# 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

I would like to thank sincerely my supervisors Dr A. M. Brodie and Dr E. W. Ainscough for their guidance and encouragement in all aspects of the research programme.

I would also like to thank Dr E. N. Baker, Massey University, for his valuable assistance with the X-ray crystallography.

The contribution of the following is also gratefully acknowledged: Dr B. F. Anderson, and Dr J. M. Waters, Massey University, for many helpful discussions; Dr W. T. Robinson, Canterbury University, for assistance with X-ray diffraction data collection and the use of Canterbury University's X-ray crystallographic instrumentation and software; Dr G. A. Gainsford (DSIR) for carrying out a crystal structure determination; Mr S. L. Ingham, B.Sc.(Hons) student Massey University, for synthetic work and carrying out a crystal structure determination; Professor A. D. Campbell, Otago University, for microanalyses; Dr H. V. Simpson and Dr G. E. Norris for proof-reading this thesis. I would also like to acknowledge the contribution made by the people I have worked with in the Department of Chemistry and Biochemistry at Massey University for their friendly encouragement and many helpful discussions.

I am grateful to the University Grants Committee for the award of a Postgraduate Scholarship.

# 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

Acknowledgements
Abstract
Contents
Abbreviations and Nomenclature
Ligand Illustrations
List of Figures
List of Tables

Page

**CHAPTER ONE:** General Introduction.......................... 1

**CHAPTER TWO:** The Reactivity of Methimazole with Copper(II)

2.1 Introduction: Copper Promoted Reactions of Ligands Containing Sulphur and Nitrogen.......................... 3
2.2 Experimental: The Preparation of $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$.......................... 6
2.3 Results: The Characterisation of $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$.......................... 7
2.4 Summary.......................... 12
References.......................... 13

**CHAPTER THREE:** The Copper Promoted Reactivity of Aliphatic Thiol-Containing Carboxylic Acids.

3.1 Introduction: Ligands Containing the SH Group.......................... 15
3.2 Experimental.......................... 17
3.3 Results.......................... 19
3.4 Copper-Disulphide Complexation.......................... 22
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).......................... 25
3.6 The Crystal Structure Determination of $[Cu(bipy)(DTDIP)]\cdot 3H_2O$ (catena-2,2′-bipyridine-μ-(2,2′-dithiodipropionato-O,O′,S)-copper(II) trihydrate).......................... 35
3.7 Summary.......................... 46
References.......................... 49

CHAPTER FOUR: The Copper promoted Reactivity of Phenylthiourea.

4.1 Introduction: The Coordination Chemistry of Copper with Thioureas........................................ 53
4.2 Experimental ((i) The Preparation of Phenylthiourea. (ii) The Preparation of [{Cu(bipy)(PC)$_2$}$_2$] from Phenylthiourea)................................ 56
4.3 Results: The Characterisation of [{Cu(bipy)(PC)$_2$}$_2$]....... 58
4.4 Discussion............................................. 60
References............................................. 62

CHAPTER FIVE: Phenylcyanamides and their Coordination Chemistry with Copper(II).

5.1 Introduction: Cyanamides as Donor Molecules............... 64
5.2 Experimental ((i) The Preparation of Phenylcyanamide. (ii) The Preparation of Ag(+) Phenylcyanamide Salts. (iii) The Preparation of Copper(II) Complexes with Phenylcyanamides).................................. 73
5.3 Results: The Characterisation of the Copper(II) Complexes.................................... 78
5.4 Infrared Spectroscopy of Systems Containing Triple Bonds............................................ 81
5.5 The Crystal Structure Determination of [{Cu(bipy)(PC)$_2$}$_2$] (bis[2,2′-bipyridine-μ-(phenylcyanamido-N,N′)-phenylcyanamido-N-copper(II)])........................... 83
5.6 The Crystal Structure Determination of [{Cu(phen)(m-Cl-PC)(Ac)}$_2$]·2H$_2$O (bis[acetato-μ-(3-chlorophenylcyanamido-N)-1,10-phenanthrolinecopper(II)] dihydrate)................ 98
References............................................. 108

CHAPTER SIX: Copper(I) Complexation by Phenylcyanamides.

