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**STRUCTURAL STUDIES ON SILVER(I) COMPLEXES
CONTAINING PHENYLCYANAMIDO LIGANDS AND
URANYL(VI) COMPLEXES WITH β -KETOPHENOLATES**

A Dissertation presented in partial fulfilment for the Degree of Master of Science in Chemistry
at Massey University

Roger Joseph Cresswell

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Abstract

This thesis is divided into two parts. In Section One studies on the interaction of phenylcyanamides with silver(I) are reported. Section Two describes the results of studies on the complexes formed from β -ketophenol ligands and the uranyl ion.

Section One

Chapter 1 is a brief overview of the use of phenylcyanamides in forming coordination complexes with transition metals.

In Chapter 2 the preparation of a series of silver complexes of the general formula $[\text{Ag}(\text{Ph}_3\text{P})_3(\text{pcyd})]$, where pcyd is a phenylcyanamido anion, is described. The crystal structures of $[\text{Ag}(\text{Ph}_3\text{P})_3(4\text{-Brpcyd})]$ and $[\text{Ag}(\text{Ph}_3\text{P})_3(4\text{-MeOpcyd})]$ have been determined, in which the silver atom occupies a distorted tetrahedral environment, and the latter complex has a very short terminal C-N bond within the 4-methoxyphenylcyanamido ligand.

Chapter 3 provides a comparison of all those transition metal complexes of phenylcyanamides that have been structurally characterised.

Section Two

Chapter 4 is a brief overview of the use of β -diketonate ligands in forming dinuclear complexes, especially those in which the uranyl ion (UO_2^{2+}) is present.

In Chapter 5 the preparation of the mononuclear complexes $[\text{UO}_2(\text{HL}^1)_2(\text{MeOH})]$, $[\text{UO}_2(\text{HL}^2)_2(\text{EtOH})]$, the heterobinuclear complexes $[\text{UO}_2\text{Mn}(\text{L}^1)_2(\text{EtOH})] \cdot 1.5\text{H}_2\text{O}$, and $[\text{UO}_2\text{Mn}(\text{L}^2)_2(\text{EtOH})] \cdot 2\text{H}_2\text{O}$ and the oxo-ligand adducts $[\text{UO}_2(\text{HL}^1)_2(\text{Ph}_3\text{AsO})] \cdot 2\text{H}_2\text{O}$, $[\text{UO}_2(\text{HL}^2)_2(\text{Ph}_3\text{PO})]$ and $[\text{UO}_2(\text{HL}^2)_2(\text{Ph}_3\text{AsO})]$ ($\text{H}_2\text{L}^1 = 1\text{-(2-hydroxyphenyl)-3-butanedione}$ and $\text{H}_2\text{L}^2 = 1\text{-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione}$) is described. The complexes have been characterized by a variety of physicochemical techniques and the crystal structures of $[\text{UO}_2(\text{HL}^1)_2(\text{EtOH})]$ and $[\text{UO}_2(\text{HL}^2)_2(\text{EtOH})] \cdot \text{EtOH}$ determined. Both complexes contain seven coordinate uranium(VI) in a pentagonal bipyramidal geometry in which the two bidentate β -diketonato ligands and the ethanol ligand make up the equatorial pentagonal plane. For the complex $[\text{UO}_2(\text{HL}^1)_2(\text{EtOH})]$ the HL^1 ligands are in a *trans* arrangement with respect to one another, whereas for the $[\text{UO}_2(\text{HL}^2)_2(\text{EtOH})] \cdot \text{EtOH}$ complex the HL^2 ligands adopt a *cis* arrangement. However, in solution variable temperature ^1H NMR spectra indicate that the *cis* and *trans* isomers are in equilibrium for both complexes.

