA^{-3}) located 1.2 Å apart in positions consistent with a second orientation of the amido nitrogen and cyano carbon atoms of the terminally bound phenylcyanamido ligand. The isotropic thermal parameters associated with the atoms originally assigned as the amido nitrogen and cyano carbon of this ligand were found to be systematically larger than the mean values of the other nitrogen and carbon atoms in the structure, indicating that the site occupancy factors orginally assigned to these atoms were probably incorrect. These observations suggested that the terminally bound phenylcyanamido ligand possessed two orientations leading to a twofold disorder of the amido nitrogen atom and cyano carbon atom. In order to refine the site occupancy factors of the atoms involved in the disorder, the atoms concerned were assigned isotropic thermal parameters fixed at 0.03 and included in one cycle of full matrix least squares refinement. This refinement produced site occupancy values for these atoms of approximately 0.5. They were thus given occupancies of 0.5 in all subsequent refinement. One cycle of least squares refinement at this stage reduced the reliability index to 0.092.

A difference map following this refinement revealed evidence for anisotropic thermal motion of the copper atom. In the next round of calculations the copper atom was assumed to vibrate according to an anisotropic thermal model while the light atoms remained limited to isotropic thermal motion. The hydrogen atoms were visible in a subsequent difference map and were included at their geometrically calculated positions using a C-H bond distance of 1.08 Å. Three further cycles of least squares refinement resulted in a reliability index of 0.0604. Anisotropic thermal parameters were applied to all non-hydrogen atoms and three further cycles of least squares refinement converged at reliability indices R and R_w of 0.0429 and 0.0430 respectively, for 1689 reflections with $I > 3\sigma(I)$. The largest parameter shifts on the last cycle were less than 0.05 of the estimated standard deviations.

For the last few cycles of refinement, a weighting scheme of the type

$$w = k / [\sigma_{(F)}^2 + gF^2]$$

was applied to the data, where $\sigma_{(F)}^2$ is the estimated standard deviation of $|F_o|$ and k and g are constants. The values of k and g were redetermined for each cycle of refinement. This resulted in a reasonable distribution of variance with respect to $|F_o|$ and sinθ with final values of 1.2365 and 0.000642 for k and g respectively. A final difference map showed no peak higher than 0.6 eA^{-3} whereas the electron density of a typical carbon atom in this structure was approximately 4.0 eA^{-3}.

STRUCTURE DESCRIPTION: An ORTEP representation of the complex $[\{Cu(bipy)(PC)_2\}_2]$ is shown in figure 5.2 together with the atomic numbering scheme. Selected bond distances and angles are given in table 5.4. The crystal structure consists of centrosymmetric dimers, separated only by normal Van der Waals distances [47]. The dimerisation occurs via the end-to-end, NCN bridging of two phenylcyanamido(1-) ligands to the two copper atoms. The two phenylcyanamido(1-) ligands in the asymmetric unit exhibit different coordination modes; a monodentate ligand which coordinates to the copper through the terminal cyano nitrogen (N3), and a bidentate ligand which bridges the two copper atoms of the dimer by bonding through the cyano (N1) and amido (N2) nitrogen atoms. The coordination is completed by the centrosymmetrically-related half of the dimer which results in an approximately planar eight membered heteroatom ring (maximum deviation 0.14Å).

The Copper Coordination Environment: The copper atom is coordinated by two bipyridyl nitrogens (Cu-N5 = 2.012(5) Å and Cu-N6 = 2.052(5) Å) and two phenylcyanamido(1-) cyano nitrogens (Cu-N1 = 1.938(5) Å and Cu-N3 = 1.942(6) Å) in a distorted basal square plane, with a longer apical bond (Cu-N2′ = 2.355(6) Å) to the amido nitrogen of the symmetry related bridging phenylcyanamido(1-) ligand. This type of coordination geometry is not uncommon for copper(II) complexes which frequently exhibit a planar arrangement of four atoms at normal covalent distances from the copper atom, with a fifth and sometimes a sixth atom at longer distances perpendicular to this plane [48].

The four basal atoms N5, N6, N1, and N3, exhibit poor planarity, as shown by the least-squares planes presented in table 5.5. The copper atom is displaced by about 0.19 Å from the best plane through these atoms, towards the apical donor atom, N2′. The configuration of the four strongly coordinated donor atoms can be described by considering the dihedral angle between the planes through atoms Cu, N5, N6 and Cu, N1, N3. For an exact square plane this angle would be 0°, whereas for tetrahedral geometry it would be 109.5°. The observed value of 16.6° arises, in part, from a tetrahedral distortion of the basal ligand plane, as well as from the 0.19 Å displacement of the copper atom out of this plane. The overall copper coordination geometry can be described as distorted square pyramidal, in which the distortion arises due to the enlarged N2'-Cu-N1 (99.7(2)°) and N2'-Cu-N3 (98.5(2)°) angles (i.e. the axial Cu-N2' bond is tilted towards the bipyridyl ligand). The phenylcyanamido(1-) ligands are arranged such that the phenyl rings are virtually orthogonal to each other (the dihedral angle between the best planes through these phenyl rings is 85.2°). In addition, the phenyl ring of the bridging ligand is approximately parallel to the phenyl rings of the bipyridyl group (the dihedral angle between the best plane through the bipyridyl group and that through the phenyl ring of the bridging phenylcyanamido(1-) ligand is 17.3°). This arrangement of ligands evidently minimises the intramolecular interactions within the dimer. An inspection of the intra- and intermolecular distances shows that the shortest H...H contacts are in fact between the phenylcyanamido(1-) H atoms of neighbouring molecules rather than within the dimer. This suggests that the basal distortion towards tetrahedral geometry arises, at least in part, to optimise the molecular packing efficiency.

The copper to bipyridyl nitrogen bond distances are consistent with observed values in previously reported structures [49-51]. The copper to phenylcyanamide distances, Cu-N1 and Cu-N3 (1.938(5) Å and 1.942(6) Å respectively) are significantly shorter than the Cu-N(bipy) distances (mean 2.03 Å), indicating strong covalent bonds between the copper and the phenylcyanamido(1-) ligands. Their equivalence suggests that the donor properties of the cyano N1 atom are not significantly modified by the involvement of the amido nitrogen, N2, in bonding to the second copper. The Cu-N2' bond is clearly elongated with a value of 2.355(6) Å. This is 0.3 Å longer than the sum of the Pauling covalent radii (1.35 Å and 0.70 Å for Cu and N respectively [47]), which represents a typical lengthening of an apical bond in a five coordinate copper(II) complex [48].

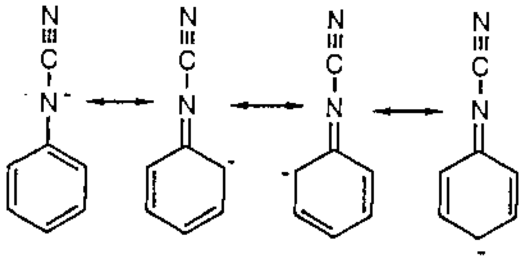
The 2,2′-Bipyridyl Ligand: The bond lengths and angles in the bipyridyl ligand agree well with the values usually found in these systems [50-53]. The pyridine rings of the bipyridyl group are individually planar but do not lie in the same plane due to a twist of 3.4° about the C19-C20 bond.

The Terminal Phenylcyanamido(1-) Ligand: The terminally bound phenylcyanamido(1-) ligand is partially disordered. The nitrogen and carbon atoms of the cyano group each occupy two positions (C8a, C8b, N4a, and N4b) with site occupancy factors of 0.5. A representation of this disorder is shown in figure 5.3. The bond lengths of each conformation are equivalent to within the limits of experimental error, with the exception of bonds N3-C8a (1.277(15) Å) and N3-C8b (1.179(14) Å). The latter bond distance agrees with the value expected for a C-N triple bond (1.158 Å) [54], whereas the former is substantially longer. There are no apparent steric or electronic reasons to explain this feature which appears chemically improbable. The remaining bond lengths, C8a-N4a, N4a-C9, C8b-N4b, and N4b-C10, agree with the corresponding bond lengths in the bridging ligand, which adopts the cyanamido $(Ph-N-C{\equiv}N)^-$ conformation. In view of this, the bond distance of 1.277(15) Å for N3-C8a, is of questionable validity, and its non-equivalence with the bond length N3-C8b is quite probably attributed to limitations in the modelling of the disorder. Thus an accurate comparison of the bond lengths and angles associated with the bridging and terminally bound phenylcyanamido(1-) ligands cannot be made. The disorder is such that the orientation of the phenyl ring is essentially the same, whereas the two orientations of the NCN group make angles to the copper of Cu-N3-C8a = 150.7(7)° and Cu-N3-C8b = 131.0(8)°. The angle between each NCN conformation is 56.1(8)° as defined by C8a-N3-C8b.

The Bridging Phenylcyanamido(1-) Ligand: The following diagram shows the two most electronically favourable resonance structures for the monodeprotonated anion of phenylcyanamide.

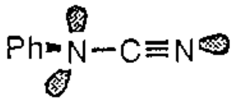
(I) (II)

The predominance of each of these forms may be inferred from the Ph-N2-C1-N2 bond distances. The observed C2-N2, C1-N2 and N1-C1 distances for the bridging ligand are 1.409(7) Å, 1.293(7) Å and 1.169(7) Å respectively. These bond distances indicate that the predominant canonical form in a description of the bonding of the phenylcyanamido(1-) ligand to copper may be written as (I). The C2-N2 bond distance of 1.409(7) Å is somewhat less than the value expected for a C-N single bond of 1.47 Å [47]. This reduction in bond length possibly arises due to some delocalisation of the negative charge on N2 onto the phenyl ring via the following resonance structures.

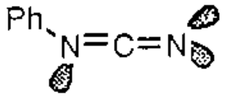


The value of 1.293(7) Å for N2-C1 is about the same as the value expected for a carbon to nitrogen double bond (1.287 Å) [47], indicating that there may be a finite contribution made to the overall electronic structure by the canonical form (II). However, this substantial shortening cannot be ascribed solely to the effect of hybridisation of the carbon and nitrogen atoms. If the effects of resonance forms (I) and (II) are accounted for, then the C1-N2 distance should have a value which corresponds to partially single-bond and partially double-bond character, and the cyano C1-N1 distance should have a value which corresponds to partially double-bond and partially triple-bond character. However, despite the shorter N2-C1 distance, the cyano distance, C1-N1, is no longer than the usual C-N triple bond length of 1.158 Å [54]. This phenomenon of markedly shortened bonds linked directly to triple bonds occurs in many other compounds, for example, HN_3, cyanates, isothiocyanates [55], $S(CN)_2$ [56], [57], H_2NCN [58], and $Se(SCN)_2$ [59]. It is still unclear what other factors are important in causing these shorter C-N distances.

It is interesting to consider the geometries of the two canonical forms (I) and (II) as follows.



(I)



(II)

In form (I), the overlap of the sp lone pair on the cyano nitrogen with an unfilled σ-type metal orbital would result in a linear M-N-C arrangement and a tetrahedral amido nitrogen. Theoretically, this situation would result in M-N-C bond angles of 180° and 109° for the cyano and amido nitrogen atoms respectively. In contrast, form (II) possesses trigonal nitrogen atoms, which would theoretically give rise to M-N-C bond angles of 120°. It is clear that neither of these two models adequately describes the bonding geometry of the bridging phenylcyanamido(1-) ligand, which has bond angles Cu'-N2-C1 = 105.6(6)°, C2-N2-C1 = 118.3(5), Cu'-N2-C2 = 116.5(6) and Cu-N1-C1 = 151.0(5)°.

The N2-C1-N1 bond angle of 172.7(7)° clearly indicates the non-linear bonding at the cyano carbon atom. This bending may arise as a result of steric repulsions.

The existing literature on metal-cyanamido complexes provides an extremely small basis for a direct comparison of the phenylcyanamido(1-) complexes reported in this study. The few crystal structures that have been reported previously are somewhat removed from $[\{Cu(bipy)(PC)_2\}_2]$ because they generally contain neutral cyanamides which are coordinated through the CN triple bond, <u>viz.</u> $[Mo_2(OCH_2\text{-t-Bu})_6(\mu\text{-NCNMe}_2)]$ [27], $[Ni(C_5H_{10}NCN)(CO)]$ [28], and $[Cp_2Mo_2(CO)_4(NCNMe_2)]$ [26] ($NCNMe_2$ = dimethylcyanamide and $C_5H_{10}NCN$ = piperidine-N-carbonitrile). The most comparable previously reported structure is that of $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-HNCN})_2](ClO_4)_2\cdot H_2O$ [18] which also possesses an end-to-end NCN ligand bridge between two copper(II) atoms ($C_9H_{21}N_3$ = N,N',N''-trimethyl-1,4,7-triazacyclononane (a tridentate cyclic amine). This structure consists of binuclear cations of $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-HNCN})_2]^{2+}$, uncoordinated perchlorate and water of crystallisation. The binuclear cation is illustrated in figure 5.1

(c) along with relevant bond distances and angles. The copper coordination environment in this particular complex is clearly dictated largely by the constraints of the tridentate cyclic amine. The resulting coordination geometry is a pseudo-trigonal-bipyramidal arrangement. The major difference between the coordination of the HNCN(1-) ligands in this structure, and the bridging phenylcyanamido(1-) ligand in $[\{Cu(bipy)(PC)_2\}_2]$, is the contrasting bridging modes. The HNCN(1-) bridges symmetrically, (mean Cu-N(cyano) = 1.98 Å) whereas the phenylcyanamido(1-) ligand is clearly asymmetrically coordinated (Cu-N(cyano) = 1.938(5) Å, Cu-N(amido) = 2.355(6) Å). The CN bond distances (1.15 Å and 1.28 Å (both mean of two) in the HNCN(1-) ligands in this complex are in agreement with the corresponding distances in the present complex and support the description of the HNCN(1-) units as $(H\text{-}N\text{-}C\equiv N)^-$.

Table 5.3 Crystallographic Data for [{Cu(bipy)(PC)$_2$}$_2$].

Formula	Cu2,C48,H36,N12
Mol. wt.	907.0
Cryst. syst.	Monoclinic
Space group	$P2_1/c$
a, Å	9.625(3)
b, Å	20.945(5)
c, Å	9.956(3)
β, deg.	97.10(2)
Z	2
V, Å^3	1992(1)
* F(000)	924
$D_{(calc)}$, gcm^{-3}	1.51
$D_{(obsd)}$, gcm^{-3}	1.53
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator $\lambda = 0.71069$ Å
Temp., K	153
Reflns. Measd	h, k, ±l
Scan type	ω/2θ
Scan range, deg.	1.6
Scan speed, deg/min.	5.86
Max. 2θ, deg.	45
Measd. Reflns.	2702
Unique reflns.($I > 3\sigma_{(I)}$)	1689
Cryst. dimensions (from centroid, mm)	±(100) 0.06
	±(010) 0.03
	±(001) 0.34
Abs. coeff., cm^{-1}	10.63
Trans. factors	Max. 0.9348 Min. 0.8653
Abs. Corr. Type	Empirical.
Wtg scheme	$1.2365 / [\ \sigma_{(F)}^2 + 0.000642F^2\ ]$
R	0.0429
R_w	0.0430

Figure 5.2 The ORTEP representation of one molecule of [{Cu(bipy)(PC)$_2$}$_2$] showing the atomic labelling.

