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SYNTHESIS AND INTERNAL REDOX REACTIONS OF
OXIMIC AND NITROSO COMPLEXES

A THESIS SUBMITTED TO THE
COUNCIL FOR NATIONAL ACADEMIC AWARDS
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
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by

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THE POLYTECHNIC OF NORTH LONDON

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BEECHAMS PHARMACEUTICALS

To Jackie, my family and friends.

"Better a diamond with a flaw than
a pebble with none."

(Confucius 551-479 B.C.)

DECLARATION

Whilst registered as a candidate for this degree
the author has not been registered as a candidate for
any other award.

N.J. HARRIS

Nigel James Harris

Synthesis and Internal Redox Reactions of
Oximic and Nitroso Complexes

ABSTRACT

$M(\text{cup})_n$ complexes have been prepared ($M = \text{Cu, Ni, Fe, Co, Mn, or } ^n\text{Zn}$; $n = 2, M = \text{Fe}; n = 3$. $\text{cupH} = \text{cupferron}$) and structures have been proposed on the basis of spectroscopic, thermal and magnetic techniques. Their behaviour towards the Lewis bases pyridine, triphenylphosphine and hydroxylamine has been investigated. All of the $M(\text{cup})_2$ complexes, except when $M = \text{Zn or Fe}$, affords adducts on reaction with pyridine, whereas the complex $\text{Fe}(\text{cup})_3$ underwent an internal redox reaction. Internal redox behaviour was also observed when the complexes $\text{Cu}(\text{cup})_2$ and $\text{Fe}(\text{cup})_3$ were treated with triphenylphosphine. On the basis of the nature of the products arising from these reactions and from a kinetic study of the reaction of $\text{Cu}(\text{cup})_2$ with the phosphine, mechanistic proposals have been made.

The structure of the metal-containing product, $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, arising from the reaction of $\text{Cu}(\text{cup})_2$ with triphenylphosphine has been elucidated by X-ray crystallography.

The reaction of hydroxylamine with $M(\beta\text{-diket})_2$ complexes ($M = \text{Cu, Ni, or Zn}$; $\beta\text{-diketH} = \text{acetylacetonone, benzoylacetone, or 1,1,1-trifluoromethylacetylacetone}$) has been studied. The nickel complex initially afforded the dihydroxylamine adduct, which upon heating underwent dehydration to give the monooximate complex. This type of complex was also obtained from the reaction of $\text{Cu}(\text{acac})_2$ with hydroxylamine. The zinc complex initially afforded the monohydroxylamine adduct, which upon heating lost hydroxylamine to give the $\text{Zn}(\beta\text{-diket})_2$ complex. The complexes $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ on treatment with hydroxylamine gave $\text{Cu}(\text{bzacM})\text{OH}$ and $\text{Cu}(\text{tfacM})\text{OH}$ and the corresponding isoxazole. On the basis of these studies involving $\text{Cu}(\beta\text{-diket})_2$ in various solvents (and/or in the presence of triphenylphosphine) mechanistic proposals have been made, which involve internal redox steps.

$\text{Cu}(2\text{-nqo})_2$ complexes effected the conversion of primary amines to secondary amines, e.g. phenylethylamine was converted to di(phenylethyl)amine and also the cyclisation of diamines, e.g. 1,5-diaminopentane was converted to piperidine. In contrast, several other types of complex were found to be ineffective. The behaviour of the quinonemonooximate complexes has been rationalised by invoking internal redox processes

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ABBREVIATIONS.

In this thesis the following abbreviations have been used:

1-nqOH	1,2-Naphthoquinone-1-monooxime
2-nqOH	1,2-Naphthoquinone-2-monooxime
Fe(1-nq) ₂	Bis(1,2-naphthoquinone-1-monooximato)iron(II)
Fe(2-nq) ₂	Bis(1,2-naphthoquinone-2-monooximato)iron(II)
Cu(1-nq) ₂	Bis(1,2-naphthoquinone-1-monooximato)copper(II)
Cu(2-nq) ₂	Bis(1,2-naphthoquinone-2-monooximato)copper(II)
py	Pyridine
Ph ₃ P	Triphenylphosphine
Ph ₃ PO	Triphenylphosphine oxide
L.B.	Lewis base
acacH	Acetylacetonone; 2,4-pentanedione
bzacH	Benzylacetone; 1-phenyl-1,3-butanedione
tfacH	Trifluoroacetylacetonone; 1-trifluoromethyl-1,3-butanedione
PhNH ₂	Aniline
PhH	Benzene
NH ₂ OH	Hydroxylamine
NH ₂ NH ₂	Hydrazine
PhCH ₂ CH ₂ NH ₂	Phenylethylamine
(PhCH ₂ CH ₂)NH	Diphenylethylamine
CCl ₃ CF ₃	Trichlorotrifluoroethane

Note:

Quinonemonooximes and nitrosophenols are tautomeric. However, throughout this thesis the term 'quinonemonooxime' has been used. This does not necessarily mean that the compound described possesses that particular structure, or exists in that form. Dative bonds have only been used when their presence clarifies the structural formulation.

<u>CONTENTS</u>	<u>Page</u>
Title	(i)
Dedication	(ii)
Declaration	(iii)
Abstract	(iv)
Acknowledgements	(v)
Abbreviations	(vi)
Contents	(vii)(viii)(ix)(x)(xi)
<u>Chapter 1 Neutral metal chelates, their reactions</u>	
<u>with Lewis bases and their use in</u>	
<u>synthesis</u>	
1.1 Introduction	2
1.2 Preparation of metal chelates	2
1.3 Reaction of metal chelates with Lewis bases	3
1.4 Photochemically initiated internal redox reactions of metal chelates	9
1.5 Aims of present work	11
<u>Chapter 2 Metal complexes of N-nitrosophenyl-</u>	
<u>hydroxylamine</u>	
2.1 Introduction and aims	16
2.2 Preparation of transition metal(II) and metal(III) cupferronates and their reactions with Lewis bases	20
2.3 Structure and properties of iron(III) and metal(II) cupferronates	22
2.3a Spectroscopic studies	22
2.3b Magnetic susceptibility measurements	23

	<u>Page</u>
2.3c Structural proposals for metal(II) cupferronates, their pyridine adducts and iron(III) cupferronate	30
2.4 Mechanistic and other studies on the triphenylphosphine-promoted internal redox reactions of $\text{Cu}(\text{cup})_2$	
2.4a Introduction	35
2.4b The effect of solvent on the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine	36
2.4c The reaction of cupH with triphenylphosphine and pyridine	38
2.4d Kinetic investigation of the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine	40
2.4e Mechanistic appraisal of the reaction between triphenylphosphine and $\text{Cu}(\text{cup})_2$	44
2.5 The reaction of $\text{Fe}(\text{cup})_3$ with triphenylphosphine and pyridine	50
 <u>Chapter 3 X-ray crystallographic study of cupferronatobis(triphenylphosphine)-copper(I)</u>	
3.1 Crystal preparation	55
3.2 Determination of the structure	55
3.3 Results and discussion	56
 <u>Chapter 4 Reaction of hydroxylamine with bis(β-diketonato)metal(II) complexes</u>	
4.1 Introduction	70
4.2 Summary of previous work on the reaction of hydroxylamine with β -diketonato metal complexes	74

	<u>Page</u>
4.3 Aims of the present investigation	80
4.4 Re-examination of the reaction of hydroxylamine with $M(\text{acac})_2$ and $M(\text{bzac})_2$ ($M = \text{Ni}, \text{Cu}$ and Zn)	80
4.5 Extension of the study to other hydroxylamine-bis(β -diketonato) metal(II) systems	81
4.6 Effect of heating $M(\beta\text{-diket})_2(\text{NH}_2\text{OH})_n$ in toluene at 115°C ($\beta\text{-diketH} = \text{acacH}$ or bzacH ; $M = \text{Ni}, n = 2$; $M = \text{Zn}, n = 1$, $\beta\text{-diketH} = \text{tfacH}, M = \text{Ni}, n = 2$). Formation of bis(monooximato)nickel(II) complexes	86
4.7 Review of the condensation behaviour of β -diketones and their metal complexes with amines and hydrazines with special emphasis towards unsymmetrical β -diketones and their complexes	88
4.8 Mechanistic rationalisation of the behaviour of copper(II) β -diketones towards hydroxylamine	95
4.8.1 The behaviour of $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ towards hydroxylamine	95
4.8.2 The behaviour of $\text{Cu}(\text{acac})_2$ towards hydroxylamine	105
4.8.3 Conclusions	106
4.9 The structure and properties of bis(monooximato)nickel(II) complexes and their pyridine adducts	108

	<u>Page</u>
4.10 The structure and properties of Cu(acacM)(Ph ₃ P) ₂ , Cu(bzacM)(Ph ₃ P) ₂ and [Cu(tfacM)OH]	112
4.11 The structure and properties of Zn(bzac) ₂ (NH ₂ OH)	114
4.12 The structure and properties of 3-trifluoromethyl-5-methylisoxazoline	114
 <u>Chapter 5 Reactions of bis(1,2-quinonemonooximato) metal(II) complexes with amines and the rationalisation of the mechanism of these reactions</u>	
5.1 Introduction	121
5.2 The preparation and studies of metal complexes of 1,2-quinonemonooximes	121
5.2.1 Preparation of metal complexes of 1,2-quinonemonooximes	121
5.2.2 Structure of metal complexes of 1,2-quinonemonooximes	123
5.3 The behaviour of metal complexes derived from the monooximes of 1,2-quinones towards Lewis bases and dienophiles	128
5.4 Reaction of metal(II) complexes of 1,2-quinone-2-monooxime with amines	138
5.4.1 The general reactions of metal(II) complexes of quinonemonooxime with primary amines	139
5.4.2 The reaction of bis(1,2-naphthoquinone- 2-monooximato)copper(II) with phenylethylamine	142

	<u>Page</u>
5.4.3 Reaction of bis(1,2-naphthoquinone-2-monooximato)copper(II) with diamines	144
5.5 A mechanistic rationalisation for the reactions of bis(1,2-naphthoquinone-2-monooximato)copper(II) with phenylethylamine and with diamines	145
5.6 Conclusions	148
 <u>Chapter 6 Experimental</u>	
6.1 General	154
6.2 Analytical techniques	154
6.3 Physical techniques	154
6.4 Metal complexes of N-nitrosophenylhydroxylamine	156
6.5 Reactions of hydroxylamine with bis(β -diketonato)metal(II) complexes	167
6.6 Reactions of amines with bis(quinone-monooximato)metal(II) complexes	181
 <u>Appendix 1</u>	
Crystal data and details of the structure determination for cupferronato-bis(triphenylphosphine)copper(II).	187
 <u>Appendix 2</u>	
Catalytic aerobic oxidation of alkenes	204
 <u>Appendix 3</u>	
Published papers	208

CHAPTER ONE

Neutral metal chelates. their reactions with Lewis bases and their use in synthesis.

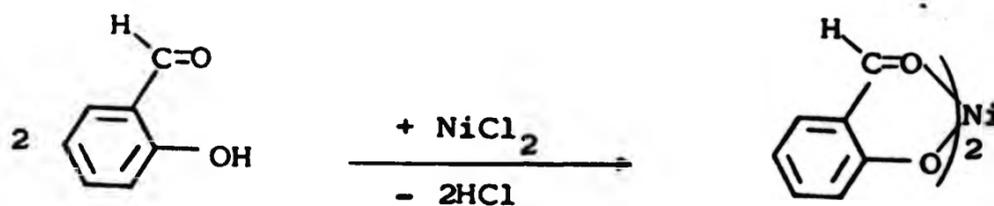
1.1. Introduction.

In this chapter the chelates considered are neutral complexes of the type ML_n incorporating mono anionic chelating ligands such as the anions of quinone mono-oximes and β -diketones. Such complexes have received considerable attention and have found application in analysis, synthesis and metal extraction.

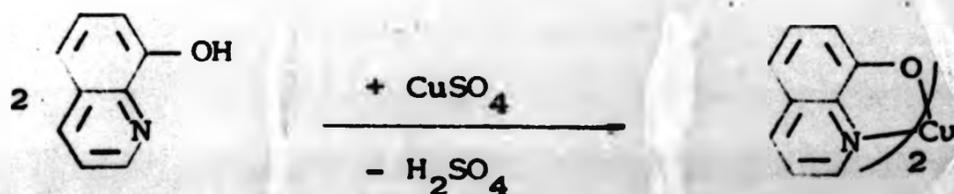
1.2. Preparation of metal chelates.

Metal chelates derived from anionic bidentate ligands are usually obtained by:

i) the direct interaction of the ligand with a metal salt in an appropriate solvent (e.g. Reactions 1.1¹ and 1.2²). This is the most common method for the preparation of chelates.

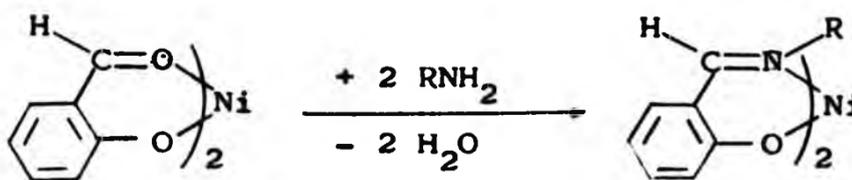


Reaction 1.1.



Reaction 1.2.

ii) Modification of the coordinated ligand (Reaction 1.3).³



Reaction 1.3.

In some cases such a modifying reaction between a metal chelate and a Lewis base can lead to complications since a variety of reactions can occur. This is dealt with more thoroughly in the following section.

1.3. Reaction of metal chelates with Lewis bases.

Metal chelates can undergo a variety of reactions with Lewis bases. In these reactions the oxidation state of the central metal atom can either (a) remain unchanged or (b) it can alter.

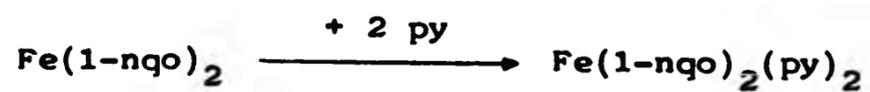
Reactions of type (a) fall into three categories;

- (i) Adduct formation.
- (ii) Ligand substitution.
- (iii) Ligand modification.

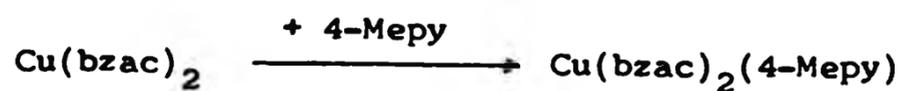
Reactions of the latter type (b) involve what is termed a Lewis-base promoted internal redox reaction.

(i) Adduct formation.

The formation of an adduct in reactions between a Lewis base and a metal chelate occurs readily, e.g. Fe(1-nqo)₂ reacts with pyridine to give Fe(1-nqo)₂(py)₂ (Reaction 1.4)⁴ and Cu(bzac)₂ reacts with 4-methylpyridine to give Cu(bzac)₂(4-Mepy) (Reaction 1.5).⁵



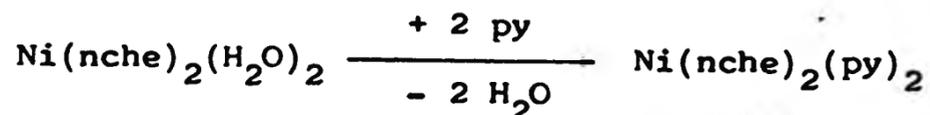
Reaction 1.4.



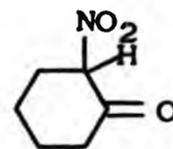
Reaction 1.5.

(ii) Ligand substitution reactions.