Abbreviations

TMTSF	tetramethyltetraselenafulvalene
DCNQI	N,N'-dicyanoquinonediimine
LMCT	ligand to metal charge transfer
pcydH	phenylcyanamide
2,3-Cl ₂ pcydH	2,3-dichlorophenylcyanamide
3-ClpcydH	3-chlorophenylcyanamide
4-ClpcydH	4-chlorophenylcyanamide
4-MepcydH	4-methylphenylcyanamide
4-BrpcydH	4-bromophenylcyanamide
4-NO ₂ pcydH	4-nitrophenylcyanamide
bipy	2,2'-dipyridyl
phen	1,10-phenanthroline
Me ₂ phen	2,9-dimethyl-1,10-phenanthroline
dppm	bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
H ₂ L ¹	1-(2-hydroxyphenyl)-1,3-butanedione
H ₂ L ²	1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione
acac	acetylacetone
hfa	1,1,1,5,5,5-hexafluoroacetylacetone
Hpicmet	benzoylpicolinoylmethane
Hnicmet	nicotinoylmethane
bhppH ₃	bis(2-hydroxyphenyl)-1,3-propanedione
LSIMS	liquid secondary ion mass spectroscopy

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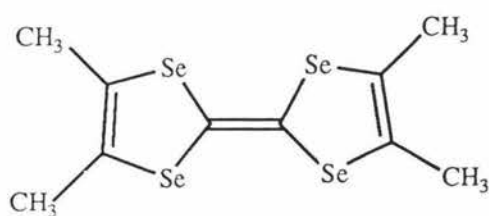
SECTION ONE
PHENYLCYANAMIDO COMPLEXES OF SILVER(I)

CHAPTER ONE

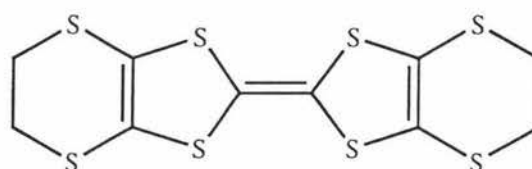
INTRODUCTION

1.1 Molecular Metals and the Cyanamide Group

The first organic superconductor at atmospheric pressure, the perchlorate salt of the radical cation of tetramethyltetraselenafulvalene (**1**) $(\text{TMTSF})_2\text{ClO}_4$ ($T_c = 1\text{K}$), was discovered in 1981¹. More recently organic superconductors based on the sulphur compound bis(ethylene dithio)-tetrathiafulvalene (**2**) have been prepared^{2,3}.



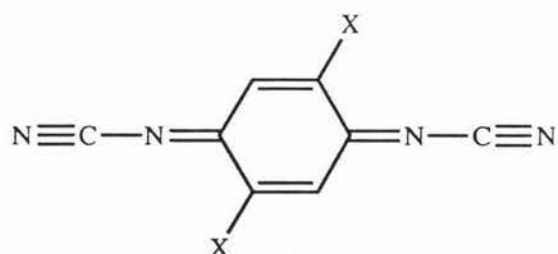
TMTSF (**1**)



(**2**)

These organic charge transfer crystals involve stacking of the radical-cations to form quasi- one-dimensional "organic metals".

The N,N'- dicyanoquinonediimines (DCNQIs) were recently synthesised to act as electron acceptors in organic charge transfer complexes⁴.



The copper salts of radical anions of 2,5- di- substituted derivatives, having stoichiometry $(2\text{-Me},5\text{-X-DCNQI})_2\text{M}$, where X = Me, I, Cl, M = Cu, exhibit metallic conductivity at low

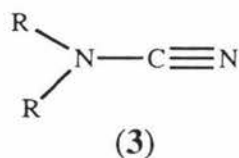
temperatures. For example, $(2,5\text{-Me}_2\text{-DCNQI})_2\text{Cu}$ has a conductivity of $\sigma = 500,000 \text{ S cm}^{-1}$ at 3.5K^5 . In the X-ray structure of this example the 2,5-Me₂-DCNQI ligands bridge copper ions that are in a distorted tetrahedral environment and are co-ordinated to four cyanamide groups (RNCN) from four individual ligands. The copper ions are arranged in chains, each surrounded by four stacks of 2,5-Me₂-DCNQI molecules (Fig 1.1).

The high electrical conductivity is attributed to the π -stacks; transverse conductivity occurs via NCN - Cu - NCN bridges within individual stacks. This multidimensionality is based on the empirical evidence of (i) no esr signal in either the X-band or Q-band, (ii) high conductivity with no phase transition point, and (iii) low temperature X-ray diffraction and XPS studies which indicate the copper exists in a mixed valence state (the average oxidation state being 1.3 per copper)⁵.