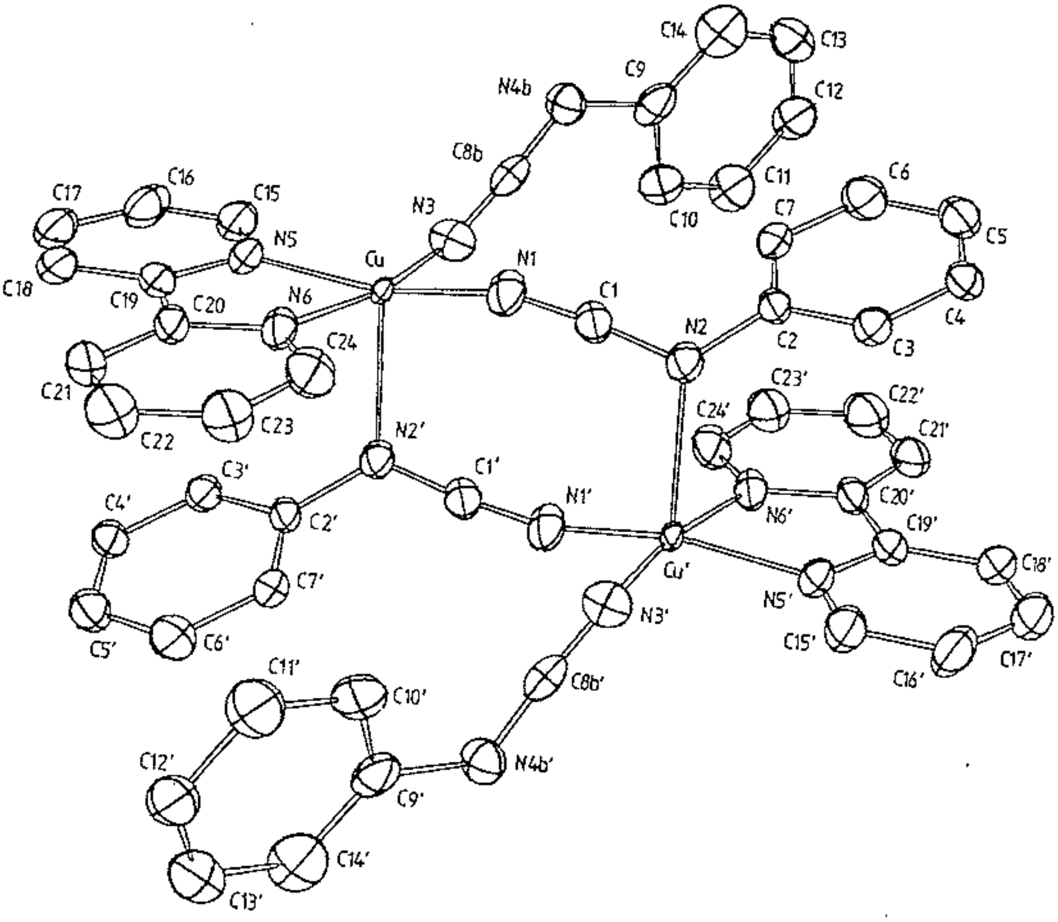


Figure 5.3 The ORTEP representation of $[\{Cu(bipy)(PC)_2\}_2]$ showing the disorder and the stereoscopic unit cell.

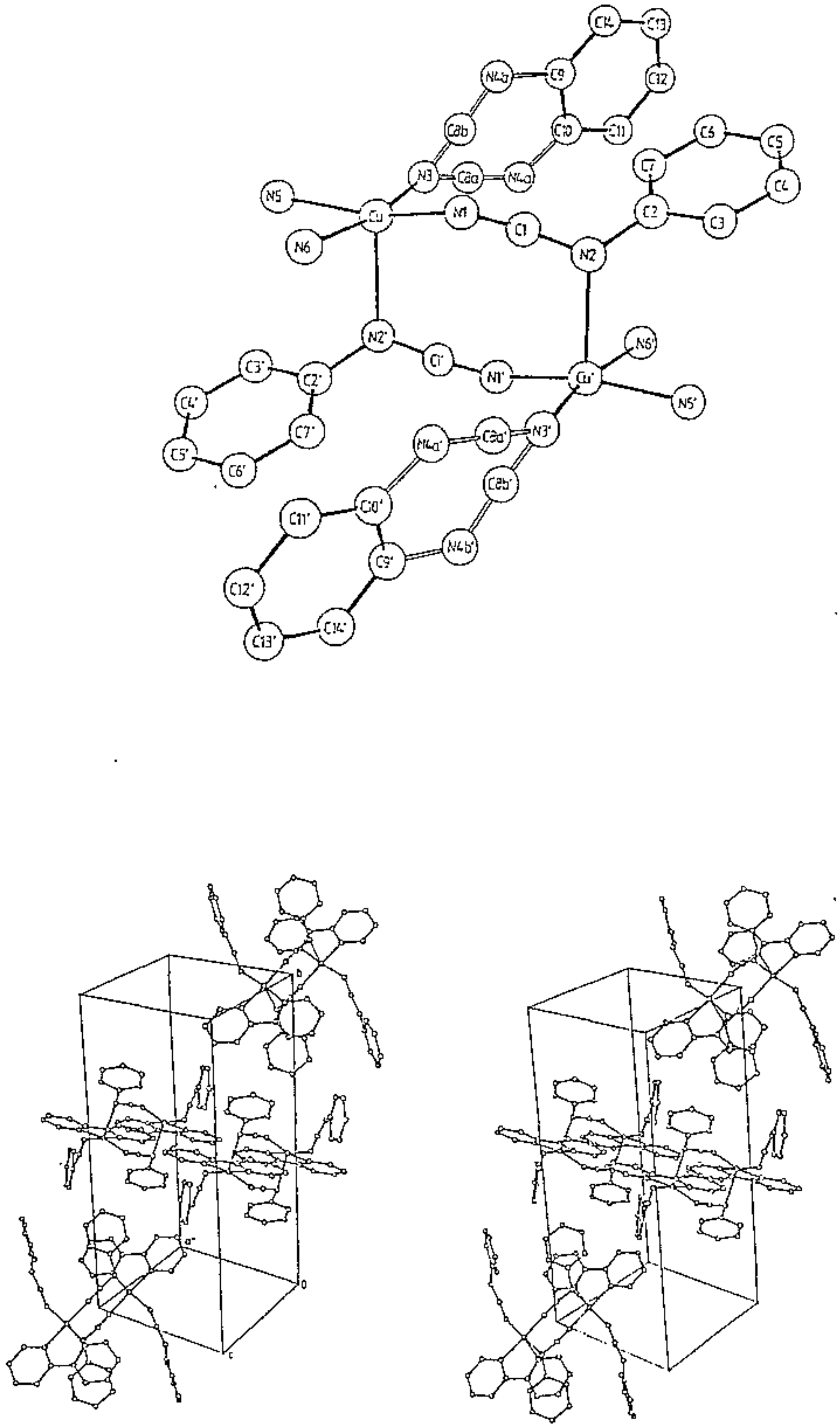


Table 5.4 Bond Lengths (Å) and Angles (deg.) in $[\{Cu(bipy)(PC)_2\}_2]$.

Cu...Cu'	5.009(6)	N4b-C9	1.413(11)
Cu-N1	1.938(5)	C9-C10	1.387(9)
Cu-N2'	2.355(6)	C10-C11	1.398(9)
Cu-N3	1.942(6)	C11-C12	1.377(9)
Cu-N5	2.012(5)	C12-C13	1.384(9)
Cu-N6	2.052(5)	C13-C14	1.376(9)
N1-C1	1.169(7)	C14-C9	1.377(9)
C1-N2	1.293(7)	N5-C19	1.341(8)
N2-C2	1.409(7)	N5-C15	1.332(8)
C2-C3	1.400(8)	N6-C20	1.359(7)
C3-C4	1.367(8)	N6-C24	1.334(8)
C4-C5	1.380(8)	C15-C16	1.386(9)
C5-C6	1.386(8)	C16-C17	1.405(10)
C6-C7	1.388(8)	C17-C18	1.369(9)
C7-C2	1.380(8)	C18-C19	1.411(8)
N3-C8a	1.277(15)	C19-C20	1.456(9)
N3-C8b	1.179(14)	C20-C21	1.387(9)
N4a-C8a	1.302(16)	C21-C22	1.374(10)
N4a-C10	1.374(11)	C22-C23	1.385(9)
N4b-C8b	1.263(16)	C23-C24	1.390(9)

N1--Cu--N3	94.3(2)	N4b--C9--C10	111.2(7)
N1--Cu--N2'	99.7(2)	N4b--C9--C14	128.0(7)
N1--Cu--N5	162.6(2)	C14--C9--C10	119.8(6)
N1--Cu--N6	92.4(2)	N4a--C10--C9	113.2(7)
N3--Cu--N2'	98.5(2)	N4a--C10--C11	127.4(7)
N3--Cu--N5	92.0(2)	C9--C10--C11	119.3(6)
N3--Cu--N6	169.7(2)	C10--C11--C12	120.1(6)
N5--Cu--N6	79.4(2)	C11--C12--C13	120.2(6)
N2'--Cu--N5	95.4(2)	C12--C13--C14	119.5(6)
N2'--Cu--N6	88.0(2)	C13--C14--C9	121.0(6)
Cu--N1--C1	151.0(5)	Cu--N5--C19	115.6(4)
N1--C1--N2	172.7(7)	Cu--N5--C15	124.6(4)
C1--N2--Cu'	105.6(6)	C19--N5--C15	119.6(5)
C2--N2--Cu'	116.5(6)	Cu--N6--C20	114.5(5)
C1--N2--C2	118.3(5)	Cu--N6--C24	124.2(4)
N2--C2--C3	117.7(5)	C24--N6--C20	120.7(6)
N2--C2--C7	124.0(5)	N5--C15--C16	123.3(7)
C7--C2--C3	118.2(5)	C15--C16--C17	117.4(7)
C2--C3--C4	120.8(6)	C16--C17--C18	119.7(6)
C3--C4--C5	120.9(6)	C17--C18--C19	119.2(7)
C4--C5--C6	119.0(6)	C18--C19--C20	123.3(7)
C5--C6--C7	120.2(6)	C18--C19--N5	120.8(7)
C6--C7--C2	120.8(6)	N5--C19--C20	115.9(5)
Cu--N3--C8a	150.7(7)	C19--C20--C21	125.7(6)
C8a--N3--C8b	56.1(8)	C19--C20--N6	113.9(6)
Cu--N3--C8b	131.0(8)	N6--C20--C21	120.4(6)
N3--C8a--N4a	175.9(1.3)	C20--C21--C22	119.3(6)
N3--C8b--N4b	175.2(1.2)	C21--C22--C23	119.7(7)
C8a--N4a--C10	123.2(1.0)	C22--C23--C24	119.2(7)
C8b--N4b--C9	128.2(9)	C23--C24--N6	120.7(6)

Table 5.5 Selected least-squares planes and deviations (Å) in $[\{Cu(bipy)(PC)_2\}_2]$.

Atoms in the Plane: Cu, N1, N3, N5, N6

Equation: $(0.1147)X + (-0.7536)Y + (-0.6472)Z - (-1.5518) = 0$

χ^2: 3856

Deviations:

Cu	0.15	N1	-0.12
N3	0.04	N6	0.05
N5	-0.12	C1	0.22
N2	0.61	N2′	2.49

Atoms in the Plane: N1, N3, N5, N6

Equation: $(0.1158)X + (-0.7523)Y + (-0.6485)Z - (-1.5926) = 0$

χ^2: 78.96

Deviations:

N1	-0.08	N3	0.08
N5	-0.08	N6	0.08
Cu	0.19	C1	0.26
N2	0.66	N2′	2.53

Atoms in the Plane: N5, C15, C16, C17, C18, C19

Equation: $(0.1778)X + (-0.7801)Y + (-0.5998)Z - (-1.3731) = 0$

χ^2: 1.22

Deviations:

N5	-0.01	C15	0.02
C16	0.01	C17	0.00
C18	0.00	C19	0.00
Cu	0.12	N1	-0.29
N2	0.29	N3	0.10
N6	-0.06	N2′	2.45

Atoms in the Plane: C2, C3, C4, C5, C6, C7

Equation: $(0.4492)X + (-0.5897)Y + (-0.6712)Z - (-0.8537) = 0$

χ^2: 8.71

Deviations:	C2	0.04	C3	-0.01
	C4	-0.02	C5	0.04
	C6	-0.01	C7	-0.02
	N1	-0.76	C1	-0.34
	N2	0.09	Cu	-0.49
	N2′	1.62		

Atoms in the Plane: C9, C10, C11, C12, C13, C14

Equation: $(-0.6369)X + (0.2154)Y + (-0.7402)Z - (-3.0112) = 0$

χ^2: 11.31

Deviations:	C9	-0.01	C10	0.01
	C11	0.02	C12	-0.05
	C13	0.05	C14	-0.01
	N3	-0.01	N4a	-0.10
	N4b	-0.24	C8a	-0.02
	C8b	-0.08	Cu	0.87
	N2′	1.42		

Atoms in the Plane: N6, C20, C21, C22, C23, C24

Equation: $(0.2242)X + (-0.7528)Y + (-0.6188)Z - (-1.5722) = 0$

χ^2: 0.47

Deviations:	N6	0.00	C20	0.00
	C21	0.00	C22	0.01
	C23	-0.01	C24	0.01
	Cu	0.29	N1	-0.09
	N2	0.54	N3	0.37
	N5	0.11	N2′	2.60

Atoms in the Plane: Cu, N1, C1, N2, Cu′, N1′, C1′, N2′

Equation: $(0.9636)X + (0.2423)Y + (-0.1129)Z - (0.0000) = 0$

χ^2: 2463

Deviations:	Cu	0.10	Cu′	-0.10
	N1	-0.14	N1′	0.14
	N2	0.07	N2′	-0.07
	C1	0.03	C1′	-0.03
	N3	2.02	C2	1.11
	N6	-1.90	N5	0.11

5.6 THE CRYSTAL STRUCTURE DETERMINATION OF $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ (bis[acetato-μ-(3-chlorophenylcyanamido-N)-1,10-phenanthroline-copper(II)] dihydrate).

CRYSTAL PREPARATION: Dark green diamond shaped crystals of the complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ were obtained by the slow evaporation of an ethanol solution as described in section 5.2. Considerable difficulty was experienced in obtaining suitable diffraction quality crystals. In general, the crystals were not single or well formed. The crystal finally chosen for the data collection exhibited some evidence of spiral growth patterns which were possibly indicative of poor mosaicity.

DATA COLLECTION: A single crystal of dimensions 0.26 x 0.25 x 0.10 mm was mounted on Canterbury University's Nicolet R3m four-circle diffractometer equipped with Mo radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. A series of ω-scans prior to the data collection revealed bad reflection profiles particularly along the (100) direction. In view of the unlikelihood of obtaining a better crystal, and the importance of this structure, it was decided to proceed with the data collection. The data collection was carried out at 153 K as described in appendix A1, and is summarised in table 5.6.

SPACE GROUP DETERMINATION: An examination of the intensity statistics revealed no systematic absences. The choice of the triclinic space group P1 was confirmed by the successful refinement of the structure.

STRUCTURE SOLUTION AND REFINEMENT: Structure solution and refinement were performed using the crystallographic software and procedures described in appendix A1.

The three dimensional Patterson synthesis yielded coordinates of the copper atom which were consistent with a subsequent direct methods structure solution. The remaining non-hydrogen atoms were located from subsequent Fourier maps. Several cycles of block diagonal least squares refinement of the atomic coordinates, individual isotropic temperature factors and scale factor were carried out. Initially, unit weights were applied and isotropic refinement resulted in a reliability index, R, which converged to 0.136. An inspection of the difference electron density map revealed two peaks well separated from the molecule situated approximately 1.4 Å apart. On the basis of the peak heights and their mutual positions they were attributed to a single disordered water molecule, the presence of which had previously been established by infrared spectroscopy (section 5.3). Each position was assigned as an oxygen atom with a site occupancy factor of 0.5. Anisotropic thermal parameters were introduced for the copper and chlorine atoms only, and two cycles of full matrix least squares refinement reduced the reliability index to 0.0643. The non-water hydrogen atoms were visible in a subsequent difference map and included in their geometrically calculated positons using a C-H bond distance of 1.08 Å. Anisotropic thermal parameters were applied to all non-hydrogen atoms and several cycles of least squares refinement resulted in convergent values for R and R_w of 0.0558 and 0.0581 respectively for 2142 reflections with $I > 3\sigma_{(I)}$. The largest parameter shifts in the final cycle were less than 0.05 of the estimated standard deviations.

For the last few cycles of refinement a weighting scheme of the type

$$w = k / [\ \sigma_{(F)}^2 + gF^2\ ]$$

was applied to the data, where $\sigma_{(F)}$ is the estimated standard deviation of |Fo| and k and g are constants. The values of k and g were redetermined for each cycle of refinement. This resulted in a reasonable distribution of variance with respect to $|F_o|$ and sinθ with final values of 4.22760 and 0.000391 for k and g respectively. A final difference map showed no peaks higher than 0.7 $eÅ^{-3}$ whereas the electron density of a typical carbon atom in this structure was approximately 4 $eÅ^{-3}$. The hydrogen atoms belonging to the water molecule could not be unambiguously located from the final difference map.