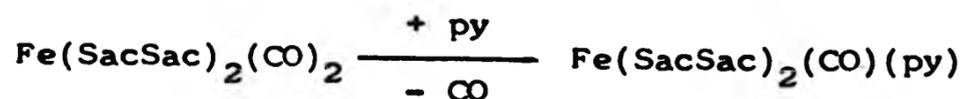
These reactions occur when the ligands in the chelate are displaced by another species which generally forms a more stable complex (e.g. Reactions 1.6 and 1.7).



ncheH = 2-nitrocyclohexanone,



Reaction 1.6.⁶



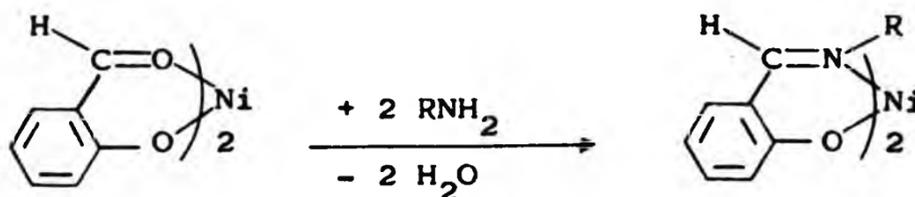
SacSacH = dithioacetylacetone, $\text{Me}-\overset{\text{S}}{\parallel}{\text{C}}-\text{CH}=\overset{\text{SH}}{\text{C}}-\text{Me}$

Reaction 1.7.⁷

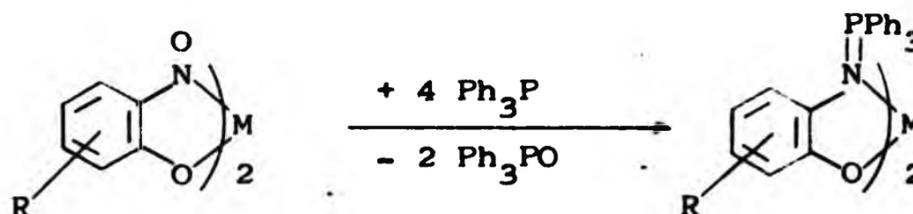
In these reactions neither the oxidation state nor the coordination number changes.

(iii) Formation of another complex through the coupling or condensation of the Lewis base with the coordinated ligand.

Examples of reactions which conform to this pattern are given in Reactions 1.3³ and 1.8.⁸



Reaction 1.3.



Reaction 1.8.

In Reaction 1.3 the amine attacks the carbonyl group to give a Schiff base complex and water. The amine attack on the carbonyl group is aided by the enhanced polarisation of the carbonyl due to its coordination to the metal, making the carbonyl group more susceptible to nucleophilic attack by the amine lone pair.⁹

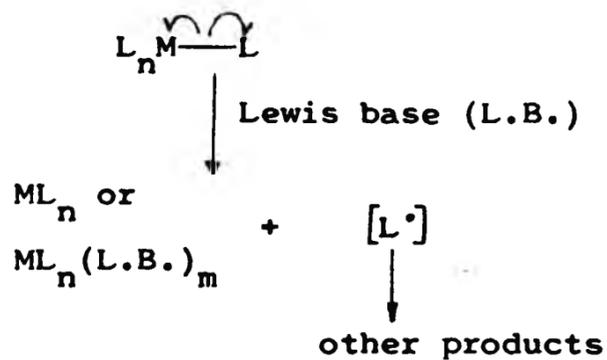
In Reaction 1.8 deoxygenation of the coordinated ligand occurs followed by coupling of the deoxygenated ligand with triphenylphosphine to give the iminophosphorane chelate. This reflects both the mode of bonding of the ligand NO group in the nitrosophenol complex and the strong affinity of trivalent phosphorus compounds for oxygen.

Mechanistically reactions such as 1.3 and 1.8 may involve initial coordination of the Lewis base to the

metal prior to its reaction with the ligand.

iv) Lewis base promoted internal redox reactions.

A generalised representation of Lewis base promoted internal redox reactions in which the metal oxidation state is reduced by one unit is illustrated in Scheme 1.1. Some examples of such reactions are given in Table 1.1.



Scheme 1.1.

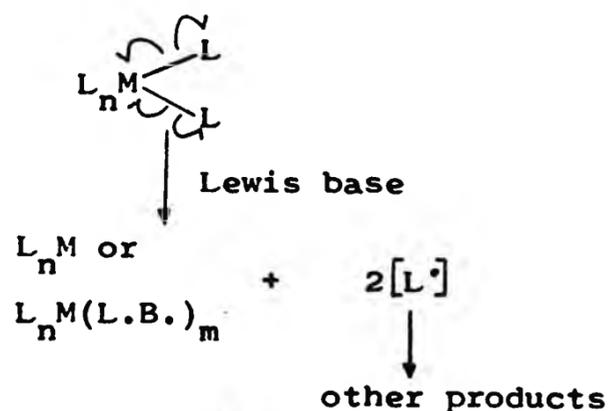
Table 1.1. Lewis base promoted internal redox reactions.

Metal complex	Lewis base	Products	Reference
$\text{Cu}(\text{dtc})_2^{\text{a}}$	Ph_3P	$\text{Cu}(\text{dtc})(\text{Ph}_3\text{P})_2$	10
$\text{Fe}(\text{dtc})_3$	RNC	$\text{Fe}(\text{dtc})_2(\text{RNC})_2$	11
$\text{Cu}(\text{acac})_2$	Ph_3P	$\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$	10
$\text{Cu}(1\text{-nqo})_2$	Ph_3P	$\text{Cu}(1\text{-nqo})(\text{Ph}_3\text{P})_2$ + 1-nH_2^{b}	12
$[\text{Ni}(\text{dtc})_3][\text{PF}_6]$	Ph_3P	$\text{Ni}(\text{dtc})_2 + \text{Ph}_3\text{PS}$ + $\text{Ph}_3\text{PC}(=\text{S})\text{NEt}_2$ + trace $\text{Ni}(\text{Ph}_3\text{P})_2(\text{dtc})$	13

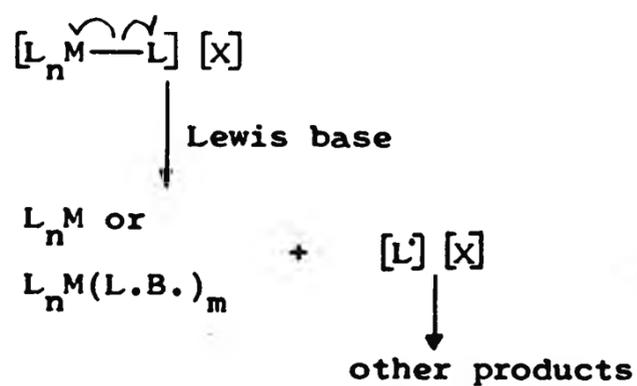
^adtc⁻ = diethyldithiocarbamate anion

^b1-nH₂ = 1-aminonaphthol

When the change in oxidation state of the metal is two, as opposed to one unit, as in Scheme 1.1, the internal redox reaction can be represented as in Schemes 1.2 and 1.3 for neutral and cationic species, respectively.



Scheme 1.2.



Scheme 1.3.

The term internal redox reaction was first used by McCleverty et al.¹¹ It was reported that nickel and iron dithiocarbamate complexes undergo Lewis base promoted internal redox reactions to give stable metal complexes with the metal in a lower oxidation state and the corresponding oxidation products. These reactions have also been referred to as redox reactions, charge transfer reactions or electron transfer reactions.^{14,15}

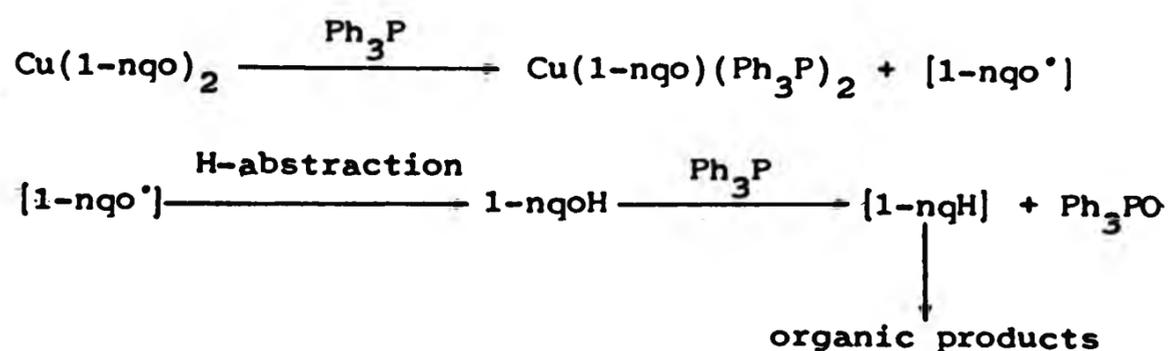
In general, with most studies of internal redox reactions, no attempt has been made to examine the reactions in full. Their mechanisms have not been rationalised and only some of the products arising from them have been characterised.

Reactions of this type occur in systems where the metal is easily reduced to a stable low oxidation state. Thus, iron(III) (d^5) complexes are readily reduced to iron(II) (d^6) complexes, copper(II) (d^9) complexes are reduced to copper(I) (d^{10}) complexes and nickel(III) (d^7) or nickel(IV) (d^6) complexes are easily reduced to square planar nickel(II) (d^8) complexes. This behaviour can give rise to novel complexes that are difficult to synthesise by other methods.

In the majority of studies of internal redox reactions reported in the literature only the metal containing products have been investigated. The products arising from the ligand radical L^\cdot have been identified only in a few cases. McCleverty observed that the reaction of $Fe(S_2CNEt_2)_3$ with RNC affords $Fe(S_2CNEt_2)_2(RNC)_2$ and $(Et_2NCS_2)_2$ and suggested that the latter is formed by dimerisation of L^\cdot . However, this is unlikely to occur on statistical grounds. Another more likely route to this compound might involve hydrogen abstraction by the radical L^\cdot to give the dithiocarbamic acid which, being unstable in air, would decompose to the thiuram disulphide. The formation of radicals of the type $EtNCS_2^\cdot$ is supported by an e.s.r. study of the reaction of piperidine with $Cu(S_2CNEt_2)_2$.¹⁸

An example of a reaction where hydrogen abstraction

may occur is that of $\text{Cu}(1\text{-nqo})_2$ with triphenylphosphine (Scheme 1.4).¹² In this case the radical nqo^\bullet , which is liberated by the internal redox process, abstracts hydrogen to give the ligand 1-nqoH . However, the reaction is complicated by the fact that the triphenylphosphine deoxygenates the NO group of the ligand to give the nitrene species 1-nqH and thence various organic products.



Scheme 1.4.

1.4. Photochemically initiated internal redox reactions of metal chelates.

All of the internal redox reactions outlined in the latter part of the previous section involve the interaction of a Lewis base with a metal chelate. There is, however, one important group of reactions where internal redox reactions occur without the presence of a Lewis base; these are photochemically initiated internal redox reactions. The solvent may act as a Lewis base but the reaction requires

photochemical radiation to initiate it. This type of reaction has previously been described as an inner sphere, or intramolecular redox process.¹⁹

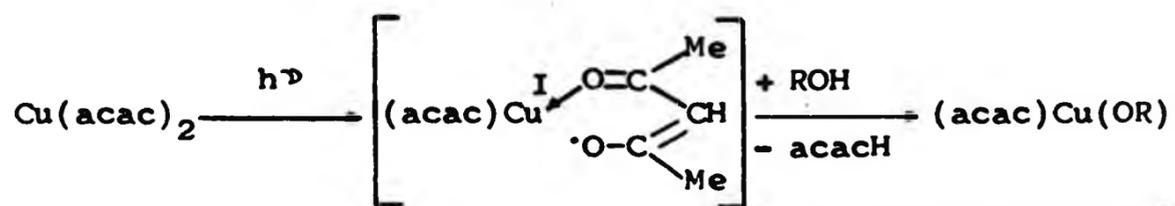
A number of photochemical studies of first row transition metal complexes have been reported (Table 1.2). One such is the photolysis of bis(acetylacetonato) copper(II) in various solvents (Scheme 1.5).²⁰

Table 1.2. Photochemically induced internal redox reactions.

Metal complex	Product	Reference
$[\text{Fe}(\text{ox})_3]^{3-}$	$[\text{Fe}(\text{ox})_2]^{2-}$	21
$\text{Co}(\text{gly})_3^{\text{a}}$	$\text{Co}(\text{gly})_2$	19
$\text{Cu}(\text{acac})_2$	$\text{Cu}(\text{acac})\text{S}_x^{\text{b}}$ + acacH	20

^agly = glycine

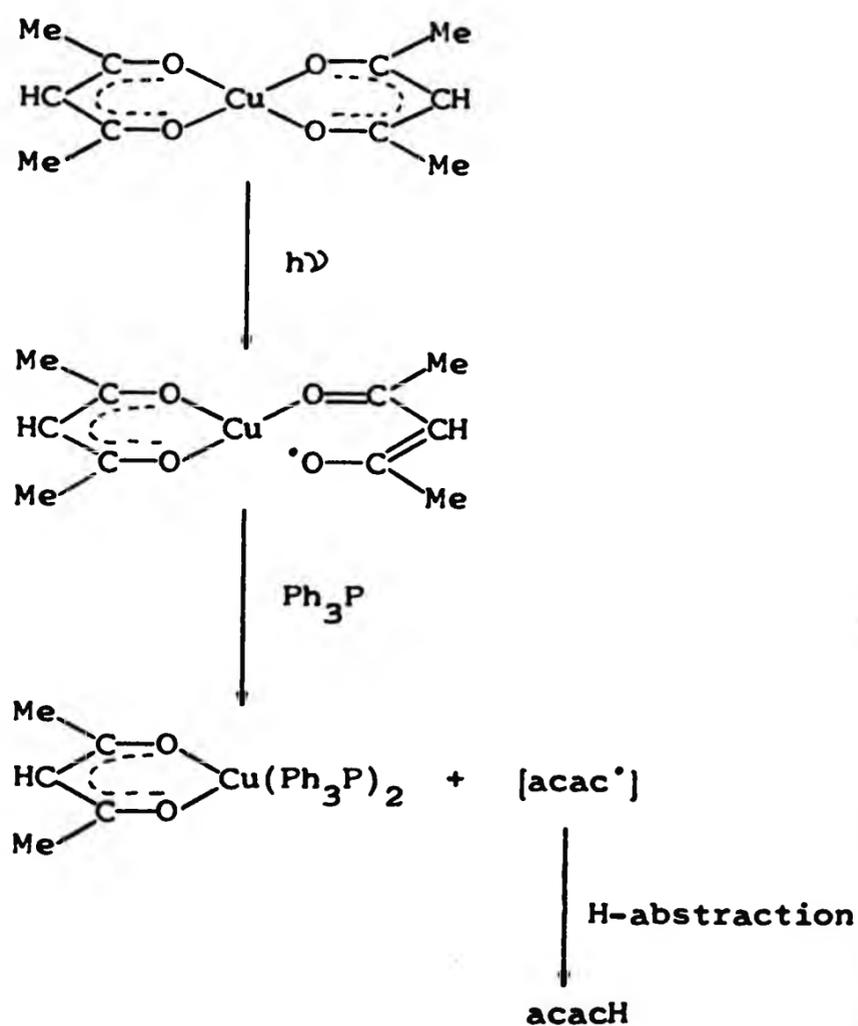
^bS = solvent



Scheme 1.5.

When the reaction is carried out in the presence of triphenylphosphine the copper(I) complex $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$ and acacH are obtained. The formation of these products can be rationalised as shown in Scheme 1.6 which is based on a scheme provided by the original authors²⁰ but

provides a more accurate picture of the reaction. As shown in Scheme 1.6 the internal redox reaction leads to a copper(I) species which reacts with the phosphine to give the isolated product $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$ and the ligand radical. Hydrogen abstraction by the latter leads to the other product i.e. the protonated ligand.



Scheme 1.6.

1.5. Aims of the present work.

From the above outline of internal redox reactions it can be seen that although they have received considerable attention their mechanisms are not clear

and often the ultimate fate of the ligand radical has not been determined. The primary aim of this work is to investigate the mechanisms of such reactions shown by complexes of N-nitrosophenylhydroxylamine, β -diketones and 1,2-quinonemonooximes.