The coordination chemistry and physicochemical properties of the related cyanamides are therefore of interest since they have an important role in the understanding of the high conductivity of radical anion salts of N,N'-dicyanoquinonediimines.

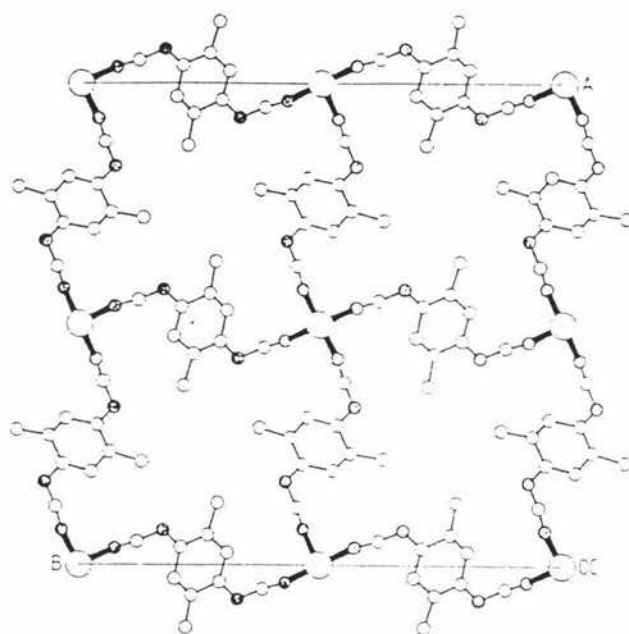
1.2 The Coordination Chemistry of Phenylcyanamides

Cyanamides (**3**) are highly reactive molecules. They are used as starting materials in a wide variety of organic syntheses. Calcium cyanamide (CaNCN) is used as a direct application fertiliser and is also the basic starting material for the industrial preparation of a great range of substances including polymers, medicinals, thiourea, dicyandiamide and melamine plastics.

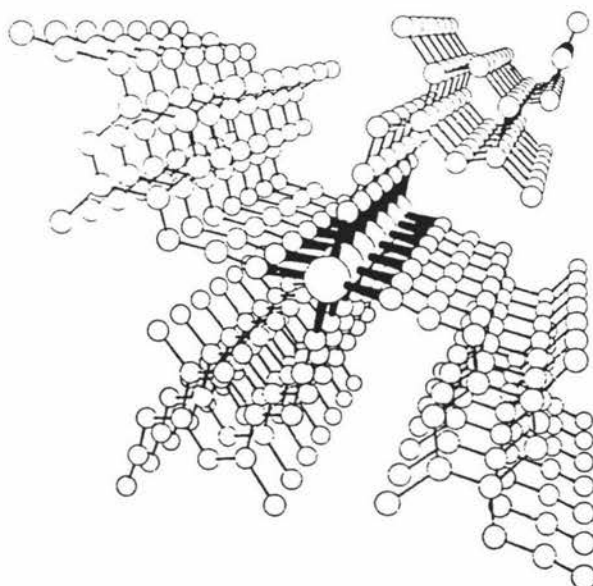


The predominant reaction of cyanamides is that of polymerisation, involving the addition of a cyanamide ion to the nitrile group of an undissociated cyanamide molecule, e.g. cyanamide (H_2NCN) slowly dimerises on standing to form dicyandiamide.

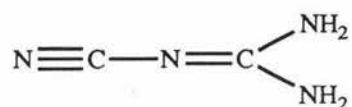
Figure 1.1 The crystal structure of $(2,5\text{-Me}_2\text{-DCNQI})_2\text{Cu}$



a, b-Projection of the crystal structure of $(2,5\text{-DM-DCNQI})_2\text{Cu}$ (H atoms omitted for clarity). $\bigcirc = \text{Cu}$, $\bigcirc = \text{C}$, $\bigcirc = \text{N}$.

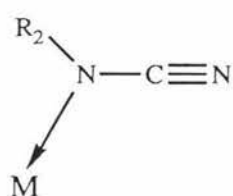


Perspective view of the crystal structure along the *c* axis: the chain of copper atoms is surrounded by four stacks of 2,5-DM-DCNQI molecules (H atoms not shown). $\bigcirc = \text{Cu}$, $\bigcirc = \text{C}$, $\bigcirc = \text{N}$.