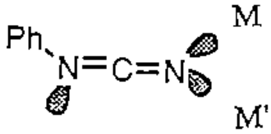
STRUCTURE DESCRIPTION: An ORTEP representation of the complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ is shown in figure 5.4 together with the atomic numbering scheme and the unit cell. Bond distances and angles are presented in table 5.7 and selected planes and deviations are given in table 5.8. The crystal structure consists of centrosymmetric dimers which are separated by normal Van der Waals distances [47]. There are two water molecules of crystallisation associated with each dimer, each of which is disordered over two positions. These water molecules are not hydrogen bonded to the rest of the molecule, which is presumably why the disorder occurs. The dimerisation occurs via the cyano nitrogen of the m-Cl-phenylcyanamido(1-) anion which asymmetrically bridges the two copper atoms. The separation of the latter is 3.247(5) Å.

The Copper Coordination Sphere: The copper atom is coordinated by two phenanthroline-nitrogen atoms (Cu-N3 = 2.014(5) Å, Cu-N4 = 2.016(5) Å), an acetate-oxygen (Cu-O1 = 1.948(5) Å) and the m-Cl-phenylcyanamido(1-) cyano nitrogen (Cu-N1 = 1.950(6) Å), in a distorted basal square plane. A longer apical bond to the m-Cl-phenylcyanamido(1-) ligand of the other half of the dimer (Cu-N1′ = 2.454(6) Å) completes the approximately square pyramidal coordination geometry. This apical Cu-N1′ bond deviates by 3.4° from the normal to the best plane through the basal atoms. The plane through atoms O1, N1, N3, and N4 shows that these four strongly coordinated atoms are not planar but that the copper atom does not deviate significantly from the best plane through them. The dihedral angle between the planes through atoms Cu, N3, N4, and Cu, N1, O1, is 7.4°, which represents a 7.4° distortion of the basal atoms, away from square planar, towards tetrahedral. This type of distortion was also observed in the structure of $[\{Cu(bipy)(PC)_2\}_2]$, and probably arises from steric interactions between the basal ligands and the apical ligand.

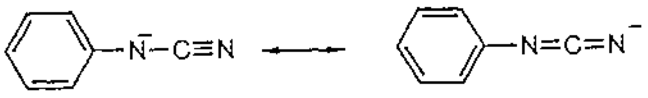
The copper to phenanthroline-nitrogen bond distances (Cu-N3 = 2.014(5) Å and Cu-N4 = 2.016(5) Å) are equivalent and agree with values previously reported for equatorial Cu(II)-N(phen) coordination [60-62]. The Cu-O1 bond distance (1.948(5) Å) is within the range of values expected for monodentate carboxylate coordination (1.946 - 1.994 Å [63]). The Cu-N1 bond distance (1.950(6) Å) is clearly shorter than the Cu-N(phen) bonds (mean 2.015 Å), indicating strong covalent bonding between the copper and the m-Cl-phenylcyanamido(1-) ligand, as observed in the previous complex [{Cu(bipy)(PC)}$_2$]. The Cu-N1′ bond distance of 2.454(6) Å is elongated by about 0.5 Å relative to the equatorial bond lengths. This pattern of coordination is similar to that in [{Cu(bipy)(PC)$_2$}$_2$], and as previously mentioned, is very common for five coordinate copper(II) complexes [42].

The m-Cl-Phenylcyanamido(1-) Ligand: This ligand forms an end-on, asymmetric bridge between the two copper atoms, where Cu-N1 = 1.950(6) Å and Cu′-N1 = 2.454(6) Å. It thus displays a different bridging mode from that seen in the complex [{Cu(bipy)(PC)$_2$}]. The phenyl ring of this ligand is planar to within the limits of experimental error, and the chlorine substituent is coplanar with this group. The chlorine atom exhibits no contacts (inter- or intramolecular) less than 2.9 Å with hydrogen atoms of neighbouring ligands. The m-Cl-phenylcyanamido(1-) and phenanthroline ligands are oriented such that they are virtually parallel to each other (the dihedral angle between the best planes through these groups is 8°). This arrangement is similar to the situation in the complex [{Cu(bipy)(PC)$_2$}$_2$], where the phenylcyanamide phenyl rings are approximately coplanar with the bipyridyl ligand. Steric repulsions between these groups are presumably minimised in this way.

The m-Cl-Phenylcyanamido(1-) ligand has bond lengths similar to those found in the phenylcyanamido(1-) ligands in [{Cu(bipy)(PC)$_2$}$_2$], and which correspond to the conformation (m-Cl-Ph-N-C≡N)$^-$. The N2-C1-N1 angle is 172.2(7)° which indicates non-linear bonding at the cyano carbon atom. This angle is similar to the corresponding angle observed in the bridging phenylcyanamido(1-) ligand in [{Cu(bipy)(PC)$_2$}$_2$], and probably arises due to steric repulsions. The electronic configurations possible for the terminal nitrogen atom suggest that for the bridging mode displayed by the present complex, the carbodiimide canonical form may result in a more efficient overlap of the nitrogen lone pairs with the copper orbitals, as follows:



This may result in an enhanced resonance contribution from form (II) relative to form (I).



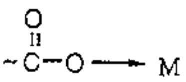
(I) (II)

As previously discussed, in an unconstrained model, this particular canonical form would theoretically give rise to C-N-Cu and C-N-Ph bond angles of 120°. The observed values (C1-N1-Cu = 149.1(5)°, C1-N1-Cu′ = 113.9(5)° and C1-N2-C2 = 120.2(6)°) are not entirely consistent with this scheme, suggesting that atom N2 is trigonal whereas the terminal nitrogen atom is not. The C1-N1 bond length is 1.196(8) Å, which is slightly larger than the value expected for a typical C-N triple bond (1.158 Å [54]) and larger than the corresponding C-N distances in the other phenylcyanamido complexes reported herein. Statistically it appears that this difference is only marginally significant [64]. However, although it is clear that neither canonical form individually describes the structure and bonding of this ligand, nevertheless the bonds in this present complex do suggest a greater contribution from the carbodiimide form relative to the others, *i.e.* the C1-N1 bond is longer (1.196(8) Å, *c.f.* 1.163 Å (mean of three complexes reported in sections 5.5, 6.4, 6.5)), the angle at N1 of (149.1(5)° represents non-linear coordination and the angles at N2 are closer to trigonal (*c.f.* values reported for the complexes in sections 5.5, 6.4, 6.5).

The copper to cyano nitrogen bond distance (Cu-N1 = 1.950(6) Å is equivalent, within the limits of experimental error, to that of the terminally bound phenylcyanamido(1-) ligand in $[\{Cu(bipy)(PC)_2\}_2]$ (1.942(6) Å). This suggests that the m-Cl-phenylcyanamido(1-) ligand has similar σ-donor properties to the monodentate phenylcyanamido(1-) ligand.

The 1,10-Phenanthroline Ligand: This ligand is strictly planar. The bond lengths and angles are consistent with the values usually found in these systems [60-62].

The Acetate Ligand: The acetate group is monodentate to the copper and exhibits bond lengths appropriate for:



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-O\longrightarrow M$$

Table 5.6 Crystallographic Data for
$[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$.

Formula	$(Cu2,C42,H30,N8,O4,Cl2)\cdot 2H_2O$
Mol. wt.	944.0
Cryst. syst.	Triclinic
Space group	PI
a, Å	8.171(5)
b, Å	10.060(6)
c, Å	13.377(7)
α, deg.	74.33(4)
β, deg.	84.79(5)
γ, deg.	72.24(4)
Z	1
V, $Å^3$	1008(1)
* F(000)	444.0
$D_{(calc)}$, gcm^{-3}	1.54
$D_{(obsd)}$, gcm^{-3}	1.51
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator $\lambda = 0.71069$ Å
Temp., K	153
Reflns. Measd.	h, ±k, ±l
Scan type	$\omega/2\theta$
Scan range, deg.	2.4
Scan speed, deg/min.	7.32
Max. 2θ, deg.	45
Measd. Reflns.	2727
Unique reflns. $(I > 3\sigma_{(I)})$	2142
Cryst. dimensions. (dist. from centroid,mm)	±(110), 0.12
	±(011), 0.13
	±(001), 0.05
Abs. corr. type	Empirical
Abs. coeff., cm^{-1}	11.74
Trans. factors	Max. 0.892 Min. 0.763
Wtg Scheme	$4.22760 / [\sigma_{(F)}^2 + 0.000391F^2]$
R	0.0558
R_w	0.0581

Figure 5.4 The ORTEP representation of $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ showing the atomic labelling and the stereoscopic unit cell.

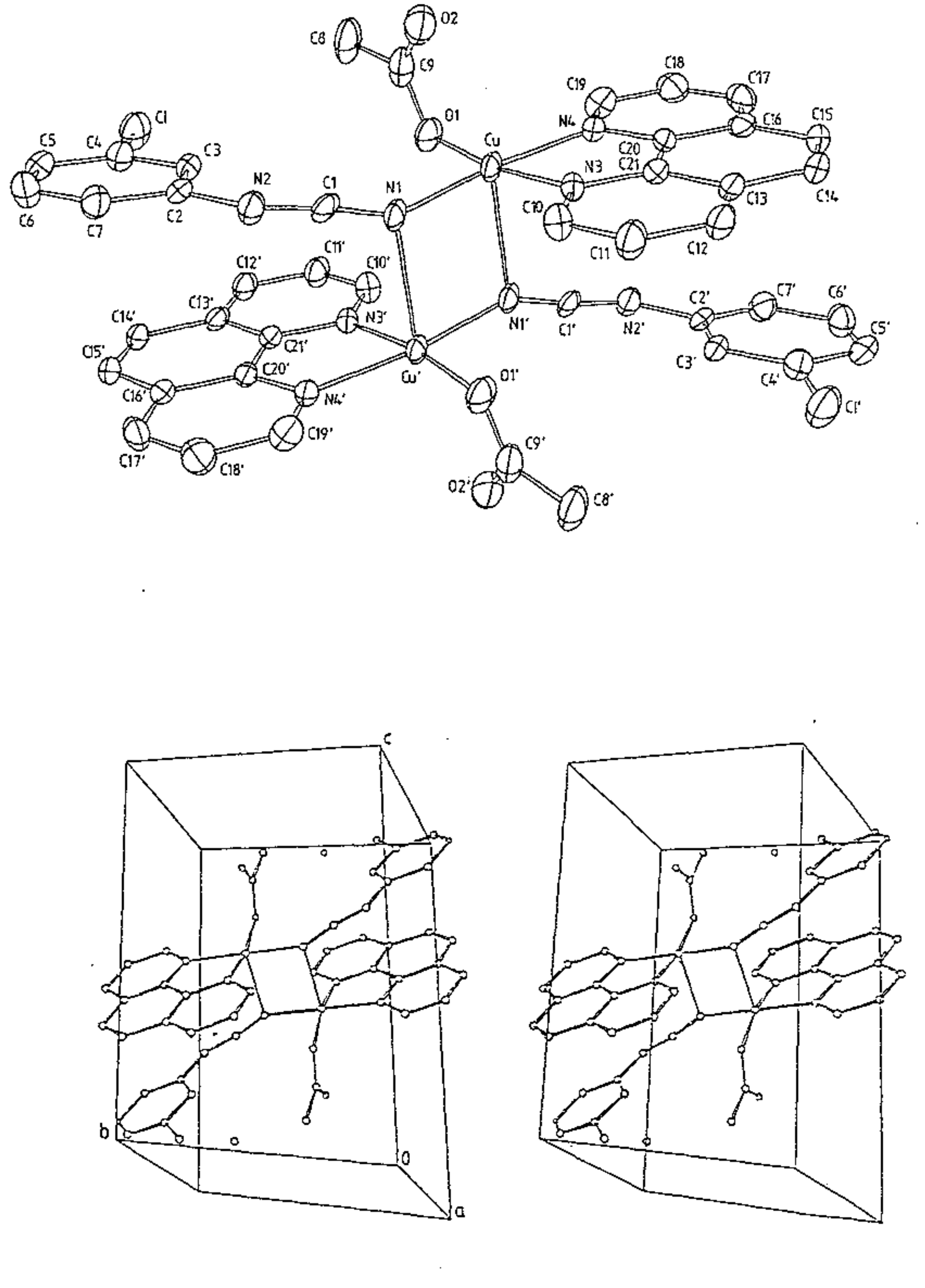


Table 5.7 Bond Distances (Å) and Angles (deg.) in $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$.

Cu...Cu′	3.247(5)	C9-O2	1.249(9)
Cu-N1	1.950(6)	N3-C10	1.330(8)
Cu-O1	1.948(5)	C10-C11	1.403(10)
Cu-N3	2.014(5)	C11-C12	1.373(9)
Cu-N4	2.016(5)	C12-C13	1.406(9)
Cu-N1′	2.454(6)	C13-C14	1.432(9)
N1-C1	1.196(8)	C13-C21	1.389(9)
C1-N2	1.269(9)	C14-C15	1.346(10)
N2-C2	1.402(9)	C15-C16	1.422(10)
C2-C3	1.400(10)	C16-C17	1.426(10)
C3-C4	1.374(9)	C16-C20	1.397(9)
C4-Cl	1.756(7)	C17-C18	1.365(10)
C4-C5	1.388(9)	C18-C19	1.404(10)
C5-C6	1.379(11)	C19-N4	1.340(8)
C6-C7	1.391(10)	N4-C20	1.356(8)
C7-C2	1.387(9)	C20-C21	1.430(9)
C8-C9	1.497(10)	C21-N3	1.360(8)
C9-O1	1.285(9)		

N1--Cu--O1	92.7(2)	Cl--C4--C5	119.0(6)
N1--Cu--N3	93.2(2)	C3--C4--Cl	118.2(5)
N1--Cu--N4	172.8(2)	C4--C5--C6	117.7(7)
N1--Cu--N1′	85.7(2)	C5--C6--C7	121.1(7)
O1--Cu--N3	172.1(2)	C6--C7--C2	119.3(7)
O1--Cu--N4	93.3(2)	C8--C9--O1	115.7(8)
O1--Cu--N1′	95.0(2)	C8--C9--O2	122.3(8)
N3--Cu--N4	81.2(2)	O1--C9--O2	122.1(7)
N3--Cu--N1′	90.7(2)	N3--C10--C11	122.4(6)
N4--Cu--N1′	89.9(2)	C10--C11--C12	119.4(6)
C1--N1--Cu	149.1(5)	C11--C12--C13	119.6(6)
C1--N1--Cu′	113.9(5)	C12--C13--C21	117.1(6)
Cu--N1--Cu′	94.3(2)	C12--C13--C14	123.6(6)
C1--N2--C2	120.2(6)	C21--C13--C14	119.3(6)
Cu--N3--C10	128.8(5)	C13--C14--C15	120.6(7)
Cu--N3--C21	113.3(4)	C14--C15--C16	121.2(6)
C21--N3--C10	117.7(6)	C15--C16--C17	124.4(6)
Cu--N4--C19	128.6(5)	C15--C16--C20	119.4(6)
Cu--N4--C20	113.5(4)	C20--C16--C17	116.2(7)
C19--N4--C20	117.7(6)	C16--C17--C18	119.3(6)
C9--O1--Cu	108.1(5)	C17--C18--C19	120.5(7)
N1--C1--N2	172.2(7)	C18--C19--N4	121.6(7)
N2--C2--C3	122.9(6)	N4--C20--C21	115.8(6)
N2--C2--C7	116.4(6)	N4--C20--C16	124.6(6)
C7--C2--C3	120.7(6)	C16--C20--C21	119.6(6)
C2--C3--C4	118.4(6)	C20--C21--N3	115.9(6)
C3--C4--C5	122.8(7)	C20--C21--C13	120.0(6)
		C13--C21--N3	124.1(6)

Table 5.8 Selected least squares planes and deviations (Å) in $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$.