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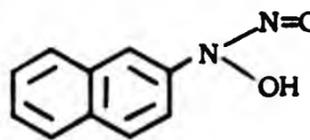
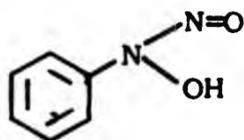
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CHAPTER TWO

Metal complexes of N-nitrosophenylhydroxylamine.

2.1. Introduction and aims.

Metal complexes of N-nitrosophenylhydroxylamine, (cupH), 1, have been extensively investigated for analytical purposes.¹ N-Nitrosophenylhydroxylamine is unstable and has a limited shelf life. As a consequence its ammonium salt, known as cupferron, is used in complexation reactions. Cupferron is used primarily for the determination of copper and iron but it has proved suitable for the determination of aluminium, bismuth, mercury, thorium, tin, titanium, vanadium and zirconium as well. The reagent gives a precipitate with most of the above metal ions even in strong acidic media. Only the aluminium(III) complex does not precipitate in the presence of acid.



By means of cupferron many metal ions may be separated, i.e. iron can be separated from aluminium and magnesium. Although cupferron makes possible several separations, the precipitates are not of stoichiometric composition. Hence, instead of being directly weighed, the precipitates are usually ignited and the metal oxide residues weighed.²

A compound closely related to cupferron, whose ammonium salt has also been used as an analytical

standard is 2-N-nitrosonaphthylhydroxylamine, (2).

Its ammonium salt, neocupferron, reacts with metal ions in the same way as cupferron. The complexes obtained are slightly less water soluble due to the larger organic group. This effect however, is negligible and therefore neocupferron is not used in preference to its phenyl analogue.

In contrast to the extensive studies of the analytical applications of complexes derived from cupferron, very little attention has been given to the study their composition, properties and reactions. The structural studies reported have been concerned with the X-ray crystallographic characterisation of the copper(II)³ iron(III)⁴ and zirconium(IV)⁵ complexes. Two rather incomplete crystallographic studies of uranium complexes of cupferron have also been reported.^{6,7} In addition some infrared spectroscopic studies of a range of metal cupferronates (Table 2.1) have been published.⁸ However, the value of these studies is limited because of the inadequate characterisation of the complexes examined.

As part of the work undertaken for this thesis the synthesis and characterisation of several metal cupferronates and their reactions with Lewis bases were investigated. In addition systematic structural and physicochemical studies of the complexes were undertaken. Also the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine was examined in depth with emphasis on product characterisation and the study of the kinetic behaviour

Table 2.1. Reported cupferron complexes.

Metal	Proposed formulation	Method of formation	Basis of formulation	Reference
K, Ag, Na, Hg.	Mcup	a	b	2
Cu	Cu(cup) ₂	c	i.r., d, b	2,3,8
Fe	Fe(cup) ₂	c	b	2
Co	Co(cup) ₂	c	i.r., b	2,8
Ni	Ni(cup) ₂	c	i.r., b	2,8
Zn	Zn(cup) ₂	c	i.r., b	2,8
Mn	Mn(cup) ₂	c	i.r., b	2,8
V	VO(OH)(cup) ₂	c	u.v., b	9
Ba, Cd, Ca, Pd, Hg, Sr, Sn	M(cup) ₂	c	b	2
Fe	Fe(cup) ₃	c	i.r., b, d	4,8
Sb, Bi, Ce, Cr	M(cup) ₃	c	b	2

See footnotes on next page.

Table 2.1.1 (continued).

Metal	Proposed formulation	Method of formation	Basis of formulation	Reference
Zr	$Zr(cup)_4$	c	b, d	2, 5
Hf	$Hf(cup)_4$	c	b	2
Ce, Pt, Sn, U	$M(cup)_4$	c	b	2
U	$[NH_4]_2 [UO_2(cup)_2Cl_2]$	c	b, d	6
	$[NH_4]_2 [UO_2(cup)_2CO_3]$	c	b, d	6
	$[X] [UO_2(cup)_3]$	c	b, d	7

^aReaction of metal hydroxide with cupferron in aqueous media

^bMetal analysis

^cReaction of metal salt (e.g. nitrate, chloride, sulphate) with cupferron in aqueous media

^dX-ray studies

and mechanism.

2.2. Preparation of transition metal(II) and metal(III) cupferronates and their reactions with Lewis bases.

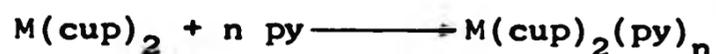
Although several transition metal(II) and metal(III) cupferronate complexes have been reported (Table 2.1) only the formulations of the copper(II) and iron(III) complexes have been satisfactorily established. The analytical results reported for all other transition metal complexes are not in accord with the proposed formulations. In most cases this is not due to the suggested non-stoichiometric character of the complexes¹⁰ but to inadequate purification.

In this study it has been possible to obtain well-defined complexes of the type $M(\text{cup})_2$ ($M = \text{Fe, Co, Cu, Ni, Zn}$ and Mn) by reaction of the metal chloride and/or sulphate with ammonium N-nitrosophenylhydroxylamine in water. Analogous reactions of the chlorides of iron(III) and chromium(III) were also examined. However, as observed by other workers,^{4,8} a well-defined product resulted only in the case of the iron. The chromium(III) product was initially a green solid but this quickly turned brown. This brown solid had an ill-defined infrared spectrum.

The complexes prepared during this study were characterised by full elemental analysis and various physicochemical methods. The latter are presented in Section 2.3 of this chapter.

Each of the metal(II) complexes, except $\text{Zn}(\text{cup})_2$,

reacted readily with pyridine at room temperature to give either the mono- or di-pyridine adducts (Reaction 2.1). Mono-pyridine adducts resulted from the copper and cobalt complexes and di-pyridine adducts from the manganese, iron and nickel complexes. As in the case of their precursors the pyridine adducts were characterised by full elemental analysis and using various physicochemical methods.



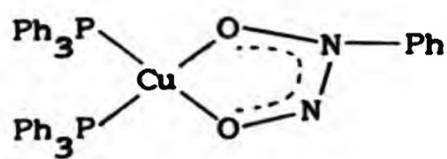
M = Zn; no reaction. M = Co or Cu; n = 1.

M = Mn, Fe or Ni; n = 2.

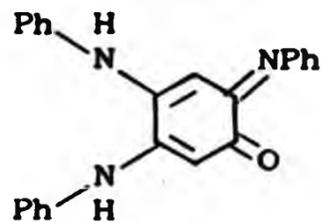
Reaction 2.1.

In contrast to their behaviour towards pyridine the metal(II) cupferronates, except $\text{Cu}(\text{cup})_2$ failed to react with triphenylphosphine and were recovered quantitatively.

The reaction of $\text{Cu}(\text{cup})_2$ with triphenylphosphine in acetone afforded the copper(I) complex $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ (3), triphenylphosphine oxide, aniline, benzene and 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (4). The formulation of the metal containing product is indicated by its diamagnetic character and elemental analysis, and has been confirmed by a full X-ray crystallographic study (see Chapter 3). The organic products were characterised by comparison with authentic samples using chromatographic techniques (g.l.c. and t.l.c.).



3



4

Triphenylphosphine also reacted with $\text{Fe}(\text{cup})_3$ in acetone to give the same organic products as those obtained from the analogous reaction of the copper(II) complex. The metal containing product obtained from this reaction was the di-triphenylphosphine adduct $\text{Fe}(\text{cup})_2(\text{Ph}_3\text{P})_2$.

The iron(III) complex also underwent a similar reaction when stirred in pyridine at room temperature. This reaction afforded the adduct $\text{Fe}(\text{cup})_2(\text{py})_2$, aniline, benzene and the quinone 4.

The nature of the products arising from the reactions of $\text{Cu}(\text{cup})_2$ with triphenylphosphine and of $\text{Fe}(\text{cup})_3$ with triphenylphosphine or pyridine is indicative of internal redox behaviour. This and the interesting character of some of the products arising from the reactions prompted a more detailed study of these systems which is presented in sections 2.4 and 2.5 of this chapter.

2.3. Structure and properties of iron(III) and metal(II) cupferronates.

2.3a. Spectroscopic studies.

Prominent bands in the infrared spectra of the complexes

$\text{Fe}(\text{cup})_3$, $\text{M}(\text{cup})_2$ ($\text{M} = \text{Ni}, \text{Fe}, \text{Co}, \text{Zn}, \text{Cu}$ and Mn), $\text{M}(\text{cup})_2(\text{py})$ ($\text{M} = \text{Cu}$ and Co) and $\text{M}(\text{cup})_2(\text{py})_2$ ($\text{M} = \text{Ni}, \text{Fe}$ and Mn) are given in Table 2.2. In all the cases the spectra show close similarities in the region $3000\text{-}600\text{ cm}^{-1}$. This indicates that the ligand coordinates to the metal in an analogous fashion in these complexes.

The complexes $\text{Ni}(\text{cup})_2$, $\text{Cu}(\text{cup})_2$, $\text{Co}(\text{cup})_2$ and their pyridine adducts gave well defined diffuse reflectance spectra (Table 2.3). The spectra of the other complexes were also recorded but these showed very broad ill-resolved bands. Additionally the solution spectra of the complexes also showed broad ill-defined bands.

2.3b. Magnetic susceptibility measurements.

The magnetic susceptibilities of the complexes were determined at room temperature using the Gouy method. Their calculated moments are given in Table 2.3.

The susceptibilities of the $\text{Co}(\text{cup})_2$ and $\text{Co}(\text{cup})_2(\text{py})$ complexes were also determined over a temperature range (115-272 K)(Table 2.4).

Before discussing the results obtained from the magnetic susceptibility measurements a brief background to the theory and application of magnetic susceptibilities is presented.

Besides enabling the determination of the oxidation state of the metal in a complex, μ_{eff} values can provide information regarding the geometry of the complex in the

Table 2.2. Main absorptions in the infrared region by metal cupferronate complexes and their pyridine adducts.

Complex	Absorption (cm^{-1})
Ni(cup) ₂	1380(w), 1300(w), 1150(m), 940(s), 760(s), 700(s), 680(w)
Fe(cup) ₂	1380(w), 1300(w), 1210(m), 1025(m), 940(s), 760(s), 700(s), 680(w)
Co(cup) ₂	1380(w), 1300(w), 1200(m), 1025(m), 930(s), 760(s), 700(s), 680(w)
Zn(cup) ₂	1380(w), 1305(w), 1220(m), 1030(m), 935(s), 760(s), 700(m), 685(w)
Cu(cup) ₂	1480(w), 1380(w), 1300(w), 1180(m), 1020(s), 920(s), 750(m), 690(m), 675(w)
Mn(cup) ₂	1455(w), 1380(w), 1300(m), 1180(m), 1025(s), 970(s), 745(m), 690(s), 680(w)
Fe(cup) ₃	1380(w), 1290(w), 1200(w), 1170(m), 1070(s), 935(s), 769(m), 680(w), 610(m)
Ni(cup) ₂ (py) ₂	3090(m), 2500(m), 1600(s), 1380(w), 1210(w), 1025(m), 920(s), 700(m), 630(w)
Fe(cup) ₂ (py) ₂	3085(m), 2500(s), 1600(s), 1385(m), 1210(w), 1010(m), 940(s), 700(m), 620(w)
Co(cup) ₂ (py)	3080(m), 2500(s), 1600(s), 1390(w), 1210(w), 1010(m), 930(s), 690(m)
Cu(cup) ₂ (py)	3085(m), 1600(s), 1575(m), 1400(m), 1210(w), 950(m), 700(m), 625(w)
Mn(cup) ₂ (py) ₂	3080(m), 2430(s), 1600(s), 1380(w), 1210(w), 1025(w), 925(s), 695(m), 620(w)

Table 2.3. Physical properties of bis(cupferronato) metal(II) complexes and tris(cupferronato) iron(III) complex.

Complex	$\mu_{\text{eff}}/\text{B.M.}$ (20 °C)	Reflectance spectra $\lambda_{\text{max}}/\text{nm}$	M_r^a	
			Found	Calc.
Fe(cup) ₂	5.11	b	319	330
Zn(cup) ₂	c	-	330	339
Ni(cup) ₂	2.83	660,460	331	338
Cu(cup) ₂	1.82	550,769	342	337
Mn(cup) ₂	6.19	b	321	329
Co(cup) ₂	3.46	460,550,650	321	333
Fe(cup) ₃	5.92	b	455	467
Ni(cup) ₂ (py) ₂	2.72	400,600,880,1075	473	491
Co(cup) ₂ (py)	4.01	350,460,500,550	394	412
Mn(cup) ₂ (py) ₂	6.10	b	473	487
Fe(cup) ₂ (py) ₂	5.09	b	455	488
Cu(cup) ₂ (py)	1.80	360,570,750	401	416

^adetermined in chloroform solution

^bill-defined

^cdiamagnetic

Table 2.4. Variable temperature magnetic data for $\text{Co}(\text{cup})_2$ and $\text{Co}(\text{cup})_2(\text{py})$.

<u>$\text{Co}(\text{cup})_2$</u>							
T/K	272	249	219	190	162	134	115
$10^6 \chi_A$	6082	6717	7763	9045	10780	13314	15761
μ_{eff}	3.64	3.66	3.69	3.71	3.74	3.78	3.81
e/K	10						
<u>$\text{Co}(\text{cup})_2(\text{py})$</u>							
T/K	272	249	219	190	162	134	115
$10^6 \chi_A$	7716	8595	9914	11592	13922	17069	20075
μ_{eff}	4.10	4.14	4.17	4.20	4.25	4.28	4.30
e/K	16						

solid state.

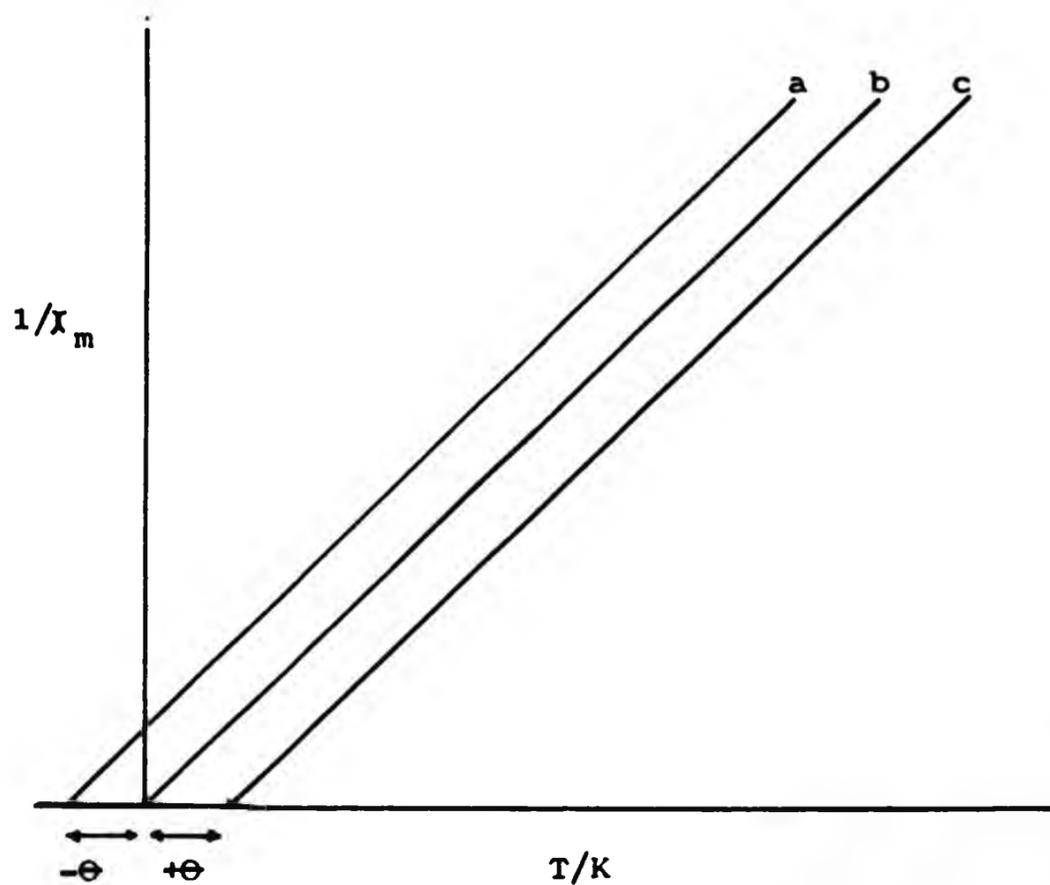
The μ_{eff} of a complex is the summation of two contributions, the spin- and the orbital-contribution. The orbital contribution is known to be dependent on the geometry of the complex.¹¹

The study of magnetic behaviour at various temperatures provides information in a different manner. Generally, magnetic properties can be affected by temperature in several ways although here only the simplest cases will be discussed:

(i) The magnetic moment can remain unchanged with temperature. Complexes which exhibit temperature independent magnetic moments are said to be magnetically dilute, i.e. the centres of magnetism are physically independent of each other.