(Dicyandiamide)

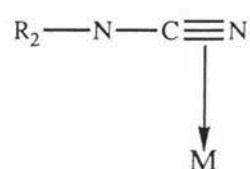
Cyanamides present a potentially versatile ligand type in that they possess two functional groups linked directly together. As monodentate ligands, they may coordinate to a metal through either the cyano group (5) or the lone pair of electrons on the amido group (4). Coordination through the cyano group may involve the σ (5a) or π (5b) electrons resulting in a μ - type bond. As bidentate ligands they may coordinate to two different metal atoms.



(4)



(5a)

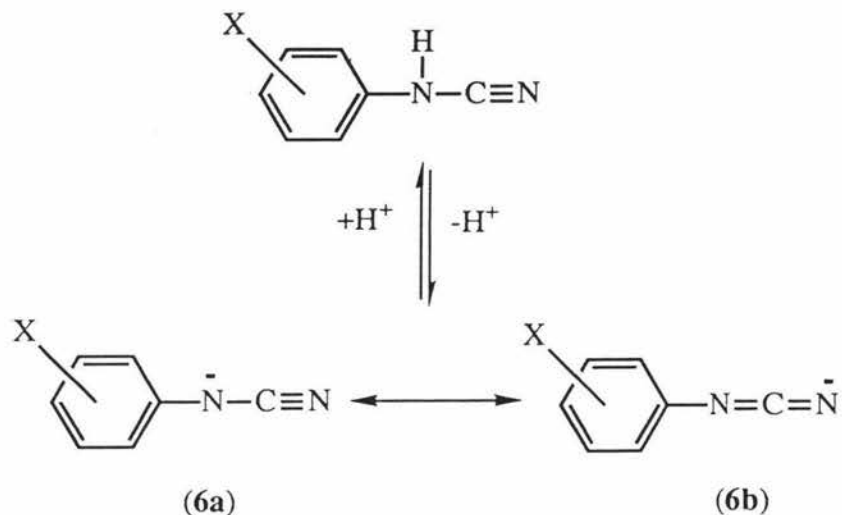


(5b)

Phenylcyanamides (6) are less prone to autopolymerisation than cyanamide and mono-alkyl substituted cyanamides, and can be synthesised readily in high yields⁶.

The amine proton of the neutral phenylcyanamides is highly acidic, due to the conjugate anion being resonance stabilised.

The anionic phenylcyanamide ligand is a strong π -donor because the nitrogen lone pairs can be delocalised into the nitrile π system.



Anionic phenylcyanamides behave like pseudohalides in their ligating properties⁷. Pseudohalides are polyatomic mesomerically stabilised monoanions which exhibit numerous parallels with the halides. Their ambidentate nature and ability to act as bridging ligands are characteristics in common with pseudohalides.

Despite their added stability and ambidentate character, the phenylcyanamides (both neutral and anionic) have received little attention - of the handful of reports published the majority have appeared since 1989⁷⁻¹⁴.

Hollebone and Nyholm, when studying the physical and spectroscopic properties of a series of transition metal pseudohalide complexes, reported a number of halogen-substituted phenylcarbodiimide complexes of copper(II), formulated as $[\text{Ph}_4\text{As}]_2[\text{Cu}(\text{L})_4]$ ¹⁵. No spectroscopic data were published to support the assertion that the ligand exists in the carbodiimide form (6b) rather than the cyanamide(6a) form.

A series of pentaammine ruthenium(III) complexes of neutral and anionic phenylcyanamides have been prepared¹⁰⁻¹². The electronic spectra of either neutral or anionic ruthenium(III) complexes show ligand to metal charge transfer (LMCT) bands arising from either one non-bonding, or two non-degenerate non-bonding electron pairs, respectively. In these complexes the neutral or anionic ligand coordinates end-on *via* the nitrile nitrogen, the carbodiimide form predominating. The short Ru - N bond distance and nearly linear Ru - N - C bond angle in the X-ray structure of

$[(\text{NH}_3)_5\text{Ru}(2,3\text{-Cl}_2\text{pcyd})][\text{SO}_4]\cdot\text{EtOH}$, where 2,3-Cl₂pcydH is 2,3-dichlorophenylcyanamide, show a significant degree of π -bonding between the cyanamide group and the ruthenium(III) ^{10,12} (Fig. 1.2).