6.1 Introduction: Copper(I) Complexes With Coordinating Anions..................................... 113
6.2 Experimental: The Preparation of Copper(I) Complexes With Phenylcyanamides......................... 116
6.3 Results: The Characterisation of the Copper(I) Complexes.. 117

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).................... 119

6.5 The Crystal Structure Description of $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ (bis[µ-(4-methylphenylcyanamido-N,N')-bis(triphenylphosphine)copper(I)])........................ 131

References.............................................. 139

CHAPTER SEVEN A Summary of Copper Complexation by Phenylcyanamides.

7.1 The Structural Features of Coordinated Phenylcyanamides... 142

7.2 Phenylcyanamides as Pseudohalides......................... 147

References.............................................. 151

APPENDIX

A1 X-ray Crystallography Summary: Data Collection, Structure Solving and Refinement, and some Definitions of Crystallographic Expressions............................ 152

A2 Instrumentation and Reagents............................ 157

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

# 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 |

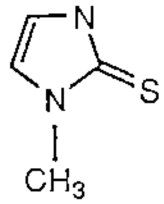
## Miscellaneous.

| | |
|---|---|
| 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) |
| $\nu$ | stretching frequency |
| nmr | nuclear magnetic resonance |
| ORTEP | the computer program used for crystal structure illustrations (see appendix A1). |
| u.v. | ultraviolet |

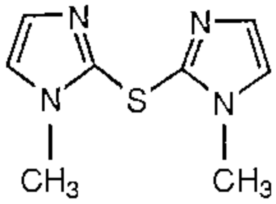
---

* Included in ligand illustrations.

# LIGAND ILLUSTRATIONS

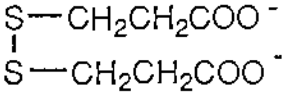


METHIMAZOLE (mimtH)



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

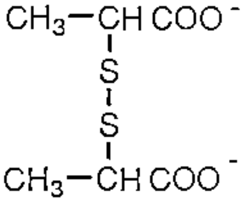
(dmimS)



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

DITHIODIPROPIONATE

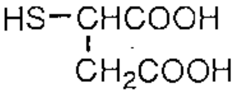
(DTDP)



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

DITHIODIISOPROPIONATE

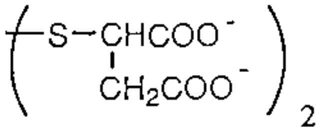
(DTDIP)



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

MERCAPTOSUCCINIC ACID

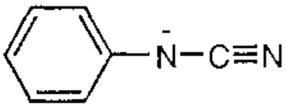
(msa)



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

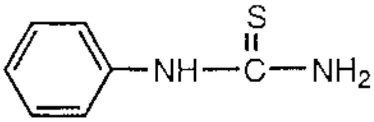
DITHIODISUCCINATE

(DTDS)



PHENYLCYANAMIDE MONOANION

(PC)



PHENYLTHIOUREA

# LIST OF FIGURES

figure page

2.1 The reactivity of 2-thiazolidinethione with copper(II)...... 4

2.2 The tautomeric forms of methimazole........................ 5

2.3 1,1'-dimethyl-2,2'-diimidazolylsulphide (dmimS)............ 5

2.4 The ORTEP representation of the $[Cu(dmimS)_2(H_2O)_2]^{2+}$ cation................................ 10

3.1 The copper(II) site of plastocyanin........................ 15

3.2 The proposed mechanism for the copper(II) catalysed scission of a disulphide bond.............................. 22

3.3 Previously reported copper(II)-disulphide structures................................................ 24

3.4 The ORTEP representation of $[Cu(bipy)(DTDP)]\cdot 2H_2O$ showing the atomic labelling...................................... 31

3.5 The ORTEP representation of $[Cu(bipy)(DTDP)]\cdot 2H_2O$ showing the coordination sphere and stereoscopic unit cell.......... 32

3.6 The ORTEP representation of $[Cu(bipy)(DTDIP)]\cdot 3H_2O$ showing the atomic labelling and the stereoscopic unit cell................................. 42