(ii) The magnetic susceptibility can change with temperature. In these cases the inverse of the molar susceptibility varies linearly with temperature. When $1/\chi_m$ is plotted against T the intersection at the temperature axis corresponds to the Weiss constant. Negative values of this constant indicate ferromagnetism and positive values antiferromagnetism (Figure 2.1). Such behaviour normally arises from interaction between magnetic centres. This can occur for instance, from metal-metal bonds or from association between adjacent molecules. Antiparallel spin alignments of the unpaired electrons in adjacent metal centres leads to subnormal magnetic moments, i.e. μ_{eff} values lower than expected for a given number of unpaired electrons.

Figure 2.1. Plots of $1/\chi_m$ vs temperature for paramagnetic ions illustrating ferromagnetic (plot a), magnetically dilute (plot b) and antiferromagnetic (plot c) behaviour (χ_m = molar susceptibility).



The effect of temperature on these types of interactions are shown qualitatively in Figures 2.2-2.4.

In Figures 2.3 and 2.4 there is discontinuity at a certain temperature, the Curie point for ferromagnetism and the Néel point for antiferromagnetism. Above these critical temperatures the magnetic interactions are suppressed as the thermal energy is greater than the

energy of interaction and normal paramagnetic behaviour is exhibited.

Figure 2.2. Temperature-dependence of magnetic susceptibility for simple paramagnetism

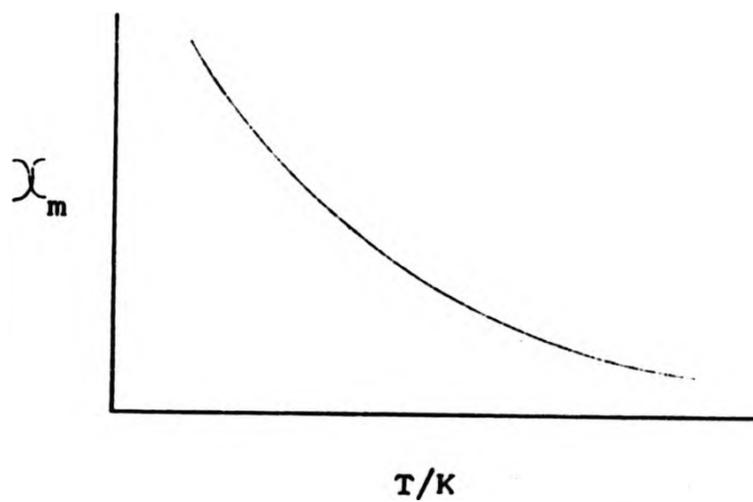


Figure 2.3. Temperature-dependence of magnetic susceptibility for ferromagnetism

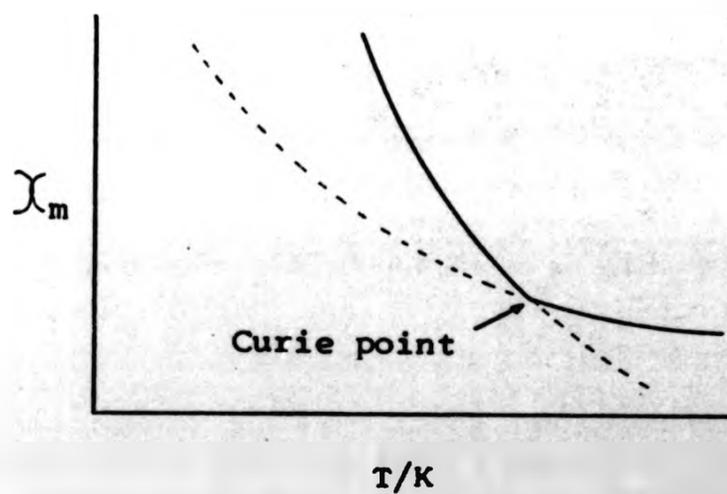
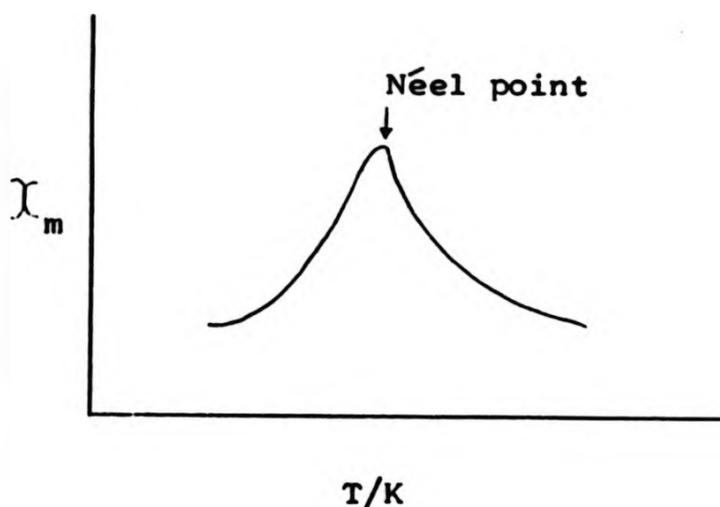


Figure 2.4. Temperature-dependence of magnetic susceptibility for antiferromagnetism



2.3c. Structural proposals for metal(II) cupferronates, their pyridine adducts and iron(III) cupferronate.

The structure of $\text{Cu}(\text{cup})_2$ was shown earlier by X-ray crystallography to be square planar.³ Its room temperature magnetic moment of 1.83 B.M. determined during this study and the presence of absorption maxima at 550 and 760 nm in the u.v./visible spectra are in accord with the square planar structure.

The pyridine adduct of the copper(II) complex, $\text{Cu}(\text{cup})_2(\text{py})$, is monomeric in chloroform and its diffuse reflectance spectrum with λ_{max} at 360, 570 and 750 nm indicates a square pyramidal structure. The spectrum compares favourably with the spectra of square pyramidal copper(II) complexes e.g. the 4-methylpyridine adducts of copper(II) β -diketonates¹² the quinoline adducts of copper(II) β -diketonates¹³ and the pyridine adduct of bis(4-methyl-1,2-benzoquinone-2-oximato)copper(II).¹⁴

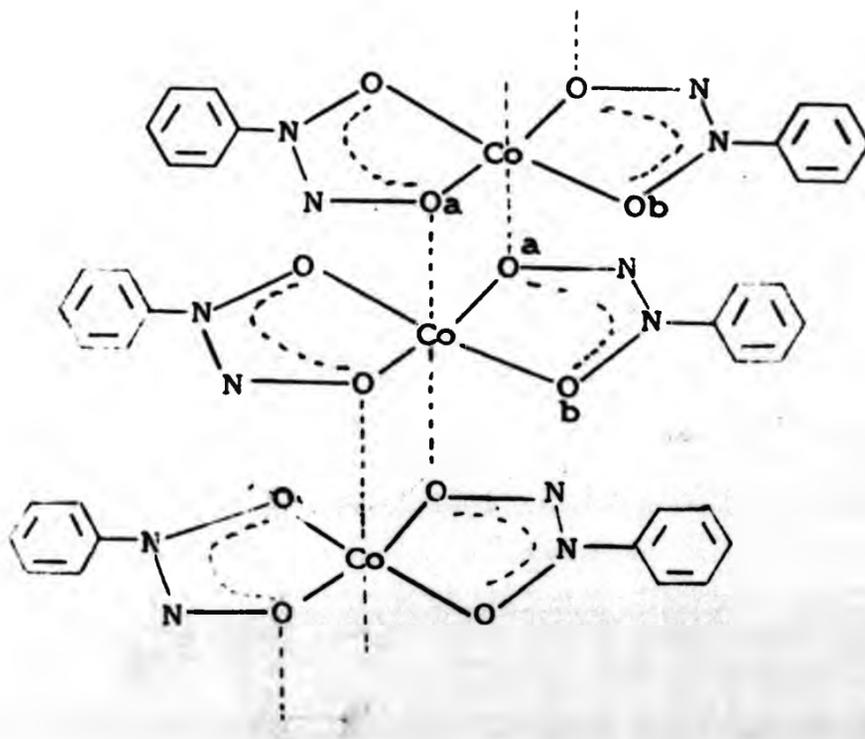
The room temperature magnetic moment of 1.82 B.M. is in accord with the proposed structure.

The Mn(II), Ni(II), Fe(II) and Zn(II) complexes, of the type $M(\text{cup})_2$, are monomeric in chloroform solution and their X-ray powder patterns are similar but differ from that of the copper(II) complex. Variable temperature magnetic measurements indicate no association in the solid state. These observations suggest that the complexes have tetrahedral or distorted tetrahedral structure. In the case of the nickel(II) complex the value of the room temperature magnetic moment (2.83 B.M.) and its diffuse reflectance spectra, which shows absorptions at 460 and 660 nm, are indicative of the distorted arrangement.¹⁵ A truly tetrahedral nickel(II) complex has a calculated magnetic moment of 4.21 B.M. at room temperature.¹⁵ However, distortions in the tetrahedral geometry reduce this by splitting the orbital degeneracy. Thus the largest magnetic moment observed for tetrahedral nickel(II) is 3.80 B.M. and generally distorted tetrahedral nickel(II) complexes have moments of about 3.00 B.M.¹⁵ In the case of the manganese(II) and the iron(II) complexes their room temperature magnetic moments are in accord with the proposed structures and their diffuse reflectance spectra were ill-defined and provided no structural information.

The decreasing magnetic moment with temperature shown by $\text{Co}(\text{cup})_2$ and the positive value of the Weiss constant, Θ , suggest antiferromagnetic behaviour and association in the solid state.¹¹ It is therefore assumed that $\text{Co}(\text{cup})_2$ has an associated structure i.e.

the cobalt is pseudo-octahedral (see Figure 2.6 and Table 2.4). This type of association in the solid state is well known for other cobalt(II) complexes, e.g. $\text{Co}(\text{acac})_2$.¹⁶ The diffuse reflectance spectrum of $\text{Co}(\text{cup})_2$ exhibits λ_{max} at 460, 550 and 650 nm which supports the proposed octahedral geometry. Cobalt(II) in an octahedral environment (e.g. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$) shows at 490 and 540 nm.¹⁷ This is significantly different from the spectra of tetrahedral cobalt(II) complexes (e.g. $[\text{CoCl}_4]^{2-}$) which have absorptions in the region 640, 680 and 700 nm.¹⁷

Figure 2.6. The structure of $\text{Co}(\text{cup})_2$



As the structure of $\text{Co}(\text{cup})_2$ is represented in Figure 2.6 the association is through the equivalent oxygen atoms a. It is possible that the association could occur through the oxygen atoms b, or a combination

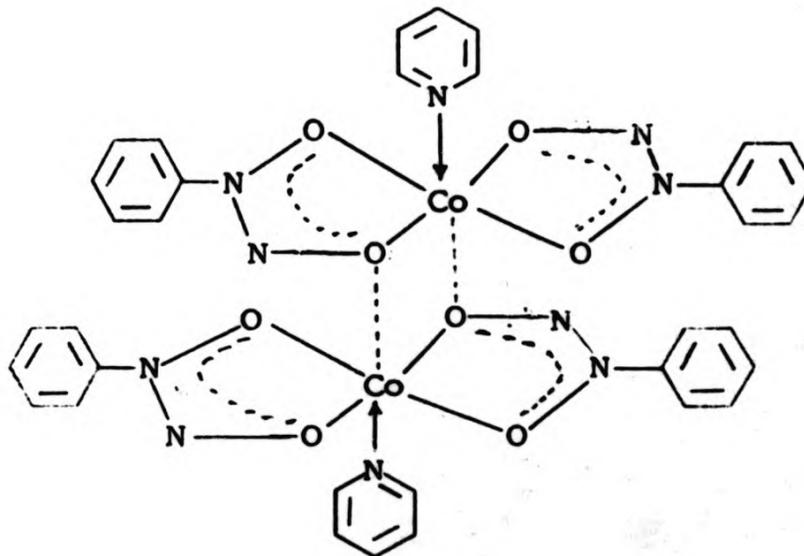
of both. However, on the basis of previous X-ray crystallographic studies³⁻⁵ and the X-ray structural characterisation detailed in Chapter 3 it is observed that the electronic charge in the chelate ring is delocalised. The N-O_a bond is longer than the N-O_b bond, indicating that the N-O_b bond has more double bond character. This suggests that O_a exhibits some sp³ hybridisation while O_b is sp² hybridised. With sp² hybridisation the lone pair on the oxygen is in the plane of the bonds and is not likely to be of the correct orientation for association. But with sp³/sp² hybridisation the electron distribution around the O_a oxygen atom allows donation to the adjacent cobalt and therefore association most likely occurs through O_a.

The pyridine derivatives, M(cup)₂(py)₂ (M = Fe, Mn and Ni) are monomeric in solution and their room temperature magnetic moments are typical of octahedral complexes.¹⁵ In the case of the Ni(II) complex this structure is also indicated by its diffuse reflectance spectrum. The pyridine derivative of the cobalt(II) complex, Co(cup)₂(py), is also monomeric in solution and associated in the solid state (Figure 2.7). The association is indicated by the decreasing value of its magnetic moment with temperature, the positive value of Θ (Table 2.4) and its diffuse reflectance spectrum which shows λ_{\max} at 350, 460, 500 and 550 nm and is typical of cobalt(II) in a pseudooctahedral environment.¹⁷

The trischelate iron complex, Fe(cup)₃, has an

observed room temperature magnetic moment of 5.90 B.M. This is indicative of iron(III) in an octahedral environment¹⁸ and compares well with other octahedral iron(III) complexes e.g. $\text{Fe}(\text{acac})_3$ which has a magnetic moment of 5.90 B.M.¹⁸

Figure 2.7. The structure of $\text{Co}(\text{cup})_2(\text{py})$



2.4. Mechanistic and other studies on the triphenylphosphine - promoted internal redox reaction of $\text{Cu}(\text{cup})_2$

2.4a. Introduction

The formation of the copper(I) product, $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, from the reaction of $\text{Cu}(\text{cup})_2$ with triphenylphosphine in acetone indicates that the copper(II) complex undergoes a Lewis base promoted internal redox reaction (Scheme 2.1). The organic products (benzene, aniline and the quinone 4) which accompany the formation of $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ must originate from the cup^\bullet radical. They could arise from the decomposition of this radical or from the decomposition of cupH which is obtained from cup^\bullet via a hydrogen abstraction reaction. The formation of triphenylphosphine oxide indicates that deoxygenation reactions involving triphenylphosphine and cup^\bullet , cupH or their decomposition products also occur. Some possible pathways to the organic products are outlined in Scheme 2.1.

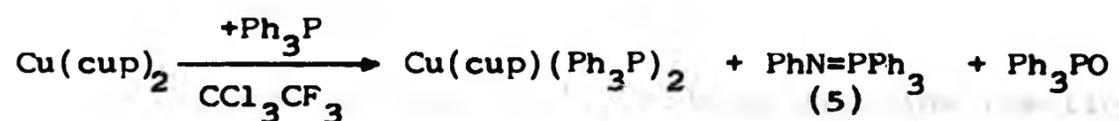
In order to clarify the mechanism of the reaction and examine which of the possible reactions in Scheme 2.1 actually occur the following aspects were investigated:

- (i) The reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine in various solvents.
- (ii) The reactions of the protonated ligand (cupH) with pyridine and triphenylphosphine.
- (iii) The kinetic behaviour of the $\text{Cu}(\text{cup})_2$ /triphenylphosphine system.

acetone which, as noted earlier, leads to the compounds $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, benzene, aniline and 4.