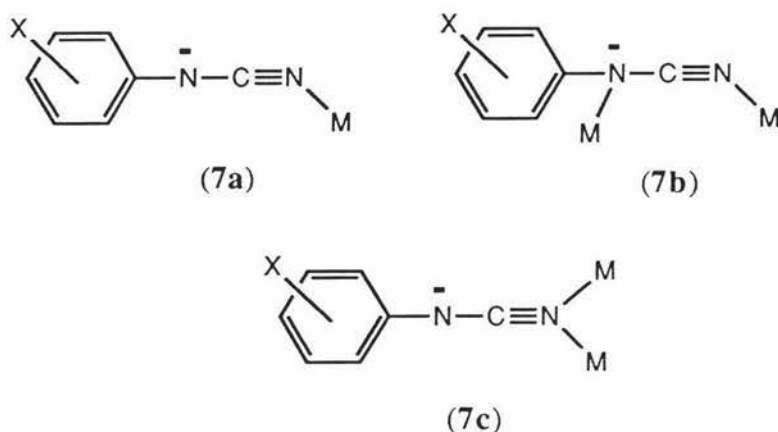
The coordination chemistry of neutral phenylcyanamide ligands to the pentaammine ruthenium(II) moiety shows they are capable of acting as π -acceptor ligands, stabilising the Ru(II) oxidation state (even though they possess π -donor properties), whereas anionic phenylcyanamides preferentially coordinate to Ru(III)¹¹.

A pentaammine mixed-valence complex $[(\text{NH}_3)_5\text{Ru(II)(L)Ru(III)(NH}_3)_5]$, where $\text{L}^{2-} = 1,4$ -dicyanamido-2,3,5,6-tetrachlorobenzene dianion was prepared in an attempt to observe electronic coupling between π -donor Ru(II) and π -acceptor Ru(III), bridged by L^{2-} , via a superexchange mechanism, but only weak coupling was measured¹³.

Two copper complexes of anionic phenylcyanamides have been prepared¹⁴ in an attempt to model the copper site in the molecular metal $\text{Cu}(\text{DCNQI})_2$. The X-ray crystal structures of $[(\text{bipy})_2\text{Cu}(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ and $[(\text{bipy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$ show the anionic phenylcyanamide ligands are bound end-on to Cu(II) and although some π interaction occurs as evidenced from a LMCT band, assigned to a cyanamido anion $p\pi \rightarrow d_x^2-y^2$ Cu(II) transition, this is predominantly a σ bonding interaction (Fig. 1.3) ¹⁴.

This group's interest in the coordinating properties of phenylcyanamides arose from the observation that the reaction of N-phenylthiourea with an ethanolic solution of copper(II) acetate / 2,2'-bipyridine resulted in the desulphurisation of the phenylthiourea to afford a complex of stoichiometry $[\{\text{Cu}(\text{bipy})(\text{pycd})_2\}_2]$ ⁸, where bipy is 2,2'-dipyridyl and pycdH is phenylcyanamide. The X-ray crystal structures of two copper(II) complexes with anionic phenylcyanamides, namely $[\{\text{Cu}(\text{bipy})(\text{pycd})_2\}_2]$ and $[\{\text{Cu}(\text{phen})(3\text{-Clpycd})(\text{CH}_3\text{CO}_2)\}_2]\cdot 2\text{H}_2\text{O}$ (phen is 1,10-phenanthroline and 3-ClpycdH is 3-chlorophenylcyanamide), were determined and revealed three different coordination modes were available to phenylcyanamido ligands when bound to copper(II)⁷ (Fig. 1.4 a,b) . These modes involve (i) terminal coordination

via the nitrile nitrogen (**7a**), (ii) μ -1,3-bridging through the amido and nitrile nitrogens (**7b**), and (iii) μ -1,1-bridging via the nitrile nitrogen (**7c**).