Atoms in the Plane: Cu, N1, N3, N4, O1

Equation: $(0.7566)X + (-0.1544)Y + (-0.6353)Z - (-1.6512) = 0$

χ^2: 951.91

Deviations:

Cu	0.01	N1	0.08
N3	-0.09	N4	0.09
O1	-0.08	N1′	2.46
C1	-0.44	N2	-0.91

Atoms in the Plane: N1, N3, N4, O1

Equation: $(0.7567)X + (-0.1545)Y + (-0.6353)Z - (-1.6532) = 0$

χ^2: 846.58

Deviations:

N1	0.08	N3	-0.09
N4	0.09	O1	-0.08
Cu	0.01	N1′	2.46
C1	-0.44	N2	-0.91

Atoms in the Plane: C16, C17, C18, C19, N4, C20

Equation: $(0.7590)X + (-0.2731)Y + (-0.5911)Z - (-2.4153) = 0$

χ^2: 3.19

Deviations:

C16	0.00	C17	0.01
C18	-0.01	C19	0.00
C20	0.00	N4	0.01
N3	0.04	O1	0.12
Cu	0.18	N1′	2.63

Atoms in the Plane: N3, C10, C11, C12, C13, C21

Equation: $(0.7524)X + (-0.2514)Y + (-0.6088)Z - (-2.3299) = 0$

χ^2: 15.92

Deviations:	N3	-0.01	C10	0.02
	C11	-0.01	C12	0.00
	C13	0.01	C21	-0.01
	N4	-0.02	Cu	0.11
	O1	0.01	N1	0.37
	N1′	2.55		

Atoms in the Plane: C13, C14, C15, C16, C20, C21

Equation: $(0.7537)X + (-0.2671)Y + (-0.6005)Z - (-2.4268) = 0$

χ^2: 3.64

Deviations:	C13	0.01	C14	-0.01
	C15	0.00	C16	0.01
	C20	-0.01	C21	0.00
	N3	0.02	N4	-0.01
	N1	0.45	O1	0.06
	N1′	2.59	Cu	0.15

Atoms in the Plane: C2, C3, C4, C5, C6, C7

Equation: $(0.7257)X + (-0.3966)Y + (-0.5621)Z - (-3.0246) = 0$

χ^2: 0.54

Deviations:	C2	0.00	C3	0.00
	C4	0.00	C5	0.00
	C6	0.000	C7	0.00
	N2	0.04	C1	0.20
	N1	0.43	Cl	0.00

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CHAPTER SIX

COPPER(I) COMPLEXATION BY PHENYLCYANAMIDES.

6.1 INTRODUCTION: COPPER(I) COMPLEXES WITH COORDINATING ANIONS

The copper(I) cation is diamagnetic and, except where colour arises from the anion or charge transfer bands, it compounds are colourless. In aqueous solution the copper(I) ion is very unstable with the disproportionation reaction

$$2\mathrm{Cu(I)} \rightleftharpoons \mathrm{Cu(II)} + \mathrm{Cu(s)}$$

being heavily in favour of Cu(II). Cuprous compounds achieve their stability through very low solubility or by the incorporation of ligands having pi-acceptor character. In contrast with the well known stereochemical 'plasticity' of the copper(II) ion, the cuprous state gives rise to more narrowly defined geometries. The usual stereochemistry is tetrahedral as in the complexes $[\mathrm{Cu(CN)_4}]^{3-}$, $[\mathrm{Cu(py)_4}]^{+}$, and $[\mathrm{CuL_2}]^{+}$ (L = phen, bipy), although lower coordination numbers are known such as 2, in linear $[\mathrm{CuCl_2}]^{-}$, and 3, as in $\mathrm{K[Cu(CN)_2]}$. In addition, $\mathrm{Cu^{I}_4}$ cluster compounds are becoming increasingly familiar. Examples of these include 'cubane' and 'step' complexes, $[\mathrm{CuXL}]_4$, where X = halide and L = phosphine or arsine [1]. Large copper(I) aggregate compounds, such as the recently reported $[\mathrm{Cu_{10}\{(EtO)_2P(S){-}N{=}C(S^{-})NHPh\}_9}](\mathrm{ClO_4})$ [2], are also attracting increasing attention. This particular complex, described as possessing a 'novel 'tent-like' structure', comprises a $\mathrm{Cu_{10}S_{18}}$ core and can be compared to other copper(I) aggregates which contain $\mathrm{Cu^{I}_4S_6}$ [3] and $\mathrm{Cu^{I}_8S_{12}}$ [4,5] centres. Phosphine and its alkyl or phenyl derivatives are among the most widely used classes of ligands for stabilising cuprous compounds. These include $\mathrm{PR_3}$, $\mathrm{PPh_3}$, mixed ligands such as $\mathrm{PMePh_2}$, and mutidentate ligands such as $\mathrm{Ph_2PCH_2PPh_2}$ (dppm) and $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe). The outcome of an interaction between the copper(I) ion and one of these phosphine ligands will generally depend on the M:L ratio, the anion present, the solvent, and frequently steric factors associated with the more bulky members of the group. In contrast, simple phosphine complexes of copper(II) are unknown. With weakly coordinating anions, such as nitrate, perchlorate, or tetrafluoroborate, mononuclear four coordinate copper(I) complexes have been reported including $[(PPh_3)_2Cu(NO_3)]$ [6], $[(PPh_3)_3Cu(BF_4)]$ [7], $[(PPh_3)_4Cu]ClO_4$ [8], and $[(PPh_3)_3(MeCN)Cu]ClO_4$ [9]. These examples show how the solvent or the anion itself tend to participate in the attainment of a four coordinate metal centre. The monodentate phosphine ligands react with copper(I) halides to give a series of compounds with various Cu:P ratios, e.g. 1:1, 1:2, 1:3, and 2:3 [10,11]. The outcome of these reactions is not always predictable. The 2:3 complexes are prepared by the reaction of CuX with PPh_3 in a 1:2 ratio. The unusual structure of $[Cu_2Cl_2(PPh_3)_3]$ has been determined and shown to contain three- and four-coordinate copper [12]. Copper(I) halides also react with the chelating phosphine ligands dppe and dppm giving compounds with a number of stoichiometries, $(CuX)_nL$ (L = dppm, dppe and X = Cl, Br, and I). Marish et al. give a detailed account of the preparation of these complexes [13]. For dppm, M:L ratios of 1:1, 1:2, 2:3, 3:4, are reported and ratios of 1:1, 1:2, 1:3, 2:3 and 3:4 for dppe. In general, X-ray crystallography has been the most widely used technique for structurally characterising copper(I)-phosphine complexes, although recent studies have shown that solid-state ^{31}P nmr and far-infrared spectroscopy are also useful techniques for obtaining structural information on these types of complexes [14-16].

Copper(I)-phosphine complexes with pseudohalides have also been studied; examples include $[Cu(PPh_3)_2(CN)]$ [17], $[\{Cu(N_3)(PPh_3)_2\}_2]$ [18], $[\{Cu(N_3)(dppe)_{1.5}\}_2]$ [19], and $[\{Cu(PPh_2(Me))_2(SCN)\}_2]$ [20]. The structures of the last three have been determined by X-ray crystallography and will be considered in more detail in following sections. It seemed reasonable, in view of the existence of these complexes, to attempt to prepare similar copper(I)-phosphines with deprotonated phenylcyanamide ligands. The results of these attempts are reported in this chapter. Much interest has been directed towards the synthetic and structural characterisation of copper(I), silver(I), and gold(I) complexes incorporating tertiary phosphine ligands with halides, pseudohalides, or weakly coordinating anions. The literature provides a comprehensive account, including the synthesis and structural characteristics, of many of these systems. However, the wide range of stoichiometries and structures dictates that more X-ray structural determinations are required to improve understanding of the factors which determine the stereochemistry of copper(I)-phosphine complexes. The aim of this section of work was to investigate the extent to which phenylcyanamide, as an anionic ligand, behaves as a pseudohalide in its reactivity with copper(I). The synthesis and characterisation of two series of copper(I)-phenylcyanamide complexes which incorporate dppe and PPh_3 respectively, have been carried out. The crystal structures of $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ and $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ are presented and compared with some previously structurally characterised halide and pseudohalide copper(I) complexes.

6.2 EXPERIMENTAL: THE PREPARATION OF COPPER(I) COMPLEXES WITH PHENYLCYANAMIDES

(a) dppe Complexes, $[\{Cu(dppe)_{1.5}(L)\}_2]\cdot 2(CH_3)_2CO$.
L = phenylcyanamide, p-chloro-, m-chloro-, p-bromo-, and p-fluorophenylcyanamide.

A solution of sodium ethoxide was prepared by dissolving sodium metal (0.02 g,1 mmol) in ethanol (5 ml). This was added to a solution of L (1 mmol) in acetone (15 ml) which was then added slowly, with stirring, to a solution of $[Cu(CH_3CN)_4]ClO_4$ (0.33 g , 1 mmol) and dppe (0.60 g, 1.5 mmol) in 30 ml of acetone. The resulting colourless solution was filtered to remove all trace of insoluble material, and upon standing immediately began to deposit the crystalline product. This was removed by filtration, washed with acetone, then air dried; yields 70-80%.

(b) PPh_3 Complexes, $[\{Cu(PPh_3)_2L\}_2]$. The phenylcyanamide complex was prepared and characterised initially. The preparation and characterisation of the remaining members of this series was then carried out by Mr S. L. Ingham (B.Sc.(Hons) student Massey University).
L = phenylcyanamide, p-chloro-, p-bromo-, p-fluoro-, and p-methylphenylcyanamide.

These compounds were prepared by combining the reagents stoichiometrically in a manner analogous to that described for the $[\{Cu(dppe)_{1.5}(L)\}_2]\cdot 2(CH_3)_2CO$ complexes;yields 70-80%.

6.3 RESULTS: THE CHARACTERISATION OF THE COPPER(I) COMPLEXES

Two series of copper(I)-phosphine complexes have been prepared and characterised. The physicochemical data for these complexes are presented in table 6.1. The monodentate phosphine ligand, triphenylphosphine (PPh_3), has given rise to the complexes of formulation $[\{Cu(PPh_3)_2(L)\}_2]$, where L is a phenylcyanamide anion.

The crystal structure determination of $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ is presented in section 6.5 and on the basis of this structure it appears that the members of this series exist as dimers. The bidentate phosphine ligand, 1,2-bis(diphenylphosphino)-ethane (dppe) has given rise to the acetone-solvated complexes $[\{Cu(dppe)_{1.5}(L)\}_2]\cdot 2(CH_3)_2CO$. The presence of the acetone molecule was inferred from the microanalytical data and the infrared spectra which each displayed a strong band at 1710 cm^{-1} consistent with the $\nu(C=O)$ frequency of acetone [21]. The crystal structure determination of a representative of this series, $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$, suggests that these complexes also exist as dimers (section 6.4). The infrared $\nu(CN)$ frequencies of the ligands in these two series show increases of up to ~60 cm^{-1} relative to those of the corresponding Ag(+) salts (section 5.2). This suggests that the cyano nitrogens of the phenylcyanamido ligands are coordinated to the copper atom [22].

Table 6.1 Physicochemical data for the copper(I) complexes.

EMPIRICAL FORMULA	M.P./°C	MICROANALYTICAL DATA (%)				IR ν(CN), cm^{-1}
		C	H	N	X	
$[Cu(PPh_3)_2(L)]$						
L						
PC	197-199	73.0 (73.2)	5.4 (5.0)	4.0 (4.0)		2163
p-Me-PC	214-216	73.5 (73.5)	5.4 (5.2)	3.9 (3.9)		2174, 2167
p-Cl-PC	219-221	69.9 (69.8)	4.8 (4.6)	3.8 (3.8)	5.0 (4.8)	2179
m-Cl-PC	201-205	69.8 (69.8)	4.9 (4.6)	3.7 (3.8)	4.9 (4.8)	2153
p-Br-PC	d	65.6 (65.9)	4.6 (4.4)	3.3 (3.6)		2175
p-F-PC	200-203	71.4 (71.1)	4.5 (5.0)	3.9 (4.0)		2161
$[Cu(dppe)_{1.5}(L)]\cdot(CH_3)_2CO$						
L						
PC	240-242	70.2 (70.4)	5.6 (5.6)	4.1 (3.4)		2165, 2126
p-Cl-PC	110-113	67.6 (67.3)	5.3 (5.4)	3.2 (3.1)	4.1 (4.2)	2166, 2140
m-Cl-PC	224-226	67.1 (67.6)	5.0 (5.3)	3.5 (3.2)	4.9 (4.1)	2163, 2139
p-Br-PC	106-108	64.1 (64.3)	5.1 (5.0)	3.0 (3.1)	9.1 (8.3)	2159, 2137
p-F-PC	232-233	67.3 (68.7)	5.6 (5.4)	3.3 (3.3)	2.0 (2.2)	2177, 2132

d decomposes at > 250°C.

calculated figures in parentheses.

6.4 THE CRYSTAL STRUCTURE DETERMINATION OF $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ (µ-(1,2-bis(diphenylphosphino)ethane)bis[4-chlorophenylcyanamido-N-1,2-bis(diphenylphosphino)ethanecopper(I)] bisacetone).

CRYSTAL PREPARATION: Transparent plate-like crystals of the complex $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ were obtained by the slow evaporation of an acetone solution as described in section 6.2. The crystals were well formed and completely extinguished polarised light.

DATA COLLECTION: A single crystal of dimensions 0.54 x 0.40 x 0.20 mm was mounted on Canterbury University's Nicolet R3m four-circle diffractometer equipped with Mo radiation (λ = 0.71069 Å) and a graphite monochromator. The data collection was carried out at 153 K as described in appendix A1, and is summarised in table 6.2.

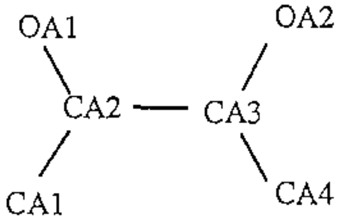
SPACE GROUP DETERMINATION: The space group Pbca was assigned unambiguously on the basis of of the systematic absences, 0kl k = 2n + 1, h0l l = 2n + 1, and hk0, h = 2n + 1.

STRUCTURE SOLUTION AND REFINEMENT: Structure solution and refinement was performed according to the methods outlined in appendix A1.

The three dimensional Patterson synthesis yielded coordinates of the copper atom consistent both with the space group Pbca and with a subsequent direct methods structure solution. The positions of the Cl and P atoms were obtained from a Fourier map phased by the copper. The remaining non-hydrogen atoms were located from subsequent Fourier maps. Several cycles of block diagonal least squares refinement of the atomic coordinates, individual isotropic temperature factors and scale factor were carried out. Initially unit weights were applied and isotropic refinement resulted in a reliability index, R, which converged at 0.143.

The Cu, Cl, P, aliphatic and non-dppe carbon atoms were assigned anisotropic temperature factors. The dppe phenyl rings (assumed to possess D6h symmetry, with C-C bonds 1.392 Å) were constrained to rigid body motion in which each phenyl ring was described by three positional and three orientational parameters and each carbon was assigned its own variable isotropic thermal parameter. The contribution of the hydrogen atoms were then included at their geometrically calculated positions using a C-H bond distance of 1.08 Å. Three cycles of full matrix least squares refinement then reduced the reliability index to 0.109. The difference electron density map following this refinement revealed six peaks of electron density well separated from the molecule. These were attributed, on the basis of their mutual positions, to a disordered solvating acetone molecule whose presence in the solid state had been previously established by infrared spectroscopy and elemental analysis (sections 6.2 and 6.3). Due to the extensive disorder, the various attempts made to refine this acetone molecule were largely unsuccessful and resulted in large thermal parameters and lack of convergence. Refinement of the individual atomic positions resulted in irregular bond lengths which were interpreted as intermediate between the two bond distances expected for acetone (C-C = 1.52 Å, C=O = 1.25 Å [23]). The acetone molecule is centred on two positions each of which possesses the three possible orientations. Each molecule is situated such that its central carbon atom simultaneously occupies the position

corresponding to the fourth member of the other molecule. The arrangement of peaks in the difference map is shown as follows, along with their numbering:



In accordance with this interpretation, the carbon atoms CA2 and CA3 were assigned site occupancy factors of 1 and the remaining positions were assigned atomic scattering factors corresponding to nitrogen atoms (mean of O and C) and site occupancy factors of 0.5. The positional parameters of the acetone molecule were fixed to aid the overall convergence of the structure. The inclusion of the acetone molecule in a final 3 cycles of least squares refinement reduced the reliability indices, R and R_w, to convergent values of

0.0673 and 0.0690 respectively for 3604 reflections with $I > 3\sigma_{(I)}$. The largest parameter shifts in the final cycle were less than 0.05 of the estimated standard deviations. For the last few cycles of refinement a weighting scheme of the type

$$w = k / [\sigma_{(F)}^2 + gF^2]$$

was applied to the data, where $\sigma_{(F)}$ is the estimated standard deviation of $|F_o|$ and k and g are constants. The values of g and k were redetermined for each cycle of refinement. This resulted in a reasonable distribution of variance with respect to $|F_o|$ and sinθ with final values for k and g of 3.6172 and 0.000300 respectively. A final difference Fourier map showed no peaks higher than 0.8 $eÅ^{-3}$ whereas the electron density of a typical carbon atom in this structure was approximately 4.0 $eÅ^{-3}$. The two highest peaks were associated with one of the phenyl rings assigned as a rigid group, suggesting a slight disordering of this group. The remaining peaks were all less than 0.60 $eÅ^{-3}$, the highest of which were associated with the disordered acetone molecule.