3.7 The ORTEP representation of $[Cu(bipy)(DTDIP)]\cdot 3H_2O$ showing the disorder of the DTDIP ligand and the hydrogen bonding network.................................. 43

3.8 Summary of the products formed from the thiol-carboxylic acids........................................ 46

4.1 The infrared spectra of phenylthiourea, $[\{Cu(bipy)(PC)_2\}_2]$, and phenylcyanamide.................... 59

4.2 The reactivity of phenylthiourea with copper(II)........... 60

5.1 Some structurally characterised cyanamide complexes......... 72

5.2 The ORTEP representation of one molecule of $[\{Cu(bipy)(PC)_2^-\}_2]$ showing the atomic labelling............ 92

5.3 The ORTEP representation of $[\{Cu(bipy)(PC)_2\}_2]$ showing the disorder and the stereoscopic unit cell................ 93

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............ 104

6.1 The ORTEP representation of $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$ showing the atomic labelling............................................ 127

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............. 128

6.3 Conformations of a bridging dppe ligand.................... 124

6.4 ORTEP representations of $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$ with and without the $PPh_3$ phenyl rings..................... 137

7.1 The coordination modes exhibited by the phenylcyanamido ligands in this study...................................... 142

7.2 Some structurally analogous azido and phenylcyanamido complexes.................................. 150

# LIST OF TABLES

Table page
2.1 Crystallographic data for $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$... 9
2.2 Bond lengths and angles in $[Cu(dmimS)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$.. 11

3.1 Crystallographic data for $[Cu(bipy)(DTDP)]\cdot 2H_2O$............ 30
3.2 Bond lengths and angles in $[Cu(bipy)(DTDP)]\cdot 2H_2O$........... 33
3.3 Selected least-squares planes and deviations in $[Cu(bipy)(DTDP)]\cdot 2H_2O$................................. 34
3.4 Crystallographic data for $[Cu(bipy)(DTDIP)]\cdot 3H_2O$........... 41
3.5 Bond lengths and angles in $[Cu(bipy)(DTDIP)]\cdot 3H_2O$.......... 44
3.6 Selected least-squares planes, deviations and torsion angles in $[Cu(bipy)(DTDIP)]\cdot 3H_2O$.................. 45
3.7 Metal-sulphur bond distances.............................. 48

5.0 Data for the phenylcyanamide ligands...................... 74
5.1 Some compounds containing the CN group.................... 65
5.2 Physicochemical data for the copper(II)-phenylcyanamido complexes................................. 80
5.3 Crystallographic data for $[\{Cu(bipy)(PC)_2\}_2]$.............. 91
5.4 Bond lengths and angles in $[\{Cu(bipy)(PC)_2\}_2]$............. 94
5.5 Selected least-squares planes and deviations in $[\{Cu(bipy)(PC)_2\}_2]$.................................. 95
5.6 Crystallographic data for $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$.. 103
5.7 Bond lengths and angles in $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$. 105
5.8 Selected least-squares planes and deviations in $[\{Cu(phen)(m\text{-}Cl\text{-}PC)(Ac)\}_2]\cdot 2H_2O$........................ 106

6.1 Physicochemical data for the copper(I) complexes.......... 118

6.2 Crystallographic data for $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2\}\cdot 2(CH_3)_2CO$........................ 126
6.3 Bond lengths and angles in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2\}\cdot 2(CH_3)_2CO$........................ 129
6.4 Selected least-squares planes, deviations and torsion angles in $[\{Cu(dppe)_{1.5}(p\text{-}Cl\text{-}PC)\}_2]\cdot 2(CH_3)_2CO$.................... 130
6.5 Crystallographic data for $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$.......... 136
6.6 Bond lengths and angles in $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$......... 138
6.7 Selected least-squares planes in $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$... 138
6.8 The configuration of the triphenylphosphine phenyl rings in $[\{Cu(PPh_3)_2(p\text{-}Me\text{-}PC)\}_2]$................................ 134

7.1 Summary of the phenylcyanamido bond lengths and angles..... 146
7.2 Some representative pseudohalides.......................... 149

A1 X-ray data collection parameters.......................... 156

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.