Several copper(I) complexes of the types $[\text{Cu}_2(\text{dppe})_3(\text{pcyd})_2] \cdot 2\text{Me}_2\text{CO}$ and $[\{\text{Cu}(\text{PPh}_3)_2(\text{pcyd})\}_2]$, where dppe is 1,2-bis(diphenylphosphino)ethane and pcyd is a phenylcyanamide anion, were synthesised and compared with previously reported halide and pseudohalide complexes. A strong parallel with the analogous azido complexes of copper (I) and copper (II)⁹ was observed. The X-ray crystal structures of $[\text{Cu}(\text{dppe})_3(4\text{-Clpcyd})_2] \cdot 2\text{Me}_2\text{CO}$ and $[\{\text{Cu}(\text{PPh}_3)_2(4\text{-Mepcyd})\}_2]$ were determined, the former consisting of centrosymmetric dimer involving terminally bound 4-chlorophenylcyanamido ligands; the latter contains μ -1,3-anionic (mode **7b**) ligands (Fig. 1.4 c,d).

1.3 This Present Study

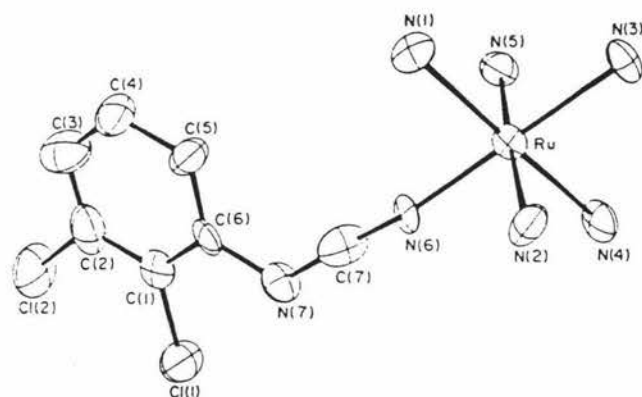
Univalent silver readily forms complexes with N-donor ligands and also tertiary phosphines and has coordination numbers of two, three and four. One of the aims of this study was to extend the coordination chemistry of anionic phenylcyanamides to include that of mixed ligand complexes of silver(I) with triphenylphosphine and phenylcyanamido ligands.

Chapter Two presents the synthesis and characterisation of some silver (I) complexes, including a series of compounds with the general formula of $[\text{Ag}(\text{Ph}_3\text{P})_3(\text{pcyd})]$. The physicochemical and spectroscopic properties of these complexes are described, including the single crystal x-ray

structures of $[\text{Ag}(\text{Ph}_3\text{P})_3(4\text{-Brpcyd})]$ and $[\text{Ag}(\text{Ph}_3\text{P})_3(4\text{-MeOpcyd})]$ respectively. This study allowed the monitoring of the influence that the phenyl substituents have on the electronic structure of the complexes.

Chapter Three involves a comparison of all the transition metal complexes of anionic phenylcyanamides that have been structurally characterised in order to investigate the nature of the bonding of phenylcyanamido ligands.

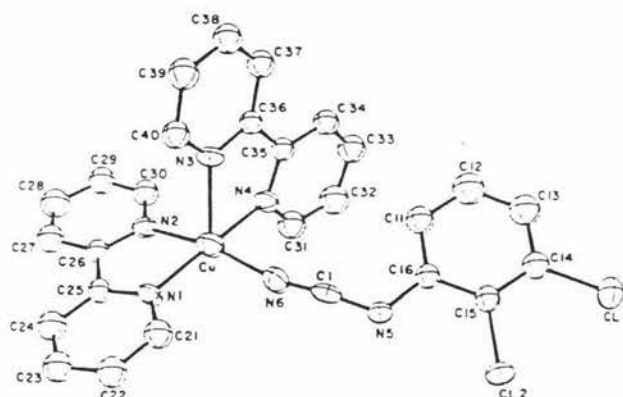
Figure 1.2 The crystal structure of the $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ ion



ref [12]