STRUCTURE DESCRIPTION:

The complex $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ exists as a dimer in the solid state. Each copper is coordinated to one chelating dppe ligand one terminal dppe ligand, and one terminal p-Cl-phenylcyanamido(1-) ligand. The terminal dppe ligand is centred on a crystallographic centre of symmetry such that it bridges the two copper atoms of the dimer. The dimer is thus centrosymmetric with the centre of symmetry located between the two methylene carbon atoms of the bridging dppe ligand. There are two disordered acetone solvate molecules associated with each dimer, and four such dimers per unit cell. An examination of all possible intermolecular distances showed that there are only the usual Van der Waals contacts [24]. All the important intramolecular distances and angles are presented in table 6.3 and selected least-squares planes, dihedral angles, and deviations are presented in table 6.4.

The Copper Coordination Environment: Views of the copper(I) coordination sphere are shown in figures 6.1 and 6.2. Each copper atom is bonded to three phosphorus atoms of the dppe ligands and one cyano nitrogen atom from the p-Cl-phenylcyanamido(1-) ligand, forming pseudo-tetrahedral CuP_3N centres.

All the N1-Cu-P and P-Cu-P bond angles exhibit deviations from the tetrahedral value of 109.5°. Deviations from the ideal tetrahedral geometry are very common in copper(I) complexes and in this case the distortion arises primarily because of the geometrical constraints imposed by the bite angle of the chelating dppe ligand. The bite angle of 89.3(1)° is among the largest of those reported for bidentate dppe, but is comparable with those found in the structures of $[\{Cu(dppe)_{1.5}(N_3)\}_2]$ (90.0(2)°) [19], and $[Cu_2(dppe)_3Cl_2]\cdot 2(CH_3)_2CO$ (89.5(2)°) [23]. The N1-Cu-P2 bond angle of 108.6(2)° is close to the tetrahedral value (109.5°) whereas the N1-Cu-P1 and N1-Cu-P3 bond angles (113.2(2)° and 116.5(2)° respectively) are considerably enlarged. This suggests that the geometry about the copper atom can be described as a distortion from tetrahedral in which the dppe ligands are pushed away from the p-Cl-phenylcyanamido(1-) ligand. The Cu-P distances are essentially equivalent, with a mean value of 2.291 Å. Similar Cu-P bond lengths have been reported for the complexes $[Cu_2Cl_2(dppe)_3]\cdot(CH_3)_2CO$ (mean value 2.295 Å) and $[\{Cu(dppe)_{1.5}(N_3)\}_2]$ (mean value 2.310 Å). Assuming Pauling covalent radii of 1.35 Å and 1.10 Å for Cu and P respectively [24] there is, for the Cu-P mean distance, a shortening of 0.16 Å which testifies to a pi-bonding component in the Cu-P interaction. The Cu-N1 bond length (1.967(7) Å) is shorter than the sum of the Pauling covalent radii (1.35 Å and 0.70 Å for Cu and N respectively), and shorter than the Cu(I)-N distance in $[\{Cu(dppe)_{1.5}(N_3)\}_2]$ (terminally bound azide, Cu-N = 2.040(13) Å). This very short Cu-N1 distance argues for appreciable copper-to-nitrogen pi back-bonding.

The p-Cl-Phenylcyanamido(1-) Ligand: The terminally bound p-Cl-phenylcyanamido(1-) ligand exhibits bond lengths consistent with $(Ph\text{-}N\text{-}C{\equiv}N)^-$. The phenyl ring is planar, within the limits of experimental error, and the chlorine atom is coplanar with this group. The bond lengths and angles are essentially very similar to those in the phenylcyanamido(1-) and m-Cl-phenylcyanamido(1-) ligands described in the structures of $[\{Cu(bipy)(PC)\}_2]$ and

[{Cu(phen)(m-Cl-PC)(Ac)}$_2$]·2H$_2$O (this work). The angle Cu-N1-C1 is 171.3(7)° which indicates an essentially linear end-on coordination of the cyanamide group.

The Terminal dppe Ligand: This ligand possesses a crystallographic centre of symmetry between the two methylene carbon atoms which constrains the C8-C8′, C8-P1, and C8′-P1′ vectors to be coplanar and the P1-C8-C8′-P1′ chain to adopt an exact trans configuration. The C8-C8′ bond length of 1.592(5) Å is marginally longer than the expected value for a C-C single bond of 1.537 Å, but this is not unprecedented for monodentate dppe ligands [25]. The P1-C(phenyl) bond distances, mean 1.825 Å, are in agreement with the P-C(phenyl) bond distances in a number of other related compounds, viz. [$Cu_2(CF_3CN_4)_2(dppe)_3$] mean P-C(phenyl) = 1.827 Å [25], [$Cu_2(Cl)_2(dppe)_3$]·2$(CH_3)_2CO$ mean P-C(phenyl) = 1.83 Å [23], and $P(C_6H_5)_3$ mean P-C(phenyl) = 1.828 Å [26]. The C-P1-C bond angles show contractions from the tetrahedral value of 109.5° (mean = 102.8°), and the Cu-P1-C bond angles show approximately corresponding expansions (mean 115.5°). The P-C8-C8′ bond angle (109.1(5)°) is very close to the tetrahedral value. An account of the theoretically possible conformations of the Cu-dppe-Cu′ chain has been presented by Gaughan et al. [19]: the conformation of the P1-C8-C8′-P1′ chain is fixed by symmetry, but centrosymmetric rotations which are possible about the C8-P1 bonds give rise to a range of Cu-P1-C8-C8′-P1′-Cu′ conformations with a corresponding range of Cu...Cu′ distances. Three such conformations are shown as follows, for different angular rotations, delta, about the C8-P1 bond.

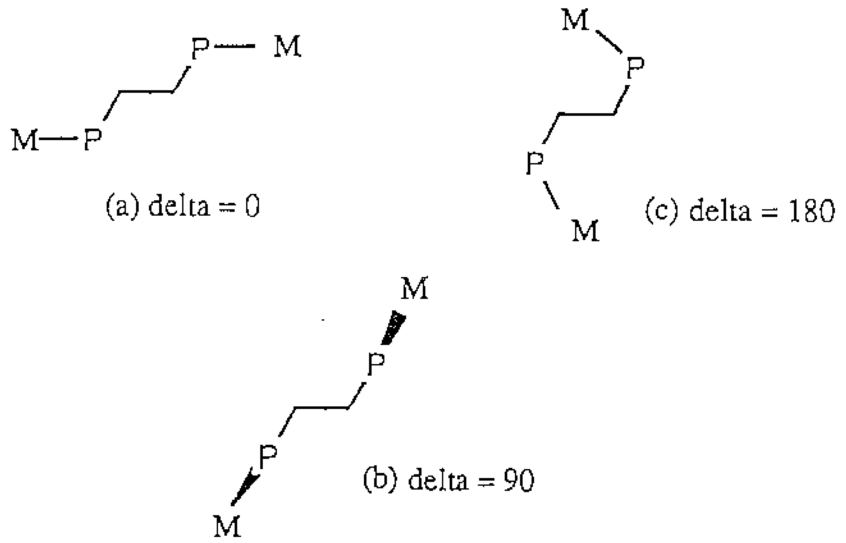


Figure 6.3 Conformations of a bridging dppe ligand.

For an idealised case in which all the bond angles are 109.5° and the C-C, C-P, and P-Cu bond lengths are 1.54 Å, 1.90 Å, and 2.30 Å respectively, the Cu..Cu′ distances are 8.23 Å, 7.53 Å, and 6.52 Å for conformations (a), (b), and (c). In conformations (a) and (c) the copper atoms are coplanar with the phosphorus and carbon atoms, whereas in (b) the copper atoms are displaced by 2.17 Å above and below the P1-C8-C8′-P1′ plane with a 90° dihedral angle between the P1-C8-C8′-P1 and Cu-P1-C8 planes. In the present structure, the Cu...Cu′ distance is 6.979(2) Å, and the copper atoms are displaced by 1.81 Å above and below the P1-C8-C8′-P1′ plane with a dihedral angle of 59° between the P1-C8-C8′-P1′ and Cu-P1-C8 planes. These values suggest that conformation (b) most closely represents the conformation of the monodentate dppe ligand in this molecule and that the dihedral angle of 59° represents a delta rotation of 59° from conformation (c) toward (b). Gaughan *et al.* conclude that conformation (c) is the most sterically unfavourable, whereas (b) is conditionally acceptable for certain values of delta, and (a) is acceptable for all values of delta. The conformation adopted by this molecule therefore reflects a compromise between an optimisation of the packing efficiency (conformation (c)) and the minimisation of intramolecular nonbonding interactions (conformations (a) and (b)).

The Bidentate dppe Ligand: The conformation of the chelate ring can be described by the torsion angles listed in table 6.4. Kilbourn *et* al. [27] have discussed the results of theoretical calculations of the conformational energies of five membered chelate rings in relation to diphosphine rings. This paper also includes a tabulation of the experimental torsion angles in a number of complexes. According to Kilbourn, the conformational energy of the dppe chelate ring is related to the torsion angle τ[C-C], and to a lesser extent, the P-M-P and M-P-C(et) angles. The displacement of the two carbon atoms with respect to the P-M-P plane does not greatly affect this energy, and a variety of conformations of equivalent stability are therefore possible. The out-of-plane displacement of atoms C9 and C10, on opposite sides of the P2-Cu-P3 plane, are -0.10 Å and +0.68 Å respectively. The conformation of the five-membered chelate ring is asymmetric, as indicated by the different τ[Cu-P] torsion angles, and follows a conformational pattern common to other structures containing this ligand. The torsion angle τ[C9-C10] of 56.5° is a typical value for bidentate dppe and falls close to the value of 60° expected for an ideally staggered conformation.

All the P-C distances and C-P-C angles are essentially equivalent, and are comparable with the corresponding values found in a number of previously reported structures [28]. The Cu-P-C angles do exhibit differences for the bidentate and monodentate ligands. The mean values of the Cu-P-C(Ph) and Cu-P-C(et) angles are 120° and 102.7° in the chelating and 117° and 111.4° in the bridging ligand, respectively. These values show that the phosphorus atoms of the bridging ligand are closer to tetrahedral symmetry than those of the chelating ligand suggesting that there is a compromise between the bite angle and the tetrahedral angles at the phosphorus.

Table 6.2 Crystallographic Data for
$[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$.

Formula.	$(Cu2,C92,H80,N4,P6,Cl2)\cdot 2((CH_3)_2CO)$
Mol. wt.	1740
Cryst. syst.	Orthorhombic
Space group	Pbca
a, Å	22.397(14)
b, Å	18.970(7)
c, Å	20.341(5)
Z	4
V, Å^3	8642(8)
F(000)	3616
D(calc), gcm^{-3}	1.34
D(obsd), gcm^{-3}	1.31
Diffractometer	Nicolet R3m
Radiation	Mo-K_α graphite monochromator $\lambda = 0.71069$ Å
Temp., K	153
Reflns. Measd.	±h,k,l
Scan type	$\omega/2\theta$
Scan range, deg.	1.2
Scan speed, deg/min.	4.88
Max. 2θ, deg.	45
Measd. Reflns.	6407
Unique reflns.($I > 3\sigma_{(I)}$)	3604
Cryst. dimensions, mm	0.54 x 0.40 x 0.20 (plate)
Wtg Scheme	$3.6172 / [\sigma_{(F)}^2 + 0.000300F^2]$
Abs. corr. type	Psi-scans
Abs. coeff., cm^{-1}	6.64
Trans. factors	Max. 0.774 Min. 0.722
R	0.0673
R_w	0.0690

Figure 6.1 The ORTEP representaton of

$[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$

showing the atomic labelling.

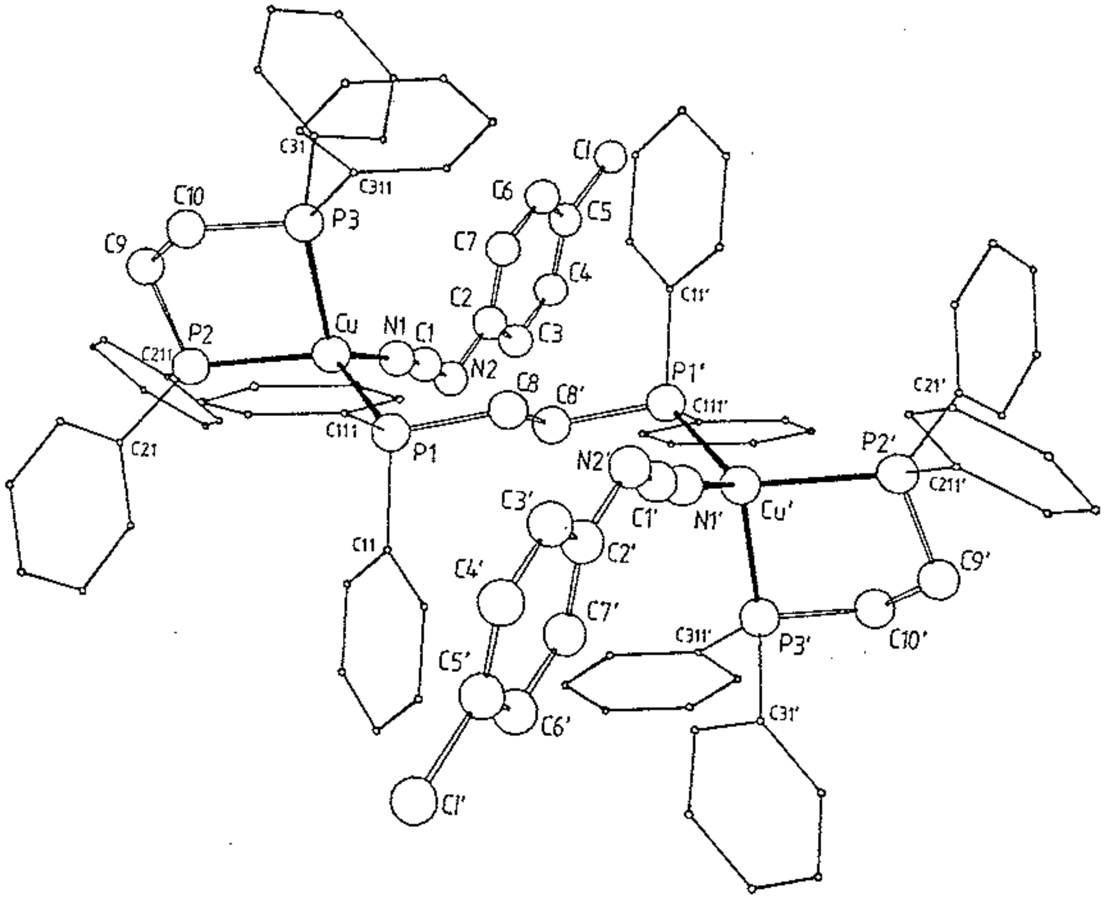


Figure 6.2 The ORTEP representation of

$[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$

showing a single molecule and the stereoscopic unit cell,

with the dppe-phenyl rings omitted for clarity.