The reaction was carried out in trichlorotrifluoroethane because this solvent does not contain any hydrogen and cannot participate in hydrogen abstraction steps with the ligand radical. This should force the ligand radical to react in a different way and thus might provide information regarding the mechanism.

The organic products from this reaction (Reaction 2.2) were phenyliminophosphorane (5), and triphenylphosphine oxide. Significantly no other organic products were detected but the copper(I) product, $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, was obtained in very high yield



Reaction 2.2.

Propan-2-ol was used as a solvent because it has strong hydrogen atom donating properties.¹⁹ This property is expected to enhance any hydrogen abstraction steps involved in the reaction. The products obtained when the reaction was carried out in propan-2-ol were aniline, benzene and triphenylphosphine oxide. Interestingly compound 4 was not produced but again the yield of $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ was very high. The yields of benzene, aniline, compound 4 and $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ produced when the reaction was carried out in pyridine were very similar to the yields obtained when acetone was used as the solvent. This suggests that the reaction follows the same pathway in acetone

as in pyridine. Because of this and the high solubility of $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ in pyridine this solvent was chosen as the reaction medium for the kinetic studies.

The reaction was also performed in an acetone/aniline (50:1) mixture to ascertain whether aniline present at the start of the reaction had any effect on the yields of the organic products and of compound 4 in particular. In this case the yield of 4 increased in comparison to its yield when acetone was used as solvent, a corresponding decrease in the yield of benzene also being observed.

2.4c. The reaction of cupH with triphenylphosphine and pyridine.

The ligand radical, cup', produced from the reaction of $\text{Cu}(\text{cup})_2$ with triphenylphosphine can abstract hydrogen from the solvent to give cupH (route A in Scheme 2.1).

As a consequence the behaviour of cupH towards triphenylphosphine and pyridine was examined in detail and in the case of the reaction with triphenylphosphine the effects of various solvents were also studied. The results are summarised in Table 2.5. CupH reacts readily with pyridine to give, aniline, benzene and compound 4. These products were also obtained from the reaction of cupH with triphenylphosphine in acetone. Significantly both systems afforded the organic products in relative yields very similar to those obtained from the reactions of $\text{Cu}(\text{cup})_2$ with triphenylphosphine in acetone or pyridine (see Table 2.5 for yields).

Table 2.5. Relative percentage yields of organic products^a from the reaction of cupH, Cu(cup)₂ or Fe(cup)₃ with triphenylphosphine or pyridine.

Reactant	Lewis base	Solvent	Relative % yield of products ^a			
			Benzene	Aniline	4	PhN=PPh ₃
Cu(cup) ₂	Ph ₃ P	acetone	42	40	11	-
cupH	Ph ₃ P	acetone	43	41	10	-
Cu(cup) ₂	Ph ₃ P/py	pyridine	42	43	11	-
Cu(cup) ₂	Ph ₃ P	acetone/aniline (50:1)	22	47	20	-
cupH	Ph ₃ P	propan-2-ol	49	50	-	-
Cu(cup) ₂	Ph ₃ P	trichlorotrifluoroethane	-	-	-	95
cupH	Ph ₃ P	trichlorotrifluoroethane	-	-	-	95
cupH	py	pyridine	42	41	12	-
Cu(cup) ₂	Ph ₃ P	propan-2-ol	48	49	-	-
Fe(cup) ₃	py	pyridine	41	42	14	-
Fe(cup) ₃	Ph ₃ P	acetone	41	42	14	-

^aExcluding triphenylphosphine oxide

The reactions of cupH with triphenylphosphine in propan-2-ol or trichlorotrifluoroethane paralleled the analogous reactions of $\text{Cu}(\text{cup})_2$ with triphenylphosphine in these solvents. Thus in propan-2-ol cupH afforded aniline and benzene but not compound 4, whereas in trichlorotrifluoroethane phenyliminophosphorane was formed. In addition to the products noted above all the reactions of cupH with triphenylphosphine afforded triphenylphosphine oxide as a major product.

2.4d. Kinetic investigation of the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine.

Before the kinetic investigation was commenced the u.v./visible spectra of $\text{Cu}(\text{cup})_2$ and $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ in pyridine were obtained. The $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ complex exhibited a λ_{max} at 415 nm. The extent of reaction was monitored by recording the change in absorbance between 350 - 700 nm at 33 °C in pyridine. A typical spectrum is shown in Figure 2.7.

For the kinetic study the same initial concentration of the $\text{Cu}(\text{cup})_2$ was used and the concentration of triphenylphosphine was varied. With the exception of the reaction using a $[\text{Ph}_3\text{P}] : [\text{Cu}(\text{cup})_2]$ ratio of 2:1 a plot of $\log(A_\infty - A_t)$ against time gave a straight line (a typical plot is given in Figure 2.8).

A series of k_{obs} values for different concentrations of triphenylphosphine were obtained. Values of k_{obs} at different concentrations of triphenylphosphine are given in Table 2.6 and plotted in Figure 2.9.

The plot of k_{obs} vs $[\text{Ph}_3\text{P}]$ gave a straight line

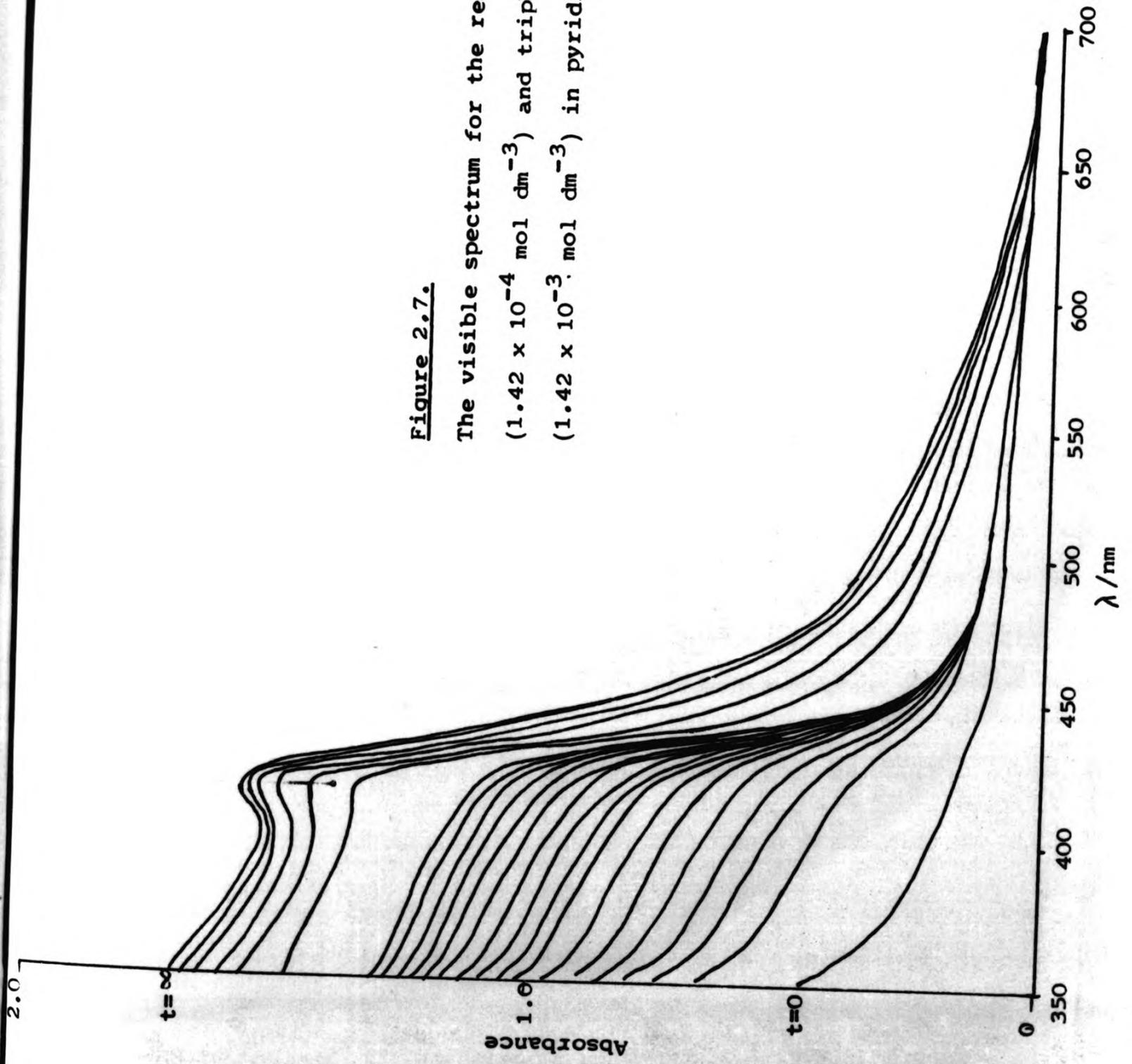


Figure 2.7.

The visible spectrum for the reaction of $\text{Cu}(\text{cup})_2$
($1.42 \times 10^{-4} \text{ mol dm}^{-3}$) and triphenylphosphine
($1.42 \times 10^{-3} \text{ mol dm}^{-3}$) in pyridine at 33°C .

Figure 2.8. A plot of $\log(A_\infty - A_t)$ vs time for a ratio of $[\text{Cu}(\text{cup})_2] : [\text{Ph}_3\text{P}]$ of 1:10 at 33 °C.

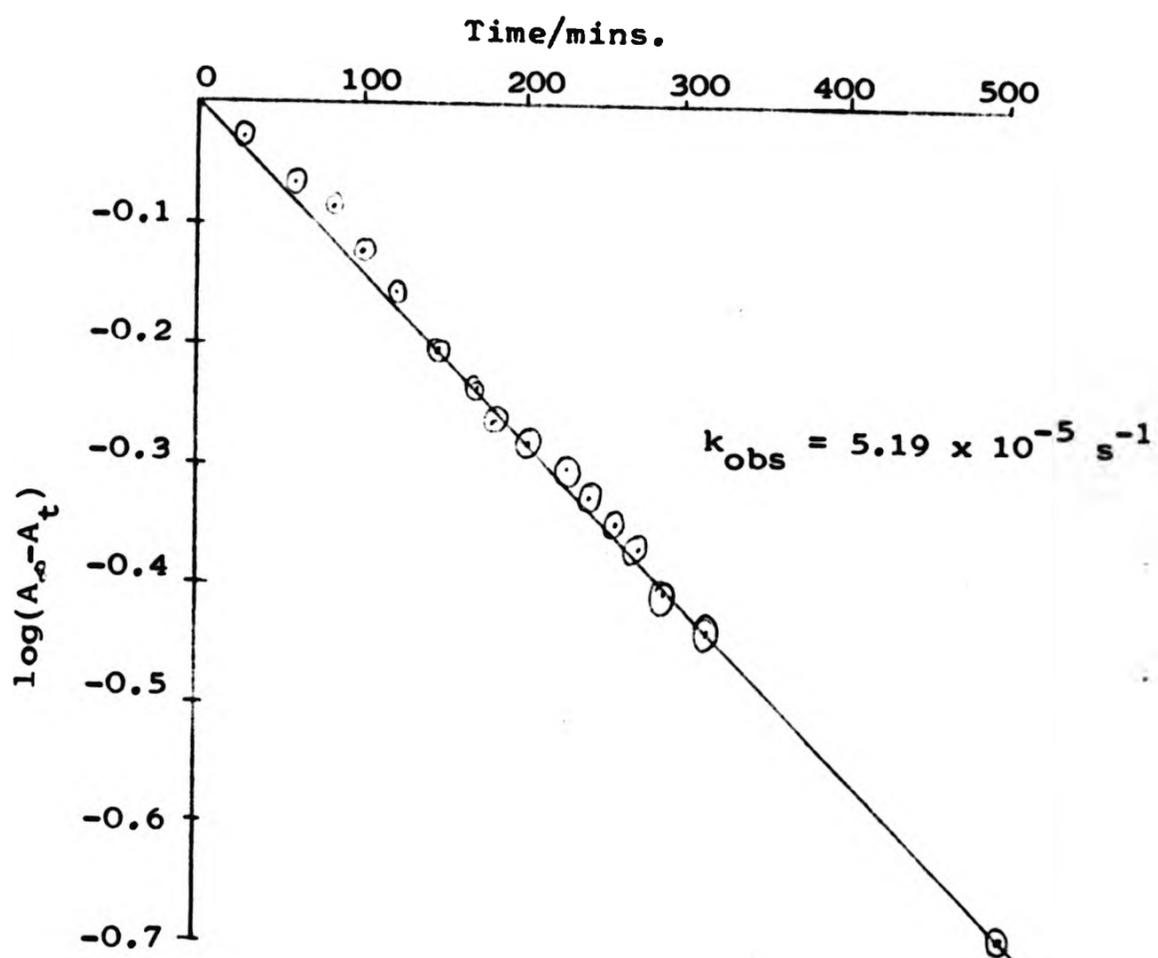
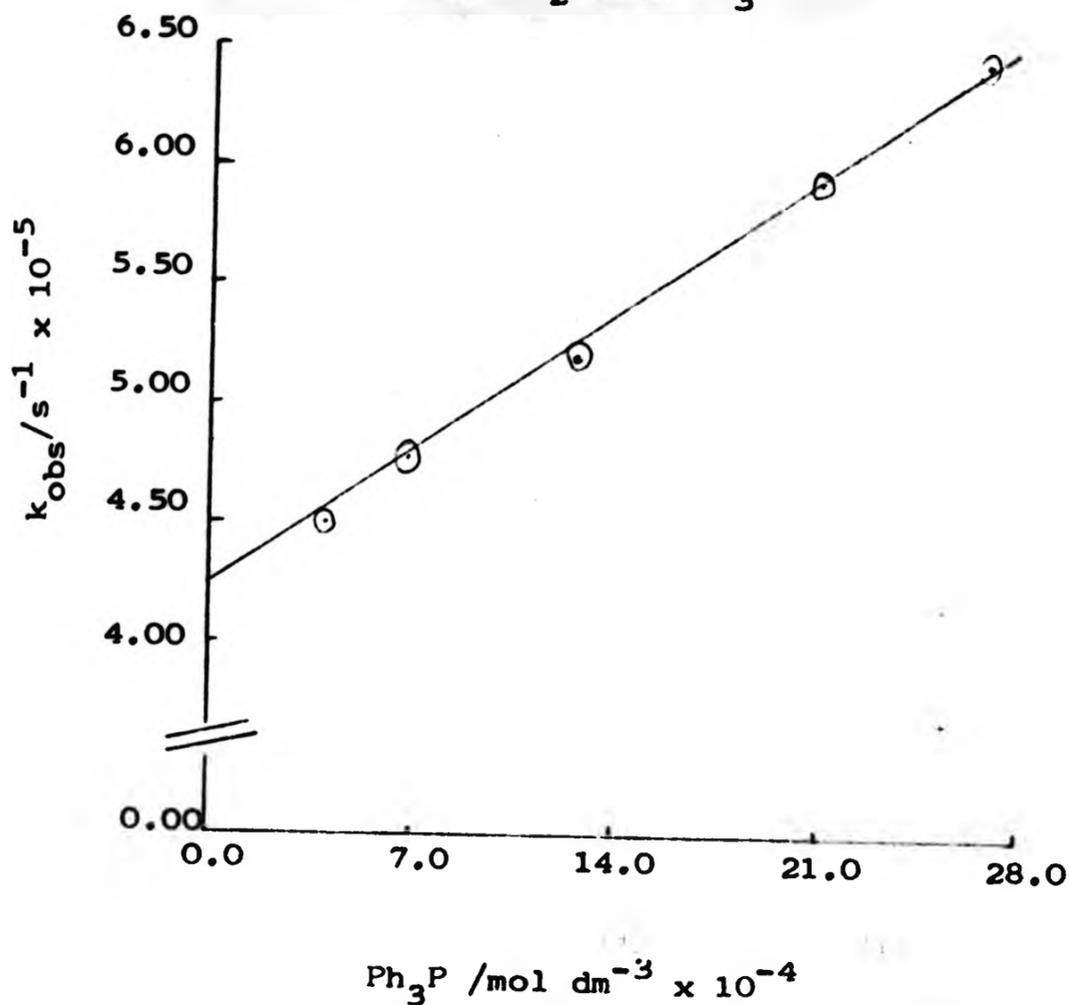


Table 2.6. Observed rate constants for the reaction between $\text{Cu}(\text{cup})_2$, $[\text{Cu}(\text{cup})_2] = 1.42 \times 10^{-4} \text{ mol dm}^{-3}$, and triphenylphosphine in pyridine.