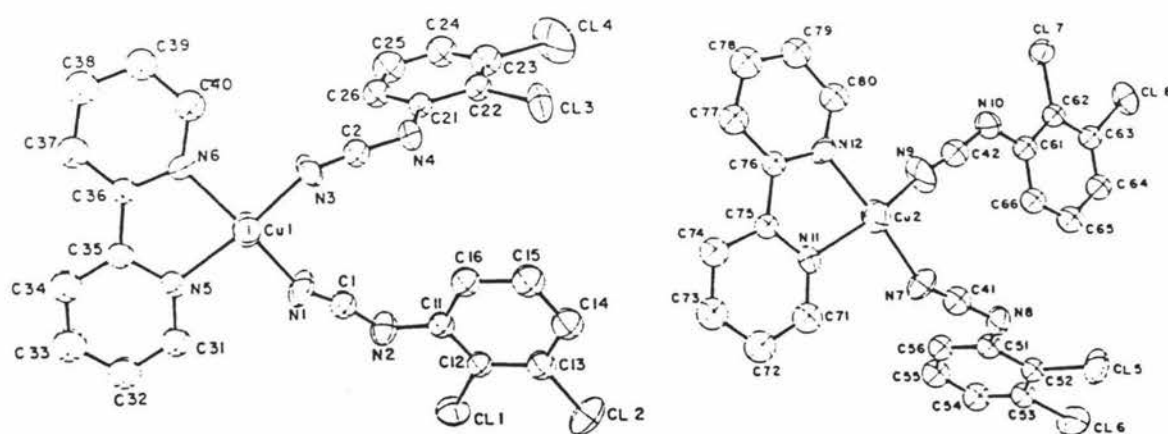
ORTEP drawing of the complex $[(\text{NH}_3)_5\text{Ru}(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ $[\text{SO}_4] \cdot \text{C}_2\text{H}_5\text{OH}$. The sulfate ion and ethanol have not been included for the sake of clarity.

Figure 1.3 Copper(II) complexes of bipyridine and phenylcyanamido ligands



(a) ref [14]

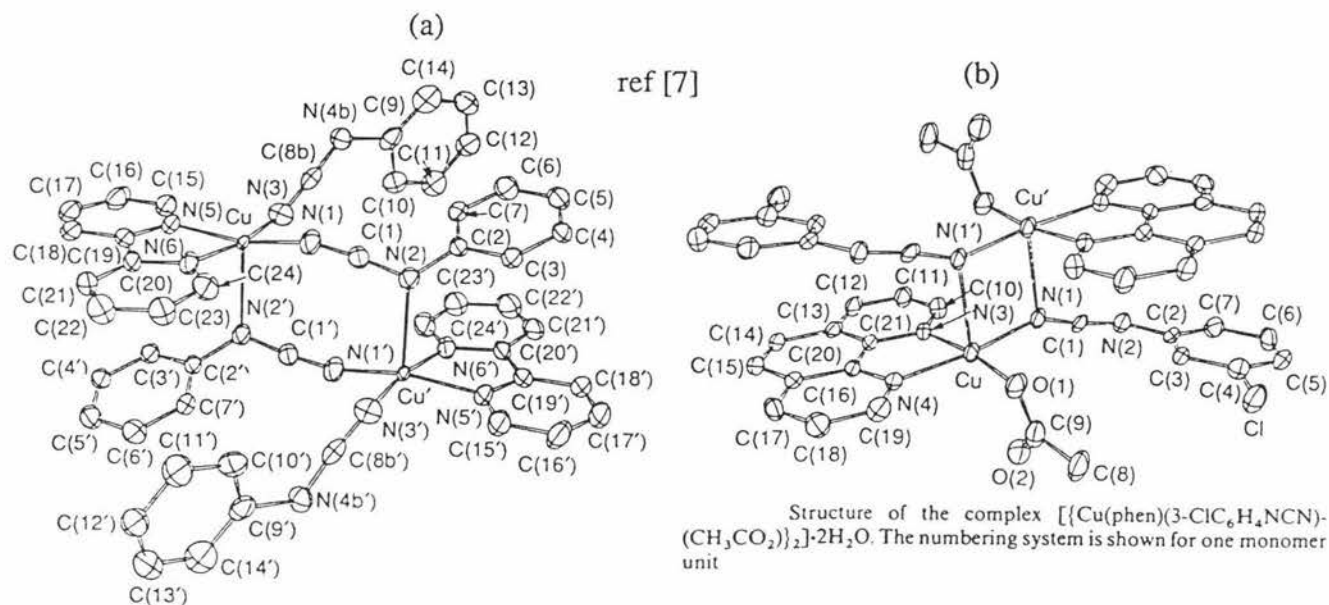
Plot of $[(\text{bpy})_2\text{Cu}(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ (1) with atom number scheme. The PF_6 anion has been omitted for clarity.