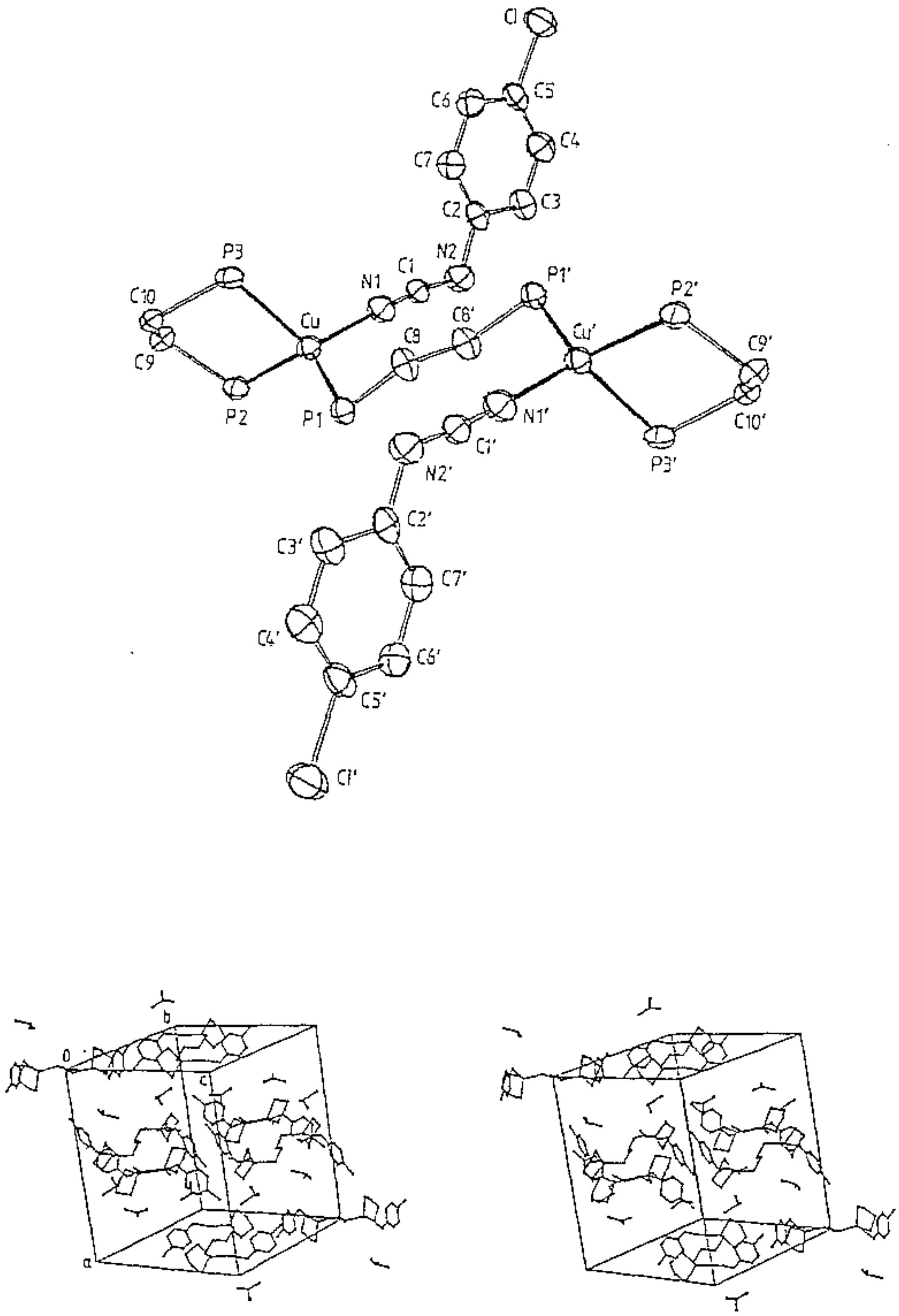


Table 6.3 Bond Distances (Å) and Angles (deg.) in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$.

Cu...Cu′	6.979(2)	N1-C1	1.155(10)
Cu-P1	2.282(2)	N2-C2	1.398(10)
Cu-P2	2.300(2)	C1-N2	1.307(11)
Cu-P3	2.292(2)	C2-C3	1.413(10)
Cu-N1	1.967(7)	C3-C4	1.363(11)
P1-C8	1.827(8)	C4-C5	1.390(12)
P1-C11	1.819(7)	C5-Cl	1.776(8)
P1-C111	1.831(6)	C5-C6	1.356(11)
P2-C9	1.845(7)	C6-C7	1.402(11)
P2-C21	1.828(8)	C7-C2	1.378(11)
P2-C211	1.825(6)	C8-C8′	1.592(5)
P3-C10	1.847(7)	C9-C10	1.545(10)
P3-C31	1.834(5)		
P3-C311	1.830(5)		

P1--Cu--P2	121.1(2)	Cu--P3--C311	125.5(2)
P1--Cu--P3	106.2(1)	C31--P3--C10	103.1(3)
P1--Cu--N1	113.2(2)	C311--P3--C10	105.0(3)
P2--Cu--P3	89.3(1)	C311--P3--C31	100.9(3)
P2--Cu--N1	108.6(2)	Cu--N1--C1	171.3(7)
P3--Cu--N1	116.5(2)	C1--N2--C2	118.9(7)
Cu--P1--C8	111.4(3)	N1--C1--N2	173.2(9)
Cu--P1--C11	120.1(2)	N2--C2--C3	117.4(8)
Cu--P1--C111	115.0(2)	N2--C2--C7	124.4(8)
C11--P1--C8	103.1(3)	C7--C2--C3	118.2(8)
C111--P1--C8	103.5(3)	C2--C3--C4	120.9(9)
C111--P1--C11	101.8(3)	C3--C4--C5	119.3(8)
Cu--P2--C9	103.6(3)	C4--C5--C6	121.6(8)
Cu--P2--C21	120.2(3)	C4--C5--Cl	118.7(7)
Cu--P2--C211	119.3(2)	Cl--C5--C6	119.7(7)
C21--P2--C9	103.3(4)	C5--C6--C7	119.0(8)
C211--P2--C9	103.8(3)	C6--C7--C2	121.0(8)
C211--P2--C21	104.2(3)	P1--C8--C8′	109.1(5)
Cu--P3--C10	101.7(3)	P2--C9--C10	110.7(5)
Cu--P3--C31	118.1(2)	P3--C10--C9	108.2(5)

Bond Distances (Å) and Angles (deg.) in the Acetone Molecule.

CA1-CA2	1.227	CA1--CA2--OA1	114.5
CA2-OA1	1.249	CA1--CA2--CA3	74.0
CA2-CA3	1.463	OA1--CA2--CA3	107.5
CA3-OA2	1.377	OA2--CA3--CA4	126.5
CA3-CA4	1.263	CA4--CA3--CA2	121.1
		OA2--CA3--CA2	109.7

Table 6.4 Selected least-squares planes, deviations (Å), and torsion angles in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$.

Dihedral Angles Between Planes of Three Atoms About Copper.

Plane 1.	Plane 2.	Angle.
Cu, P1, P2	Cu, P3, N1	82.9
Cu, P2, P3	Cu, P1, N1	81.2
Cu, P2, N1	Cu, P1, P3	75.0

Torsion Angles in the dppe Ring.

τ[Cu-P2]	-3.2	τ[P2-C9]	34.8
τ[C9-C10]	-56.5	τ[P3-C10]	49.2
τ[Cu-P3]	-22.1		

Atoms in the plane: Cu, P2, P3

Equation: $(0.1848)X + (-0.0342)Y + (-0.9822)Z - (-0.9531) = 0$

χ^2: 0.00

Deviations:				
	C9	-0.10	C10	0.68
	P1	1.85	N1	-1.65

Atoms in the Plane: C2, C3, C4, C5, C6, C7

Equation: $(-0.1939)X + (-0.9132)Y + (-0.3586)Z - (-3.2355) = 0$

χ^2: 4.47

Deviations:				
	C2	0.01	C3	-0.01
	C4	0.01	C5	0.00
	C6	0.00	C7	0.00
	N1	0.01	N2	-0.01
	C1	0.00	Cl	0.01
	Cu	-0.21		

6.5 THE CRYSTAL STRUCTURE DESCRIPTION OF [{Cu(PPh$_3$)$_2$(p-Me-PC)}$_2$] (bis[μ-(4-methylphenylcyanamido-N,N')bis(triphenylphosphine)-copper(I)]).

The crystal structure determination of [{Cu(PPh$_3$)$_2$(p-Me-PC)}$_2$] was carried out by Mr S. L. Ingham ((B.Sc.(Hons) student Massey University). The crystallographic data are presented in table 6.5, and ORTEP representations of the structure are presented in figure 6.4.

STRUCTURE DESCRIPTION: The complex [{Cu(PPh$_3$)$_2$(p-Me-PC)}$_2$] exists as a centrosymmetric, ligand bridged dimer with four such dimers per unit cell. An inspection of all possible non-bonding contacts revealed no unusual features.

A view of the copper coordination environment is shown in figure 6.4. The two NCN bridges (from the two p-me-PC ligands) link the two copper atoms of the dimer as observed in the structure of [{Cu(bipy)(PC)$_2$}$_2$] (section 5.5). The resulting eight-membered ring, in contrast to this latter complex, is distinctly non-planar (table 6.7). Each copper centre is coordinated by two triphenylphosphine phosphorus atoms (P1 and P2), a terminal cyano nitrogen atom (N1) from the p-methylphenylcyanamido(1-) ligand, and an amido nitrogen atom (N2') from the symmetry related p-methylphenylcyanamido(1-) ligand. Each copper thus possesses a four coordinate geometry which can be best described as a distorted tetrahedron with an enlarged P-Cu-P bond angle of 121.5(1)°. The enlargement of the P-Cu-P bond angle no doubt arises, at least in part, from the effects of steric repulsions between the phenyl rings. It is difficult to separate steric effects from sigma- or pi-bonding effects, and the repulsion between electron pairs bonded to the copper atom will also influence the coordination geometry. The nature of the anion and the resulting Cu-P bonding must therefore be an important factor. This effect on the coordination geometry can be discussed in terms of the electron-pair repulsion theory [29]. This suggests that the electronegativity of a ligand will affect the size of the bonding orbital(s) between that ligand and the central atom. As the electronegativity of the anionic ligand increases, the size of the bonding orbital(s) decreases, resulting in more available space for the enlargement of the P-Cu-P angle. Lippard et al. [30] have listed the P-Cu-P angles for a series of mononuclear complexes of formulation $[(PPh_3)_2CuX]$, and shown that the enlargement of the P-Cu-P bond angle does correspond to the increasing electronegativity of the anionic ligand X.

All the P-Cu-N bond angles also exhibit deviations from the tetrahedral value of 109.5°. The origin of these deviations may be associated with the effects of steric repulsions between the bridging ligands and the triphenylphosphine phenylic hydrogens. The Cu-P bond distances are Cu-P1 = 2.285(2) Å and Cu-P2 = 2.256(2) Å which are not unusual and within the range reported for other copper(I)-triphenylphosphine complexes (Cu-P = 2.24-2.29 Å for 23 Cu(I) complexes with two PPh_3 ligands per Cu atom [28]). A comparison with the sum of the Pauling covalent radii of Cu (1.35 Å) and phosphorus (1.10 Å) [24] shows that in the present case there is a significant reduction in the Cu-P bond lengths indicating that these bonds possess a certain pi-character.

The copper to amido nitrogen (Cu-N2') bond distance of 2.089(5) Å compares closely with the mean Cu-N value reported for µ-diazido-tetrakis(triphenylphosphine)dicopper(I) of 2.103 Å [18]. The copper to cyano nitrogen bond distance is 2.043(3) Å which is longer than the value of 1.967(7) Å observed in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)2CO$, suggesting weaker σ-donor properties of the bridging p-methylphenylcyanamido(1-) ligand relative to the monodentate p-Cl-phenylcyanamido(1-) ligand, in these copper(I) phosphine complexes. This situation contrasts with that in the complex $[\{Cu(bipy)(PC)_2\}_2]$, in which the bridging and terminally coordinated phenylcyanamido(1-) ligands had approximately equal Cu-N(cyano) bond distances.

The Triphenylphosphine Ligands: The phenyl rings of the triphenylphosphine ligands are all planar, within the limits of experimental error. The C-C bond lengths and angles are as expected for phenyl rings [26].

The P-C bond distances range from 1.816(7) Å to 1.842(6) Å with a mean value of 1.829 Å. These values are in excellent agreement with those reported for other copper(I)-triphenylphosphine complexes viz. μ-diazido-tetrakis(triphenylphosphine)dicopper(I), mean P-C = 1.83 Å [18], octahydrotriboratobis(triphenylphosphine)copper(I), mean P-C = 1.828(3) Å [30], as well as for free triphenylphosphine, mean P-C = 1.828 Å [26]. On the basis of the P-C bond distances and the C-P-C and P-C-C bond angles, the geometries of the triphenylphosphine groups in the present structure are very similar to that of free triphenylphosphine itself. The triphenylphosphine molecules exhibit the expected pyramidal configuration about the phosphorus which, owing to the unequal rotation of the phenyl rings about the P-C bonds, possesses no symmetry. This can be appreciated by considering the angles that the normals to each phenyl ring make with the specified P-C bonds. These angles compare with values of 117.8°, 85.6°, and 115.2° for triphenylphosphine itself [26] (table 6.8).

P-C(Ph)	Phenyl Ring.	Angle, deg.
P1-C111	A	86.4
P1-C121	B	98.4
P1-C131	C	115.0
P2-C211	D	98.4
P2-C221	E	109.8
P2-C231	F	82.7

where phenyl ring A = C121, C122, C123, C124, C125, C126

B = C131, C132, C133, C134, C135, C136

C = C111, C112, C113, C114, C115, C116

D = C231, C232, C233, C234, C235, C236

E = C211, C212, C213, C214, C215, C216

F = C221, C222, C223, C224, C225, C226

Table 6.8 The Configuration of the PPh_3

Phenyl Rings in $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$

The p-Methylphenylcyanamido Ligand: The phenyl ring of the p-methylcyanamido(1-) ligand is planar, within experimental error, and the methyl substituent is displaced by 0.1 Å from this plane. The NCN group deviates slightly from linearity as indicated by the N1-C1-N2 bond angle of 175.1(3)°. In contrast, the azido ligands of μ-diazido-tetrakis(triphenylphosphine)dicopper(I) [18] and diazido-μ-1,2-bis(diphenylphosphino)ethane-bis(1,2-bis(diphenylphosphino)ethane)-dicopper(I) [19] show lesser deviations from linearity, with N-N-N bond angles of 177.8(1.0)° (mean of two) and 179(1)° respectively. The corresponding NCN bond angle in the complex $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ (this work) also deviates from linearity (173.2(9)°). This suggests that the slightly non-linear bonding at the cyanamido-carbon atom arises due to the extra steric bulk of the p-Cl- and p-Me-phenylcyanamido(1-) ligands relative to the azide ligand.

The C1-N1, C1-N2, and N2-C2 bond distances are 1.164(7) Å, 1.297(7) Å, and 1.398(7) Å respectively, which indicates that the cyanamide configuration, $(Ph\text{-}N\text{-}C{\equiv}N)^-$, most adequately describes the bonding within the p-methylphenylcyanamido(1-) ligand. The value of 1.164(7) Å compares closely with that expected for a typical C-N triple bond (1.158 Å [31]) and agrees, within experimental error, with the value of 1.155(10) Å found for the p-Cl-phenylcyanamido(1-) ligand in the complex $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ (this work). The C1-N2 bond distance of 1.297(7) Å is shorter than that expected for a CN single bond on the basis of the Pauling covalent radii (1.472(5) Å [24]), indicating that some multiple bond character is associated with this interaction. This observation is consistent with the other phenylcyanamido(1-) ligands reported in this study. A comparison of the p-Cl-phenylcyanamido(1-) ligand in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ and the p-Me-phenylcyanamido(1-) ligand in the present structure, shows that in spite of the different co-ligands and different coordination modes, these ligands adopt very similar structural configurations.

Table 6.5 Crystallographic Data for $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$.

Formula	(Cu2,C88,H74,P4,N4)
Mol. wt.	1437
Cryst. syst.	Monoclinic
Space group.	$P2_1/n$
a, Å	15.003(2)
b, Å	13.844(2)
c, Å	18.711(2)
β, deg.	101.22(1)
Z	2
V, Å^3	3812(2)
* F(000)	1492
D(calc), gcm^{-3}	1.25
D(obsd), gcm^{-3}	1.24
Diffractometer	Enraf Nonius CAD4
Radiation	Cu-K$_\alpha$ graphite monochromator λ = 1.5418 Å
Temp., K	293
Reflns. Measd.	$\pm h,k,l$
Scan type	$\omega/2\theta$
Max. 2θ, deg.	50
Measd. Reflns.	8452
Unique reflns.($I > 3\sigma(I)$)	3443
Cryst. dimensions., mm	0.3 x 0.4 x 0.3
Abs. corr. type	Empirical
Abs. coeff., cm^{-1}	17.2
Wtg scheme	$6.79 / [\ \sigma_{(F)}^2 + 0.00062F^2\ ]$
R	0.073
R$_w$	0.094

Figure 6.4 ORTEP representations of $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ with and without the PPh_3 phenyl rings.