$\text{Ph}_3\text{P} / \text{mol dm}^{-3}$	$k_{\text{obs}} / \text{s}^{-1}$
2.84×10^{-4}	4.45
7.10×10^{-4}	4.61
1.42×10^{-3}	5.19
2.13×10^{-3}	5.80
2.84×10^{-3}	6.24

Figure 2.9. A plot of k_{obs} vs $[\text{Ph}_3\text{P}]$ for the reaction of $\text{Cu}(\text{cup})_2$ with Ph_3P



graph with a positive intercept on the k_{obs} axis. The intercept (k_1) and the gradient of the plot (k_2) had values of $4.22 \times 10^{-5} \text{ s}^{-1}$ and $7.42 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The fact that the plot does not extrapolate to zero indicates that the reaction proceeds by a first order pathway and a second order pathway. The overall reaction rate is given by equation 2.1.

$$\text{rate} = k_1 [\text{complex}] + k_2 [\text{complex}] [\text{Ph}_3\text{P}]$$

Equation 2.1.

The consequence of these kinetic data are discussed further in Section 2.4e.

2.4e. Mechanistic appraisal of the reaction between triphenylphosphine and $\text{Cu}(\text{cup})_2$.

The studies described in Section 2.4d strongly suggest that the initial step of the reaction between triphenylphosphine and $\text{Cu}(\text{cup})_2$ corresponds to a Lewis base promoted internal redox reaction of the copper(II) complex (Scheme 2.1).

The kinetic study indicates that the internal redox reaction proceeds via first order pathways (Routes B and C, Scheme 2.2) and a second order pathway (Route A, Scheme 2.2).

The rate determining step for the second order route involves substitution of the pyridine in $\text{Cu}(\text{cup})_2(\text{py})$ for triphenylphosphine, to give the adduct $\text{Cu}(\text{cup})_2(\text{Ph}_3\text{P})$. This then reacts rapidly with more triphenylphosphine to give $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ and the radical cup^\cdot .

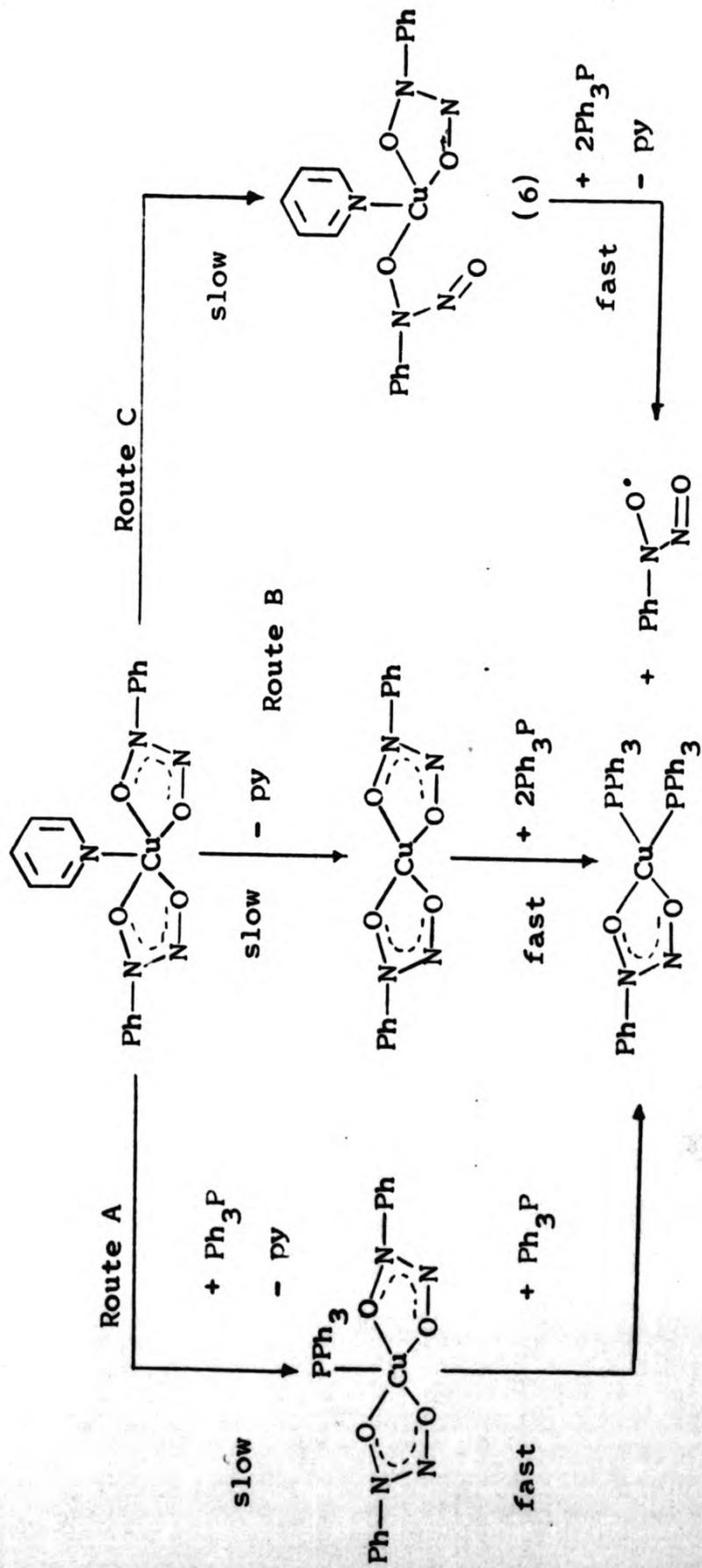
For the first order pathway there are two possible mechanisms :

(i) $\text{Cu}(\text{cup})_2(\text{py})$ dissociates to $\text{Cu}(\text{cup})_2$ and pyridine.

This is the rate determining step. The $\text{Cu}(\text{cup})_2$ then reacts very quickly with triphenylphosphine to give the copper(I) complex, $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, and cup^\cdot .

(ii) One of the cupferronato ligands in $\text{Cu}(\text{cup})_2(\text{py})$ partially dissociates to give an intermediate that contains two types of cupferronato ligand, one bonded in the usual bidentate fashion and the other coordinated in a monodentate manner. This is the rate determining step. This intermediate, 6, then reacts quickly with triphenylphosphine to

Scheme 2.2. Suggested mechanism (Route B) and possible alternatives (Routes A and C) for the triphenylphosphine promoted internal redox reaction of $\text{Cu}(\text{cup})_2$ in pyridine.



give the products. A similar intermediate to 6 is proposed in the reaction of bis(β -diketonato) copper(II) complexes with hydroxylamine (cf. Chapter 4). However, it must be noted that pyridine alone is not capable of reducing the copper(II) to copper(I). The reduction is promoted by triphenylphosphine.

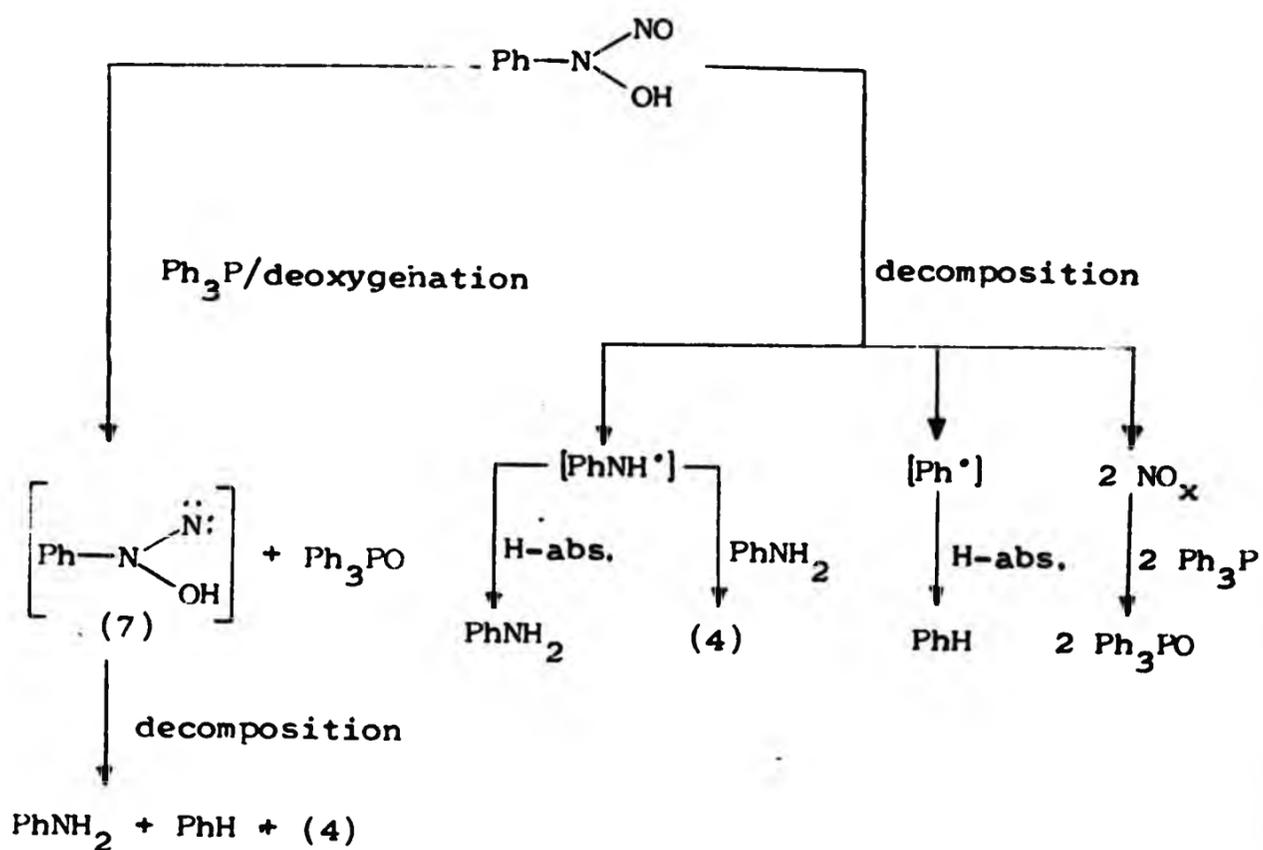
From the results of the kinetic study it is not possible to differentiate between the two first order mechanisms.

The fate of the ligand radical, cup', arising from the initial internal redox reaction and the subsequent processes (cf. Scheme 2.1) depend on the solvent used. In acetone the ligand radical abstracts hydrogen from the solvent to give the protonated ligand, which then decomposes to give benzene, aniline and compound 4. This behaviour is indicated by the formation of the same products and in almost identical relative yields from the reaction of cupH itself with triphenylphosphine in acetone.

The formation of benzene, aniline and compound 4 from cupH may occur via two routes (Scheme 2.3). The protonated ligand may undergo deoxygenation by triphenylphosphine to give triphenylphosphine oxide and a reactive species such as 7, which then decomposes to yield the other organic products. Alternatively cupH could decompose to give initially phenyl and anilino radicals as well as nitrogen oxides. The latter then react with triphenylphosphine to give triphenylphosphine oxide.

The formation of benzene, aniline and compound 4

Scheme 2.3. Possible routes for the fate of cupH produced from the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine



from the reaction of cupH with pyridine and the close similarity of the yields of these products to those obtained from the reactions of $\text{Cu}(\text{cup})_2$ with triphenylphosphine and $\text{Fe}(\text{cup})_3$ with pyridine (Section 2.5) indicates that the $\text{Cu}(\text{cup})_2$ /triphenylphosphine reaction most probably proceeds via the route involving decomposition of cupH and then deoxygenation. The tendency of cupH to decompose has been noted earlier but the products from the decomposition have not been identified.²⁰

Compound 4 has been obtained previously from the

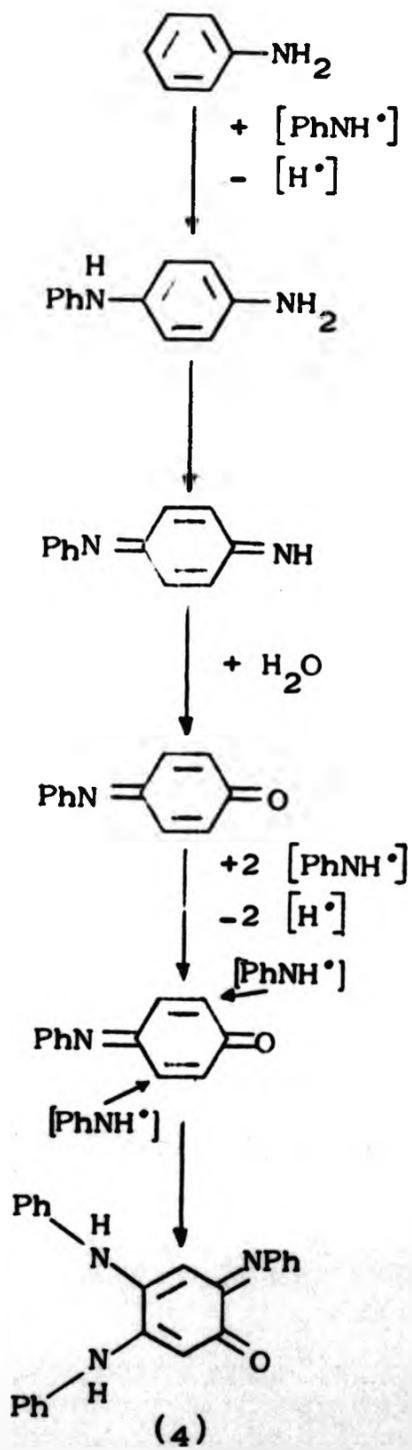
reaction of bis(quinonemonooximato)copper(II) complexes with aniline. Its formation has been rationalised as indicated in Scheme 2.4 by reactions involving the anilino radical and aniline itself.²¹ This Scheme could also account for the formation of compound 4 from the reactions involving $\text{Cu}(\text{cup})_2$, $\text{Fe}(\text{cup})_3$ or cupH with aniline.

In this study support for this mechanism has been obtained by studying the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine in a mixture of acetone and aniline (50:1). Under these conditions the yield of compound 4 increased relative to its yield in acetone alone, thus supporting the suggestion that aniline is involved in its formation.

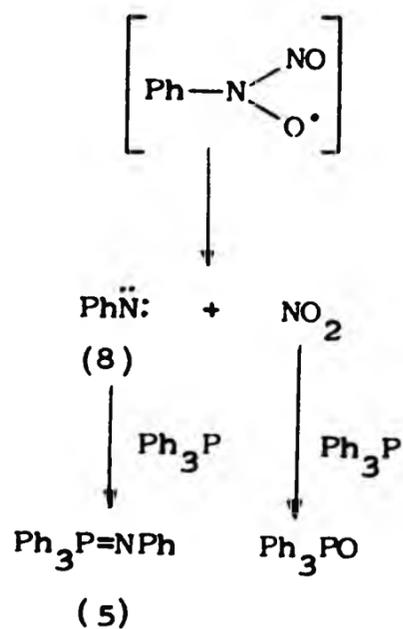
In propan-2-ol the reaction between $\text{Cu}(\text{cup})_2$ or cupH and triphenylphosphine gave aniline, benzene and triphenylphosphine oxide. In this solvent the formation of compound 4 is completely suppressed. This reflects (i) the relative amounts of propan-2-ol and aniline in the reaction mixture and (ii) the strong hydrogen atom donating properties of the propan-2-ol.