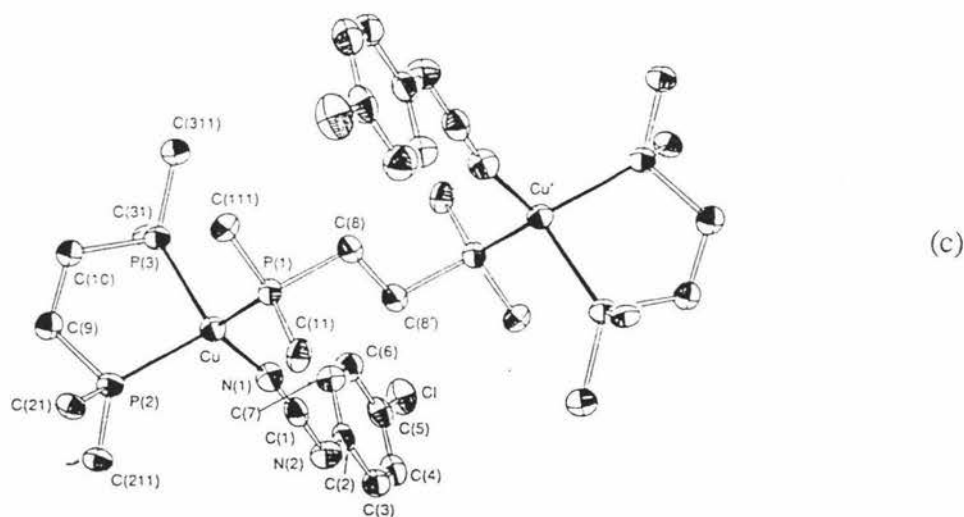
Plot of the two inequivalent configurations of $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$ (2) with atom number scheme.

(b) ref [14]

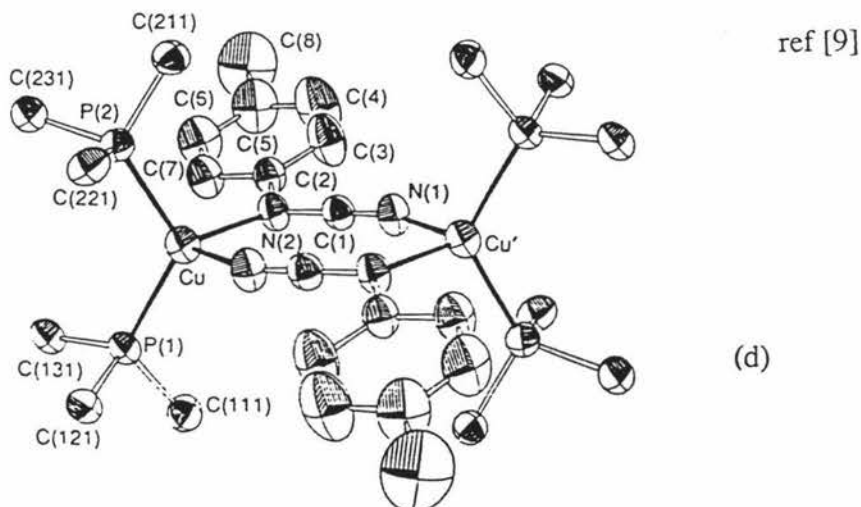
Figure 1.4 Phenylcyanamido complexes of copper(I) and copper(II)



Structure of the complex $[\text{Cu}(\text{bipy})(\text{PhNCN})_2]_2$ showing the numbering system used



The structure of the complex $[\text{Cu}_2(\text{dppe})_2(4\text{-ClC}_6\text{H}_4\text{NCN})_2]$, showing the numbering system used. Ellipsoids are drawn at the 50% probability level. Only the first atoms of the phenyl rings of the dppe ligands are shown, the remainder having been omitted for clarity



The structure of the complex $[\text{Cu}(\text{PPh}_3)_2(4\text{-MeC}_6\text{H}_4\text{NCN})_2]$, showing the numbering system used. Ellipsoids are drawn at the 50% probability level. Only the first atoms of the phenyl rings of the