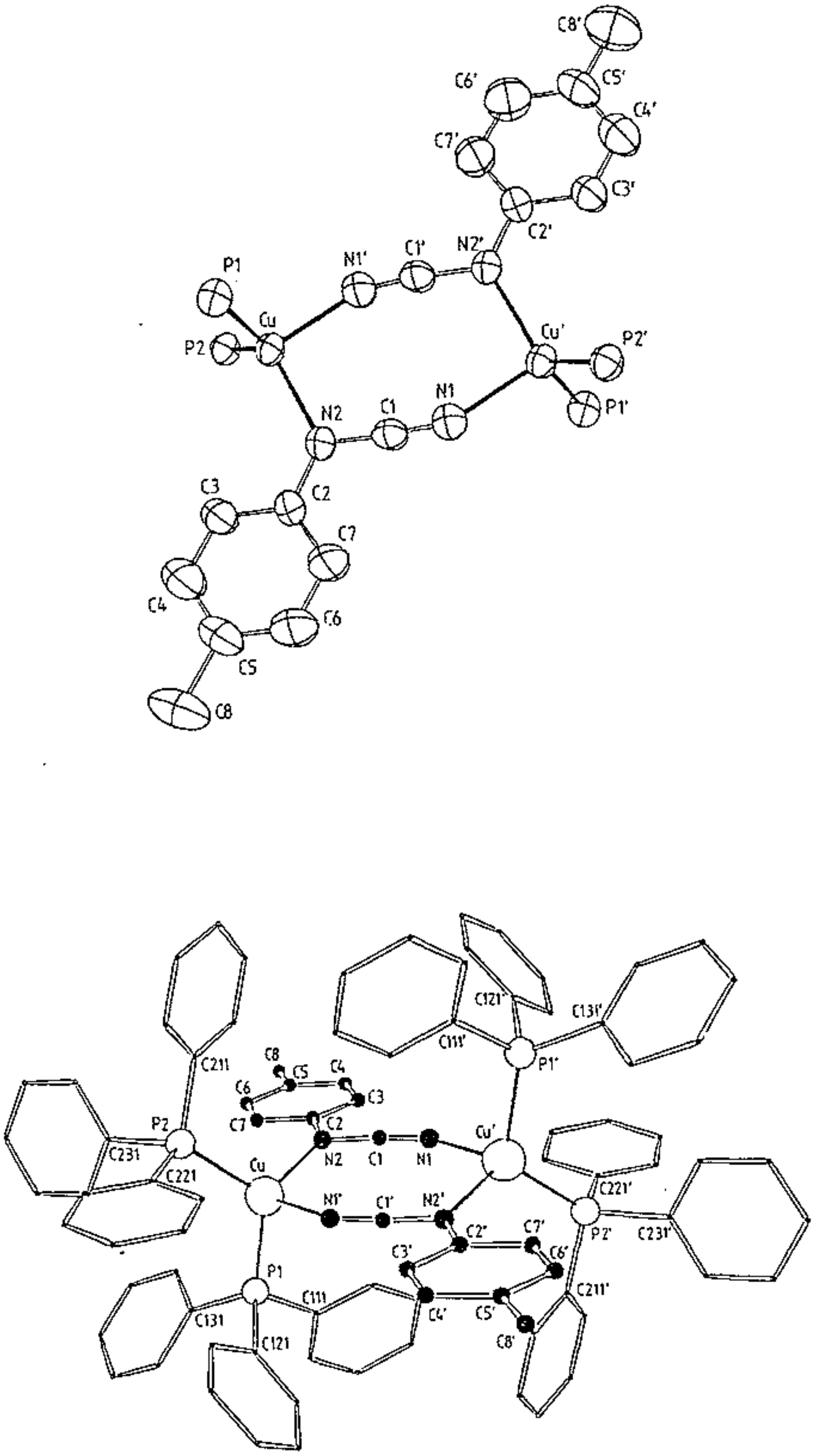


Table 6.6 Bond Lengths (Å) and Angles (deg.) in
$[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$.

Cu-P1	2.285(2)	C1-N1	1.164(7)
Cu-P2	2.256(2)	C1-N2	1.297(7)
Cu-N1	2.043(3)	C2-N2	1.398(7)
Cu-N2′	2.089(5)	C2-C3	1.384(9)
P1-C111	1.824(6)	C3-C4	1.375(10)
P1-C121	1.816(7)	C4-C5	1.368(11)
P1-C131	1.827(6)	C5-C6	1.376(12)
P2-C211	1.825(6)	C5-C8	1.512(12)
P2-C221	1.835(6)	C6-C7	1.387(10)
P2-C231	1.842(6)	C7-C2	1.376(10)

N2--Cu--N1′	94.9(2)	Cu--P2--C211	115.2(2)
P1--Cu--P2	121.5(1)	Cu--P2--C221	111.3(2)
P1--Cu--N1′	98.0(2)	Cu--P2--C231	119.9(2)
P1--Cu--N2	112.5(1)	C1--N1--Cu′	156.8(3)
P2--Cu--N1′	110.3(2)	N1--C1--N2	175.1(3)
P2--Cu--N2	114.6(1)	Cu--N2--C1	112.6(2)
Cu--P1--C111	115.7(2)	Cu--N2--C2	127.6(4)
Cu--P1--C121	108.0(2)	C1--N2--C2	117.9(4)
Cu--P1--C131	122.2(2)		

Table 6.7 Selected least-squares planes and deviations in
$[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$.

Atoms in the Plane: C2, C3, C4, C5, C6, C7

Equation: $(0.5100)X + (0.8545)Y + (-0.0990)Z - (3.3999) = 0$

χ^2: 0.00

Deviations:

C2	0.00	C3	0.00
C4	0.00	C5	0.00
C6	0.00	C7	0.00
N1	0.80	N2	0.06
C1	0.83	C8	0.10
Cu	0.64		

Atoms in the Plane: Cu, N1, C1, N2, Cu′, N1′, C1′, N2′

Equation: $(-0.2328)X + (0.6572)Y + (-0.7169)Z - (-1.3216) = 0$

χ^2: 7117247

Deviations:

Cu	0.51	Cu′	-1.36
N2	-1.48	N2′	0.63
N1	1.03	N1′	-0.13
C1	0.90	C1′	-0.10
C2	-2.42	C3	-3.57
C7	-4.17		

CHAPTER SIX REFERENCES

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CHAPTER SEVEN

A SUMMARY OF COPPER COMPLEXATION BY PHENYLCYANAMIDES

7.1 THE STRUCTURAL FEATURES OF COORDINATED PHENYLCYANAMIDES

The X-ray structural analyses have shown that the phenylcyanamido monoanion may coordinate to a metal in a number of different ways, the simplest being as a terminal group (I)

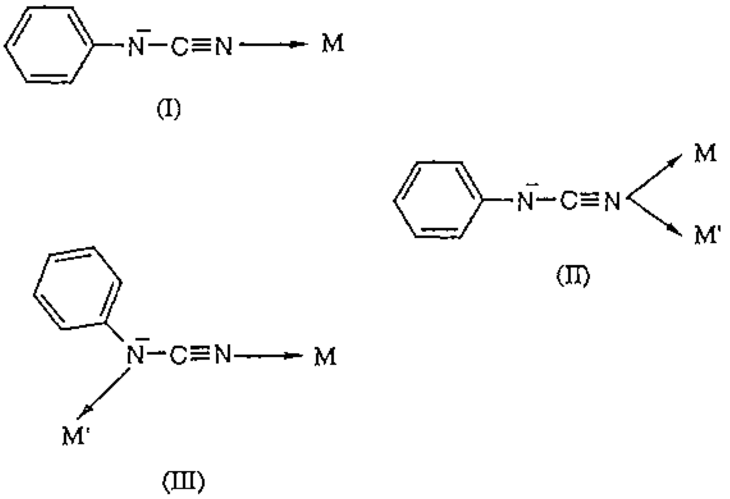
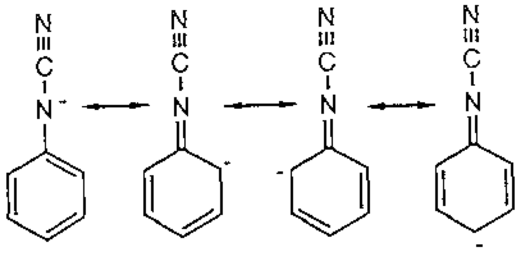


Figure 7.1 The coordination modes exhibited by the phenylcyanamido ligands in this study.

Bridging may occur in the short mode (II) or the long mode (III). The complex $[\{Cu(bipy)(PC)_2\}_2]$ contains both bridging (III) and terminal (I) ligands. The observed C-N bond lengths and some important angles are summarised in table 7.1 for Ph-N2-C1-N1. The mean C1-N1 bond length is 1.171 Å which is consistent with that of a CN triple bond (1.158 Å [1]). The mean value of the N2-C1 bonds is 1.292 Å which is about the same as that expected for a CN double bond (1.287 Å) [2]. The Ph-N2 bond lengths in these complexes agree, within the limits of experimental error, the mean being 1.402 Å, which is also shorter than the distance expected for a single bond (1.47 Å [2]). This observation may be attributed to the partial delocalisation of the negative charge onto the phenyl ring via the following resonance structures.



The N2-C1 bond distances represent substantial shortenings which cannot be explained solely by the effects of hybridisation of the carbon and nitrogen atoms. As discussed in section 5.5, this phenomenon of unusually short CN bonds is not uncommon in species which contain CN triple bonds. The reasons behind these shorter CN distances are unclear.

The N2-C1-N1 bond angles indicate that the bonding at the C1 atom is generally slightly non-linear (mean 173.3°). The observed values may be compared to those in the complex $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-}HNCN)_2]^{2+}$ [3] (176.9° mean of two), in which the HNCN(1-) anion is bridging the copper(II) atoms (mode (III)). This suggests that the extra steric bulk associated with the phenyl ring introduces increased steric forces which are responsible for the larger deviations from 180° in the N2-C1-N1 angles.

The phenyl rings of all the phenylcyanamido ligands are planar, as expected. The NCN groups are generally slightly non-coplanar with the attached phenyl rings, although the p-chloro-phenylcyanamido ligand in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ is an exception to this. The Ph-N2-C1 bond angles are all very close to the trigonal value of 120°. The M-N1-C1 and M-N2-C1 bond angles are quite varied and illustrate the geometrical flexibility of phenylcyanamide coordination.

The C1-N1 bond distance in the complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ exhibits the largest deviation from the mean value. The C1-N1 bond distance of 1.196(8) Å in this complex is the longest C1-N1 distance observed, although statistically, it is not significantly longer than the others and is still indicative of CN triple bond character. The observed ir ν(CN) frequency is very similar to the values observed for the $[\{Cu(bipy)(L)_2\}_2]$ series which suggests a similar bond order (table 5.2).

A comparison of the bond data for the complexes $[\{Cu(bipy)(PC)_2\}_2]$ (A), $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ (C), and $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ (D) shows that the bond lengths in the phenylcyanamido ligands agree with each other within the limits of experimental error. The ligands in these complexes are coordinated via modes (I) and (III). The complex $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ (B) displays coordination mode (II) and the corresponding bond data shows a number of interesting differences:

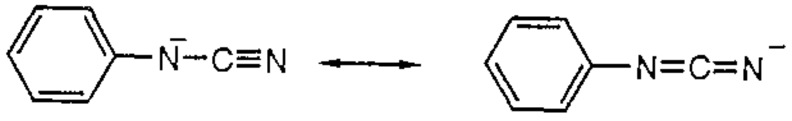
(i) the C1-N1 distance is longer, 1.196(8) Å, cf. 1.163 Å (mean of compounds (A), (C) and (D));

(ii) the C1-N2 distance is shorter, 1.269(9) Å, cf. 1.299 Å (mean of compounds (A), (C) and (D));

(iii) the angle at N2 is more trigonal, 120.6(6)°, cf. 118.4° (mean of compounds (A), (C) and (D));

(iv) The angle at N1 is also more trigonal, 149.1(5)°, cf. 151.0(5)°, 171.3(7)° and 156.8(3) for compounds (A), (C) and (D) respectively.

These four observations, individually, do not represent statistically significant differences. However, overall there is an interesting trend consistent with the suggestion that the m-Cl-PC ligand in $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ exhibits a hybridisation different from the ligands in complexes (A), (C) and (D), namely that there is an enhanced resonance contribution from form (II) relative to form (I):



The findings for the present structures indicate that in general, the ligands are best represented by the phenylcyanamide configuration (I) as opposed to that of the phenylcarbodiimide (II). The possible relationship between the ligand hybridisation and the coordination mode poses an interesting question which requires further research. The crystal structure determination of free phenylcyanamide itself would provide a useful basis for comparison with the results presented in this thesis. In addition, synthetic work to investigate further the factors which influence the ambivalence of phenylcyanamido(1-) ligands towards copper is clearly important. These projects are proposed as future research for workers in our laboratory.

Table 7.1 Summary of Phenylcyanamido Bond Lengths and Angles.

COMPOUND	MODE	Ph-N2	N2-C1	C1-N1
(A)*	I	-	-	-
(A)	III	1.409(7)	1.293(7)	1.169(7)
(B)	II	1.402(9)	1.269(9)	1.196(8)
(C)	I	1.398(10)	1.307(11)	1.155(10)
(D)	III	1.398(7)	1.297(7)	1.164(7)
MEAN		1.402	1.292	1.171

COMPD	MODE	N1-C1-N2	C1-N2-Ph	C1-N1-Cu	Cu-N2-C1	C1-N1-Cu'
(A)	III	172.7(7)	118.3(5)	151.0(5)	105.6(6)	-
(B)	II	172.2(7)	120.2(6)	149.1(5)	-	113.9(5)
(C)	I	173.2(9)	118.9(7)	171.3(7)		
(D)	III	175.1(3)	117.9(4)	156.8(3)	112.6(2)	-
MEAN		173.3	118.8			

(A) $[\{Cu(bipy)(PC)_2\}_2]$

(B) $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$

(C) $[\{Cu(dppe)_{1.5}(m\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$

(D) $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$

notes.

(1) * A disordered terminal PC ligand (bond data not considered accurate).

(2) the accepted values for typical single, double and triple CN bonds are 1.47 Å [2], 1.287 Å [2] and 1.158 Å [1] respectively.

7.2 PHENYLCYANAMIDES AS PSEUDOHALIDES

The classical representatives of the pseudohalide series are compounds such as cyanide (CN^-), and triatomic isosteric ions of general formula type $[ABC]^-$ - azide (N_3^-), fulminate (NCO^-), cyanate (CNO^-), thiocyanate (NCS^-), selenocyanate ($NCSe^-$), tellurocyanate ($NCTe^-$) - which are characterised by linear or nearly linear structures. To these classical representatives the non-linear pseudohalides of general formula $A(BC)_n^-$ can be added: dicyanamide ($N(CN)_2^-$) and tricyanomethanide ($C(CN)_3^-$) are two such examples. Pseudohalides are negative, polyatomic, mesomerically stabilised monoanions which exhibit numerous parallels with the halides. Table 7.2 gives a summary of the most important representatives of the series of pseudohalide ions.

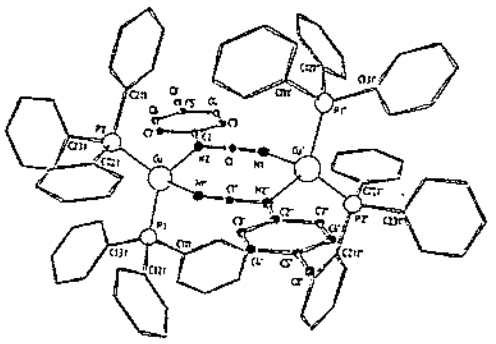
The isosterism of the triatomic linear pseudohalides, ABC^-, involves a number of parallels in the physical properties of these ions which extends to marked analogies in their reactivity and coordination chemistry. The ambidentate nature and ability to act as bridging ligands are important common characteristics of pseudohalides. These features are perhaps the most intriguing aspects of the structures presented in this study showing that, with copper, in true pseudohalide fashion, there is a marked tendency for phenylcyanamido(1-) ligands to act as bridging groups resulting in the formation of dimers. The coordinative similarity to azide in particular is highlighted by the structural comparisons presented in figure 7.2. There is in fact an exact parallel between the copper(I) complexes reported here and those which have been reported for the azide ion. In figure 7.2, complexes (i) and (ii) are essentially isostructural with complexes (iv) and (v) respectively. The structures of $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ (i), $[\{Cu(N_3)(PPh_3)_2\}_2]$ (iv) [4] and $[\{Cu(NSC)((CH_3)PPh_2)_2\}_2]$ [5] all consist of centrosymmetric dimers with end-to-end ABC^- bridges. In addition, the complexes $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ (ii), $[\{Cu(dppe)_{1.5}(N_3)\}_2]$ (v) [6] and $[\{Cu(dppe)_{1.5}(Cl)\}_2]\cdot 2(CH_3)_2CO$ [7], also possess structures which are analogous to each other. In these structures, the chloride, azide, and p-chlorophenylcyanamide ligands are all terminally coordinated. This parallel between phenylcyanamide(1-) and azide continues for copper(II) compounds by comparing the structure of $[\{Cu(bipy)(PC)_2\}_2]$ (iii), reported in the present work, with that of the recently reported azide complex, $[\{Cu(L)(N_3)_2\}_2]$ (vi) (where L = N,N,',N''-trimethyl-1,4,7-triazacyclononane) [8]. These complexes are presented in figure 7.2 and show similar arrangements of the anionic ligands.