When the reaction between $\text{Cu}(\text{cup})_2$ or cupH and triphenylphosphine is carried out in trichlorotrifluoroethane the radical cup^{\bullet} cannot abstract hydrogen from the solvent. In this case the radical decomposes to give the phenylnitrene, 8, and NO_2 (Scheme 2.5). The nitrene species, 8, couples with the triphenylphosphine to yield the iminophosphorane, 5, and reaction of triphenylphosphine with NO_2 yields triphenylphosphine oxide.

Scheme 2.4. Mechanism for the formation of
 2-hydroxy-5-phenylamino-2,4-diphenylimino-
 1,4-benzoquinone, 4.



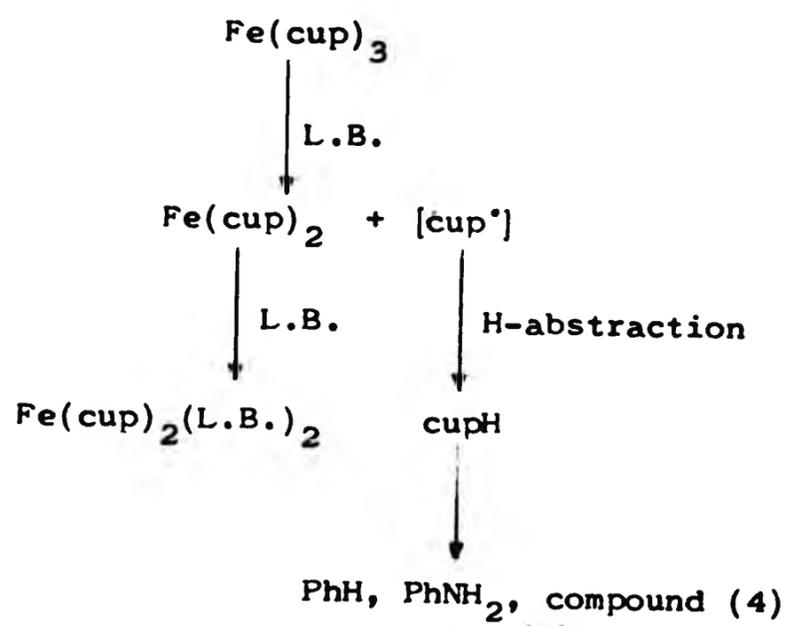
Scheme 2.5. Possible mode of decomposition of the cup[•] radical in trichlorotrifluoroethane



2.5. The reaction of Fe(cup)₃ with triphenylphosphine and pyridine.

The reaction of Fe(cup)₃ with triphenylphosphine or pyridine gave aniline, benzene and compound 4. In both cases the yields were very similar to those obtained from the reaction of Cu(cup)₂ with triphenylphosphine. This indicates that the reaction proceeds via a similar pathway. Thus the Lewis base induces an internal redox reaction of the iron(III) complex which gives the iron(II) species Fe(cup)₂(L.B.)₂ (L.B. = Ph₃P or py) and the ligand radical abstracts hydrogen from the solvent to give cupH as illustrated in Scheme 2.6. Deoxygenation of cupH by triphenylphosphine leads to the organic products.

Scheme 2.6. Mechanism for the Lewis base promoted internal redox reaction of $\text{Fe}(\text{cup})_3$



L.B. = Ph_3P or py

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CHAPTER THREE

X-ray crystallographic study of cupferronabis
(triphenylphosphine)copper(I).

3.1. Crystal preparation.

Cupferronabis(triphenylphosphine)copper(I) was precipitated as a pale yellow solid from the reaction mixture resulting from the interaction of $\text{Cu}(\text{cup})_2$ with triphenylphosphine in acetone. Recrystallisation of the solid from pyridine yielded pale yellow cubic crystals which preliminary intensity measurements indicated were suitable for study.

3.2. Determination of the structure.

The intensity measurements were made using a Philips PW 1100 four circle diffractometer using a $\Theta/2\Theta$ scan mode and employing $\text{Mo-K}\alpha$ radiation. The intensity of three reflections were measured at five hourly intervals during the data collection and these showed no significant variation. Altogether 4853 intensities were recorded, $3.0^\circ \leq \Theta \leq 25.0^\circ$. L_p operations were applied. No absorption corrections were made. Equivalent reflections were averaged to give 4642 unique observed intensities. The unit cell dimensions were derived from angular measurements of 25 strong reflections at $2.0^\circ \leq \Theta \leq 20.0^\circ$.

The dimensions were;

$$a = 10.097(4), b = 12.955(4), c = 14.740(6) \text{ \AA}.$$

$$\alpha = 88.384(3), \beta = 104.438(3), \gamma = 103.332(5)^\circ$$

The crystal showed no symmetry and was therefore determined to be triclinic. Relative molecular mass = 724.5 g mol^{-1} ,

molecular formula = $C_{42}H_{35}CuN_2O_2P_2$, $D_{2=2} = 1.326 \text{ g cm}^{-3}$

The structure was solved by using the Patterson method and refined by full-matrix least-squares calculations (Shelex 76¹) with anisotropic thermal parameters assigned to the Cu, P, N and O atoms and the ligand phenyl ring C_1-C_6 atoms. The refinement converged to $R = 0.042$ and $R_w = 0.045$, $R = \sum |F_o - F_c| / \sum |F_o|$, $R_w = \sum |F_o - F_c| w^{1/2} / \sum |F_o| w^{1/2}$, $w = 1/\sigma^2(F_o)$.

The final coordinates, temperature factors, bond lengths, bond angles inter- and inter-molecular distances are given in Tables 1-7 of Appendix 1.

3.3. Results and discussion.

A perspective view of the molecule together with the atomic numbering is given in Figure 3.1. Some bond lengths and bond angles are shown in Figures 3.2 and 3.3 respectively.

The complex has a distorted tetrahedral geometry about the copper atom. The O-Cu-O bond angle is 75.1° , which is considerably less than the idealised tetrahedral angle of 109.5° . This small angle is comparable with the O-M-O bond angle determined in the $Fe(cup)_3$ and $Cu(cup)_2$ complexes^{2,3} (Figures 3.4 and 3.5).

The Cu-O₁ bond length is 2.102 Å and the Cu-O₂ bond length is 2.078 Å. Comparable bonds in $Cu(cup)_2$ are 1.87 Å and 1.90 Å long, respectively. These are shorter by approximately 0.2 Å. However, the bond lengths between the other atoms in the chelate ring are comparable in the two complexes.

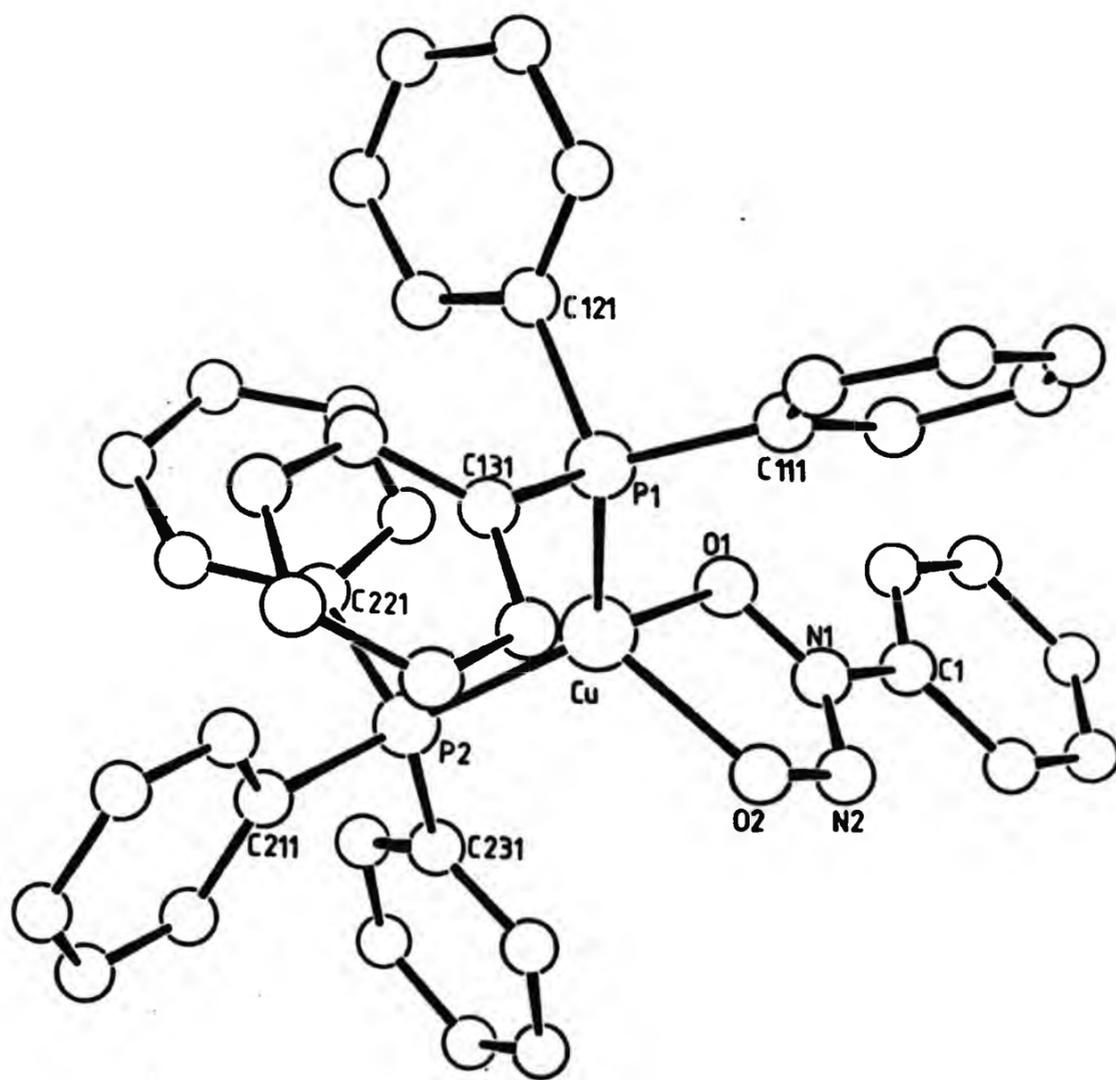


Figure 3.1. A view of cupferronatobis(triphenylphosphine)copper(I)

Figure 3.2. Some bond lengths (Å) in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

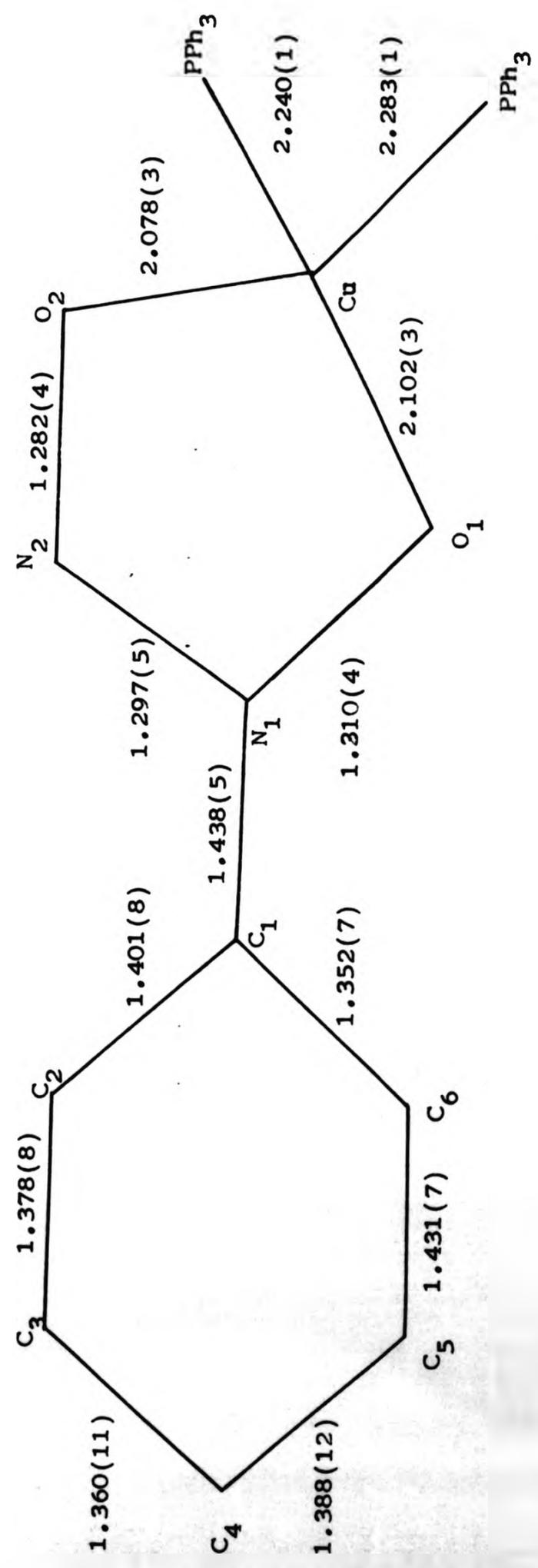


Figure 3.1. Some bond angles ($^{\circ}$) in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