In addition to the established members of the series, efforts to extend the pseudohalide concept by the discovery of new pseudohalide-like anions are important. The phenylcyanamide monoanion is not an indigenous member of the pseudohalide series, although the results of the present work show that it definitely does possess ligating properties which are closely comparable to those of the classical pseudohalides. It thus seems appropriate that the expression 'organo-pseudohalide' be coined to describe the ligand classification for the phenylcyanamide monoanion. In a description of structural type, the phenylcyanamide monoanion may be expressed as $(X)A(CN)^-$, where X = Ph. This emphasises the resemblence to the non-linear representatives of the pseudohalide series which are formulated as $A(BC)_n^-$. It remains to establish the full extent of this analogy, and whether phenylcyanamides form compounds similar to the various types of metal halides. The compounds tentatively formulated as $Cu^{II}L_2$ (L = p-Br-PC and m-Cl-PC, (section 5.2)) are therefore important. Work to fully characterise and extend this series of compounds would establish further halide-like chemical behaviour. One interesting related result is the series of compounds formulated as $[Et_4As]_2[ML_4]$ (Et_4As = tetraphenylarsonium cation; M = Cu(II), Ni(II), Zn(II); L = 2-chlorophenylcarbodi-imide and 2,4,6-trichlorophenylcarbodi-imide), reported by Hollebone et al. [9]. On the basis of magnetic data and the electronic spectra of these complexes in solution, Hollebone et al. proposed four-coordinate tetrahedral structures which are similar to those formed by cupric halides. In view of the present results, it appears likely that the description of these anions as phenylcarbodi-imides is incorrect and a description in terms of the phenylcyanamide structure is more appropriate. The results of Hollebone et al. do provide evidence for pseudohalide behaviour. Further structural studies to characterise unambiguously a representative of these compounds is clearly needed.

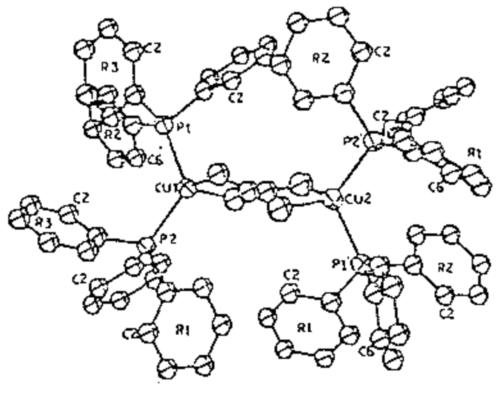
Table 7.2 Some Representative Pseudohalides.

Name	formula	structural type
cyanide	CN^-	AB^-
azide	N_3^-	ABC^-
fulminate	CNO^-	
cyanate	NCO^-	
thiocyanate	NCS^-	
selenocyanate	$NCSe^-$	
tellurocyanate	$NCTe^-$	
dicyanamide	$N(CN)_2^-$	$A(BC)_2^-$
dicyanophosphide	$P(CN)_2^-$	
tricyanomethanide	$C(CN)_3^-$	$A(BC)_3^-$
nitrosodicyanomethanide	$(C(CN)_2NO^-)$	

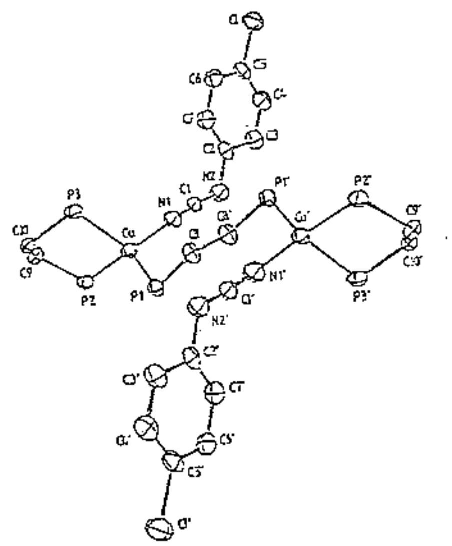
Figure 7.2 Some Structurally Analogous Azido and Phenylcyanamido Complexes.



(i) $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ (section 6.5)

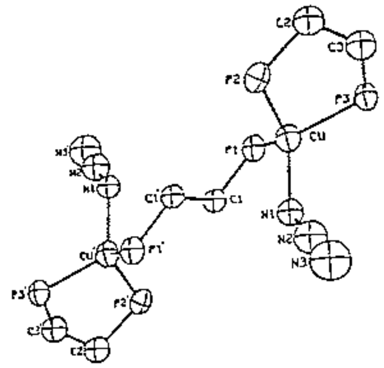


(iv) $[\{Cu(PPh_3)_2(N_3)\}_2]$ ref. [4]

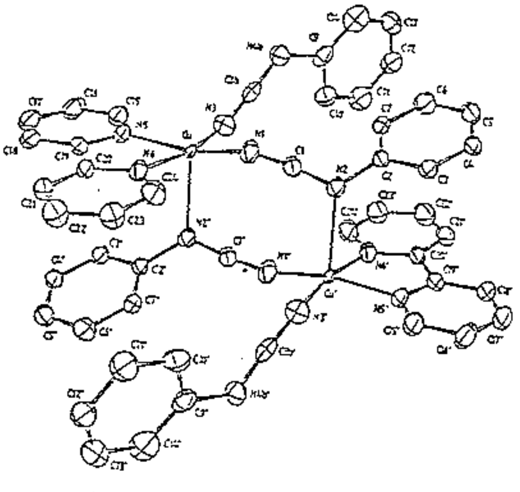


(ii) $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$

(section 6.4)

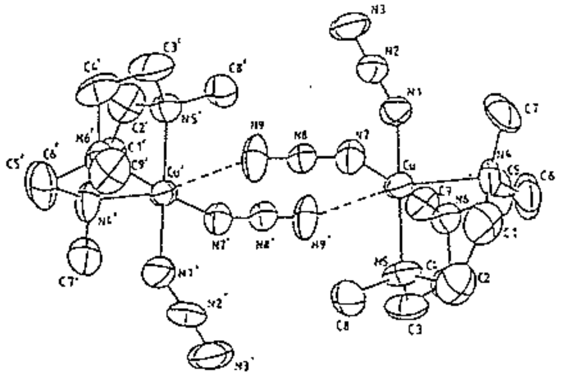


(v) $[\{Cu(dppe)_{1.5}(N_3)\}_2]$ ref. [6]



(iii) $[\{Cu(bipy)(PC)_2\}_2]$

(section 5.5)



Molecular geometry and atomic labeling scheme of a pair of $LCu(N_3)_2$ molecules. The dotted lines indicate weak Cu--N interactions.

(vi) $Cu(C_9H_{21}N_3)(N_3)_2$ ref. [8]

CHAPTER SEVEN REFERENCES

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APPENDIX A1.

X-RAY CRYSTALLOGRAPHIC SUMMARY: DATA COLLECTION, STRUCTURE SOLVING AND REFINEMENT, AND SOME DEFINITIONS OF CRYSTALLOGRAPHIC EXPRESSIONS

SUMMARY: The results of seven crystal structure determinations are presented in this thesis. The structure determinations of the complexes $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ and $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ were carried out by Mr S. L. Ingham (B.Sc.(Hons) student Massey University) and Dr G. Gainsford (DSIR) respectively. The crystal structures of these complexes are presented in sections 6.5 and 2.3 together with the associated crystallographic data.

The X-ray intensity data used for the structure determination of $[Cu(bipy)(DTDP)]\cdot 2H_2O$ were collected by Dr Ward Robinson of Canterbury University, and are summarised in table 3.1. The structure determination and refinement of this structure was then carried out at Massey University with the assistance of Mr D. Lewandoski, whose contribution constituted part of the research requirements for his B.Sc.(Hons) degree.

The X-ray intensity data used for the structure determinations of the complexes $[\{Cu(bipy)(PC)_2\}_2]$, $[Cu(bipy)(DTDIP)]\cdot 3H_2O$, $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$, and $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ were collected at Canterbury University according to the general method outlined below.

DATA COLLECTION: Intensity data for the compounds $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$, $[Cu(bipy)(DTDIP)]\cdot 3H_2O$, $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$ and $[\{Cu(bipy)(PC)_2\}_2]$ were collected at 153 K using a Nicolet R3m four circle automatic single crystal diffractometer equipped with Mo radiation (λ = 0.71069 Å) and a graphite monochromator. The intensity of each peak was calculated from the equation

$$I = FC - 2(BGL + BGR)$$

where FC = full count (integration of total peak) BGL = left background count BGR = right background count

The standard deviations, σ were estimated from counting statistics according to the equation

$$\sigma(F_o^2) = (Lp)^{-1}[C + B + (0.02P)^2]^{\frac{1}{2}}$$

in which Lp is the Lorentz-polarisation factor, C is the count accummulated during the scan, B is the total background count, and P is the net count for the reflection (scan minus background). N1 machine-centred reflections with $2\theta_{min} < 2\theta < 2\theta_{max}$ were used in a least squares refinement of the unit cell parameters and orientation matrix. Three strong reflections (intensity controls: C1, C2, C3) were measured after every 100 reflections to monitor crystal stability. No significant variation in the intensities of these intensity controls occurred during any of the data collections. These same reflections were used as orientation controls by accurately redetermining their angular settings after every 100 intensity measurements. Reorientation was not required during any data collection. A total of N2 reflections were measured using the $\omega/2\theta$ scan technique ($5° < 2\theta < 45°$) and a fixed scan speed. The intensity data were corrected for Lorentz and polarisation effects and also for absorption effects using either an empirical absorption method [1], or an analytical one based on psi-scan data. Merging of the equivalent reflections yielded N3 unique reflections. The agreement index, R_{merge}, for all unique reflections, is given by the following expression.

$$R_{merg} = [\Sigma(N\Sigma(w(F_{(mean)} - F)^2)) / \Sigma((N - 1)\Sigma(wF^2))]^{\frac{1}{2}}$$

The inner summations are over N equivalent reflections averaged to give $F_{(mean)}$; the outer summations are over all the unique reflections and the weight, w, is given by $(\sigma_{(F)})^{-2}$. A total of N4 reflections satisfied the $I > 3\sigma_{(I)}$ criterion of observability and no allowance was made for extinction.

STRUCTURE SOLUTION AND REFINEMENT: For the complexes $[\{Cu(bipy)(PC)_2\}_2]$, $[Cu(bipy)(DTDIP)]\cdot 3H_2O$, $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$, and $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$, structure determination was performed at Canterbury University using a Data General computer and the SHELXTL-86 (G.M. Sheldrick, 1986) crystallographic computing package which includes atomic scattering factors and all programs required for data reduction and structure determination. The refinement of the structures was then completed at Massey University using the SHELX-76 (G.M. Sheldrick, 1976) computer program and Massey University's Prime 9955 computer. For refinement of the structures, the atomic scattering factors used for the light atoms were those incorporated in the SHELX-76 program. Those for the Cu ion were taken from 'International Tables For Crystallography' and were corrected for both real and imaginary anomalous dispersion [2].

Structure refinement was carried out using a least squares process which minimises the funtion

$$\Sigma w(|F_o| - |F_c|)^2$$

where w is the weight applied to each reflection. For each structure refinement, unit weights were used initially, then towards the end of each structure refinement, a weighting scheme of the type

$$w = k / [\sigma_{(F)}^2 + gF^2]$$

was applied to the intensity data where $\sigma_{(F)}$ is the e.s.d. of $|Fo|$ and k and g are constants. The agreement between the set of observed structure factors, F_o, and the calculated structure factors, F_c, was assessed by the reliability index, R, such that

$$R = \Sigma|(|Fo| - |Fc|)| / \Sigma(|F_o|)$$

and the weighted reliability index, R_w, where

$$R_w = \Sigma w^{\frac{1}{2}}(|F_o| - |Fc|) / \Sigma w^{\frac{1}{2}}|F_o|$$

Molecular diagrams were obtained using the computer graphics program ORTEP [3]. Least squares planes were calculated with reference to an orthogonal coordinate system where X, Y and Z, refer to a, b and c*. The quantity minimised was $\Sigma_i P_i^2$, where P_i is the perpendicular distance of atom i from the plane. The quantity χ^2 was calculated as an index of the planarity of the group, where

$$\chi^2 = \Sigma_i P_i^2 / \sigma^2(P_i)$$

REFERENCES

[1] Program ABSORB was used: a locally adapted (Canterbury University) version of the program by L. Templeton and D. Templeton (described in abstracts; American Crystallographic Association. Storrs, CT (1973); No. E10) using the analytical method of: J. De Meulenaer, H. Tompa, Acta Cryst., 19, 1014 (1965).

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[3] ORTEP: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations; Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

Table A1. X-ray Data Collection Parameters.

	N1	$2\theta_{min}$	$2\theta_{max}$	C1	C2	C3	N2	N3	N4	Abs. Corr.	R_{merge}
(a)	25	24	33	(500)	(080)	(006)	2789	1914	1689	Empirical	0.0191
(b)	21	13	23	(300)	(030)	(004)	2727	2640	2142	Empirical	0.0530
(c)	16	6	23	(1200)	(0120)	(0010)	6407	5628	3604	Empirical	0.0161
(d)	16	7	23	(700)	(060)	(007)	2674	3604	1924	Psi-scans	0.0132

(a) $[\{Cu(bipy)(PC)_2\}_2]$

(b) $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$

(c) $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$

(d) $[Cu(bipy)(DTDIP)]\cdot 3H_2O$

N1 The no. of refln.s such that $2\theta_{min} < 2\theta < 2\theta_{max}$ used in the least squares refinement of the unit cell parameters and orientation matrix.

C1, C2, C3 The refln.s used as intensity and orientation controls.

N2 The total no. of refln.s measured.

N3 The no. of unique refln.s.

N4 The no. of unique refln.s such that $I > 3\sigma_{(I)}$.

R_{merge} The merging R factor.

APPENDIX A2

INSTRUMENTATION AND REAGENTS

INSTRUMENTATION

Electronic spectra: Solution and solid state electronic spectra were recorded over the range 1100-350 nm using a Shimadzu MPS UV-160 spectrophotometer. Solid state spectra were run as nujol mulls on Whatman filter paper, with a nujol filter paper blank in the reference compartment.

Infrared spectra: A Pye Unicam SP-3-300 infrared spectrophotometer was used to record spectra which were run as nujol mulls using KBr discs.

Electron spin resonance spectra: Frozen solution samples at 113 K were recorded using a Varian E-104A esr spectrometer equipped with a variable temperature accessory. Spectral g values were calibrated with a diphenylpicrylhydrazyl standard.

Magnetic moments: A Cahn Faraday balance no. 7550 was used to determine magnetic susceptibilities.

Molar conductivities: Measurements were carried out using a Philips PW 9509 digital conductivity meter.

Microanalyses were carried out by Professor A. D. Campbell at Otago university.

REAGENTS

Unless otherwise specified, solvents and copper salts were reagent grade chemicals and used as supplied. In spectroscopy, analar or spectroscopic grade solvents were used. The following chemicals were used as supplied by the respective manufacturers:

Aldrich Chemical Co.

2,2'-bipyridyl
1,10-phenanthroline monohydrate
methylsulphate monohydrate
mercaptoacetate sodium salt
2-mercaptopropionic acid
1,2-bis(diphenylphosphino)ethane
3-mercaptopropionic acid
p-bromoaniline
triphenylphosphine

Sigma Chemical Co.

mercaptosuccinic acid
p-fluoroaniline
methimazole

BDH Chemicals.

o-chloroaniline
m-chloroaniline
p-chloroaniline
aniline
ammoniumthiocyanate

May and Baker Ltd. (England)

piperidine

Riedel-De Haen Ag
Seelze-Hannover

lead acetate trihydrate