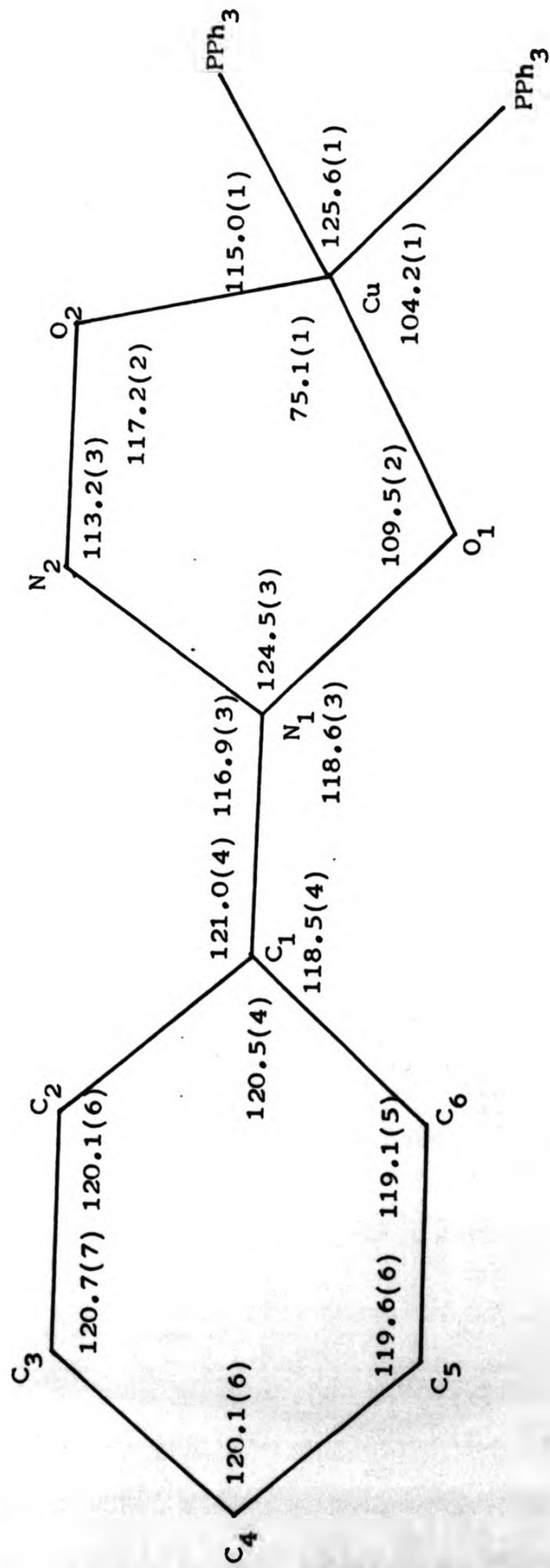
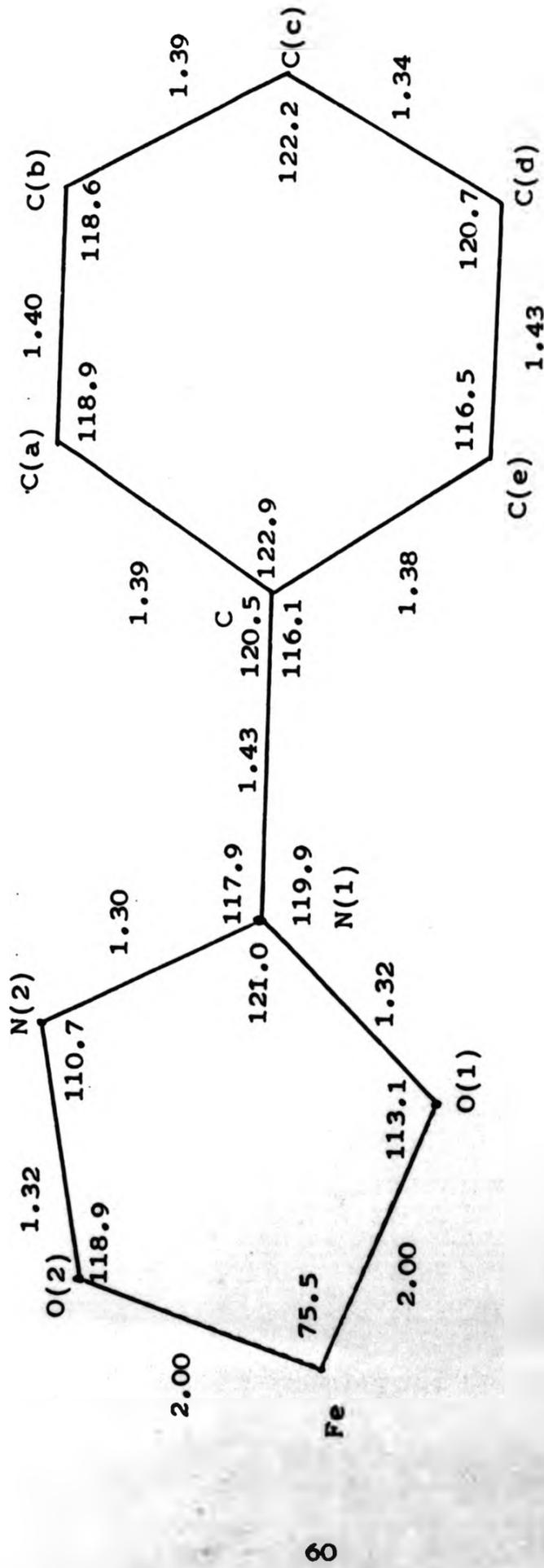
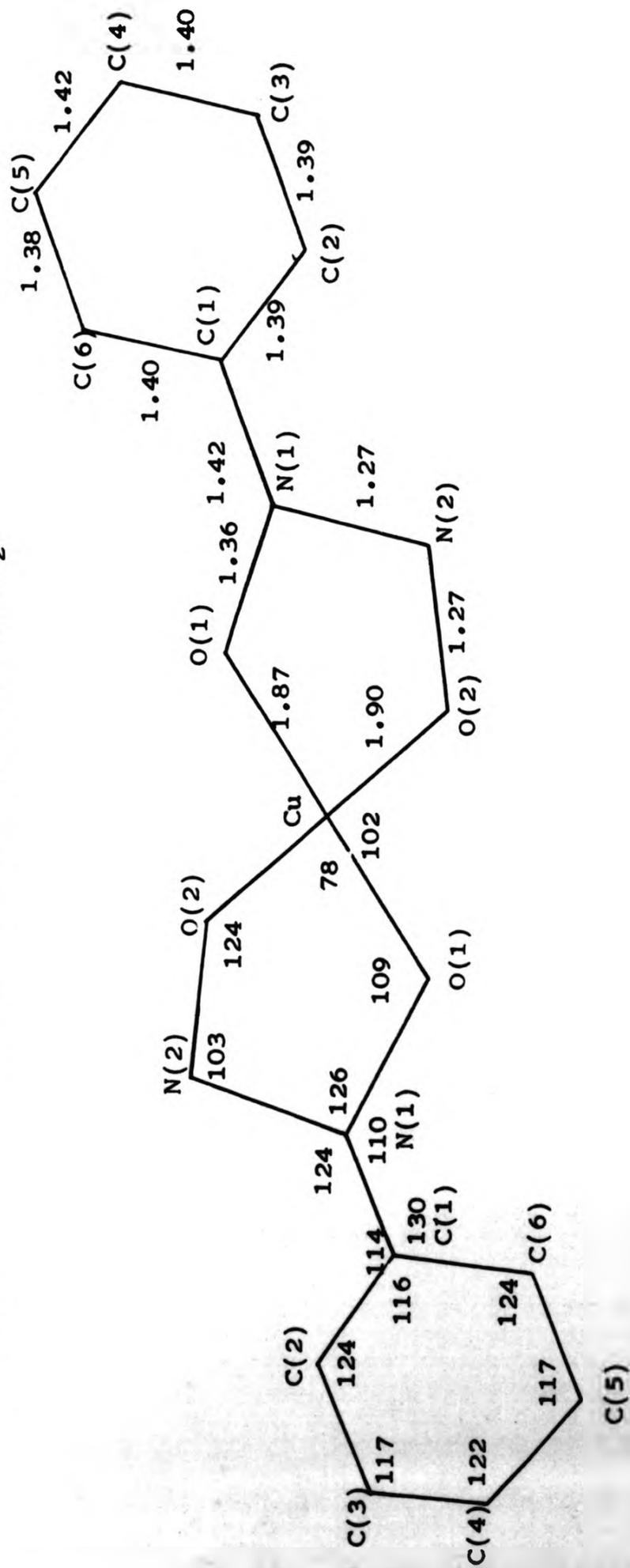


Figure 3.4. Bond lengths (Å) and angles (°) in $\text{Fe}(\text{cup})_3^2$



Bond lengths (Å) and angles (°) are average values for three crystallographically independent cupferron groups.

Figure 3.5. Bond lengths (Å) and angles (°) in $\text{Cu}(\text{cup})_2^3$



The P_1 -Cu- P_2 bond angle is 125.6° ; this is much greater than the idealised angle of 109.5° . The Cu- P_1 and Cu- P_2 bond lengths are 2.240 and 2.283 Å, respectively. These figures are comparable with those of previously studied copper(I) complexes (cf. Table 3.1).

The differences and similarities described here indicate that the cupferronate ligand is more weakly bound to the copper atom in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ than in $\text{Cu}(\text{cup})_2$, but the structure of the ligands in these complexes, and in $\text{Fe}(\text{cup})_3$, is similar.

The Cu-O bonds in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ are longer, i.e. weaker, than in $\text{Cu}(\text{cup})_2$ because of the lower oxidation state of the metal in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$. The ligands in $\text{Cu}(\text{cup})_2$ are attracted more strongly to the copper atom than the cupferronate ligand in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$.

The O_1 -Cu- O_2 bond angle is less than the idealised tetrahedral bond angle due to the constraint arising from the 5-membered ring structure of the chelate ligand.

The large P-Cu-P bond angles of the complexes listed in Table 3.1 have been attributed as being mainly due to steric factors involving the bulky triphenylphosphine groups.⁴ The view has been put forward that the largest P-Cu-P angles occur when the chelating ligand is planar (e.g. NO_3^-) but non-planar or bulky ligands constrain the angle to smaller dimensions due to Ph_3P -ligand interactions.⁴ In keeping with this the P-Cu-P bond angle of 125.6° , found for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$, is greater than the corresponding bond

Table 3.1. Molecular dimensions of $\text{CuY}(\text{Ph}_3\text{P})_2$ complexes.

Compound	Cu-P (Å)	P-Cu-P (°)	Reference
$\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$	2.240(1), 2.283(1)	125.6(0)	present work
$\text{Cu}(\text{1-nqo})(\text{Ph}_3\text{P})_2^{\text{a}}$	2.230(3), 2.241(4)	124.5(1)	5
$\text{Cu}(\text{O}_2\text{CCH}_3)(\text{Ph}_3\text{P})_2$	2.233(2), 2.240(3)	133.4(1)	6
$\text{Cu}(\text{hfa})(\text{Ph}_3\text{P})_2^{\text{b}}$	2.236(2), 2.239(2)	127.1(6)	7
$\text{Cu}(\text{NO}_3)(\text{Ph}_3\text{P})_2$	2.256(3)	131.2(1)	8
$\text{Cu}(\text{S}_2\text{CSPH})(\text{Ph}_3\text{P})_2$	2.255(2), 2.258(2)	128.5(8)	9
$\text{Cu}(\text{S}_2\text{CSEt}_2)(\text{Ph}_3\text{P})_2$	2.247(2), 2.266(2)	125.7(1)	10
$\text{Cu}(\text{B}_5\text{H}_8)(\text{Ph}_3\text{P})_2$	2.266(3), 2.284(3)	123.4(1)	11
$\text{Cu}(\text{B}_3\text{H}_8)(\text{Ph}_3\text{P})_2$	2.274(2), 2.288(2)	199.9(7)	12

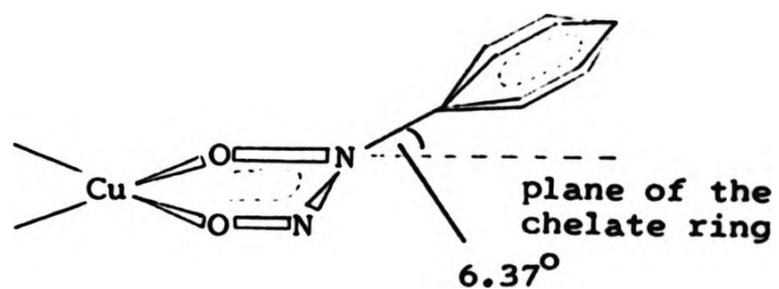
^a1-nqoH = 1,2-naphthoquinone-2-monooxime

^bhfaH = hexafluoroacetylacetone

angles in complexes containing bulky, non-planar borane ligands.

The X-ray structure determination of $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$ shows that the phenyl group has a maximum deviation of 6.37° from the plane of the chelate ring (Figure 3.6).

Figure 3.6. Representation of angular deviation of the phenyl group from the chelate ring in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$.



The bond lengths between atoms in the chelate ring indicate intermediate bond order when compared to ideal single and double bonds between corresponding atoms. The literature values of bond lengths are given in Table 3.2.

Table 3.2. Literature values of bond lengths.

Bond	Length (Å)	Compound	Method used. S=spectroscopy C=crystallography	Ref.
C-N	1.472	NMe_3	S	13
C=N	1.253	$\text{MeC}(\text{NOH})\text{Et}$	S	13
N-N	1.418	$\text{N}_2\text{H}_6\text{SO}_4$	C	14
N-O	1.414	$\text{HONCH}_2\text{NH}_2$	C	15
N=N	1.240	N_2F_2	S	15
N=O	1.212	HNO	S	15

The amount of double bond character between atoms in the chelate ring can be calculated by Pauling's method (Equation 3.1).¹⁶

$$r = r_1 - \frac{(r_1 - r_2) 3b}{(2b + 1)}$$

b = double bond character

r = actual bond length

r₁ = single bond length

r₂ = double bond length

Equation 3.1.

The actual values for the bond lengths are obtained from measurements of compounds that contain as close as possible the relevant bond. For example the literature value of the N=O bond length is obtained from HNO. In this compound the N=O bond is as close to pure double bond as possible, there is no chance of an intermediate bond order. All of the literature bond lengths were obtained from compounds in which the bond order is as close to the theoretical bond order as possible.

If b = 1, then the bond is pure double bond, if b = 0, then the bond is pure single bond. Solving for b for the atoms in the chelate ring gives;

$$C_1-N_1, b = 0.02; N_1-N_2, b = 0.41;$$

$$N_2-O_2, b = 0.37; N_1-O_1, b = 0.26.$$

So all the bonds in the ring have some double bond character, i.e. there is delocalisation around

the chelate ring. This is expected for this type of chelating ligand and agrees well with results for other cupferron complexes.^{2,3,17}

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and Ions', 1956.

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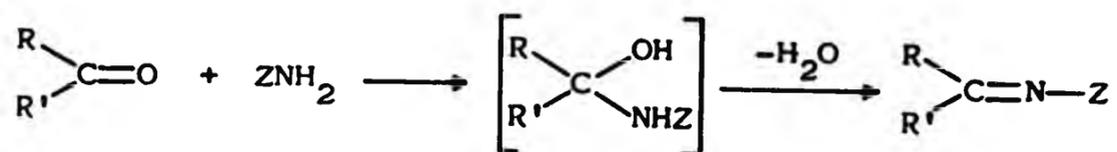
17. W. Mark, Acta Chem.Scand., 1970, 24, 1398.

CHAPTER FOUR

Reaction of hydroxylamine with bis(β -diketonato)metal(II) complexes.

4.1. Introduction.

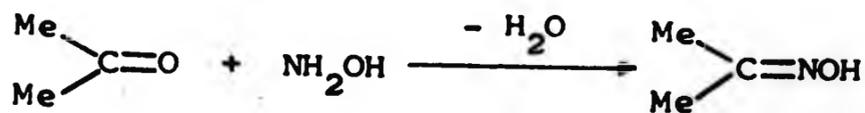
The reactions of aldehydes and ketones with primary amines, hydroxylamine and hydrazines are of considerable importance in organic chemistry because of their analytical and synthetic value. In general such reactions can be represented as indicated in Reaction 4.1.¹



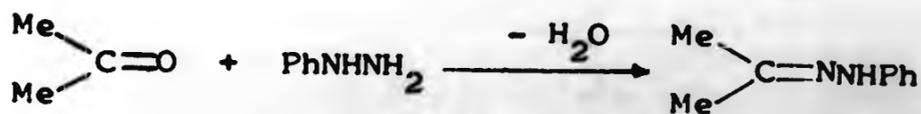
Z = e.g. NH₂, alkyl or aryl; R = alkyl; R' = alkyl or H

Reaction 4.1.

The reactions of hydroxylamine and hydrazines afford oximes and hydrazones, respectively (e.g. Reactions 4.2 and 4.3).² These products are stable and often crystalline

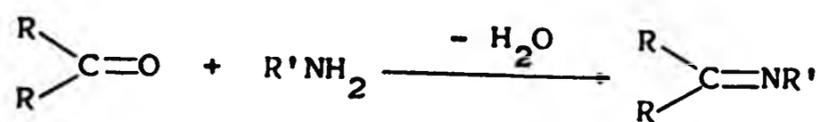


Reaction 4.2.



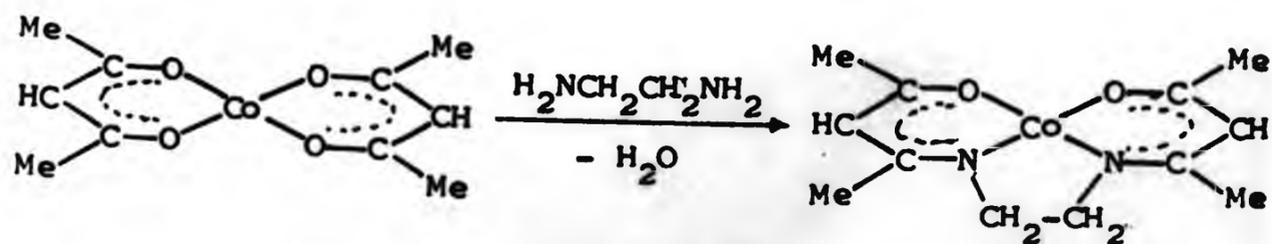
Reaction 4.3.

solids. In contrast the products arising from the reactions of amines are generally stable only if there is at least one aryl group on the nitrogen or carbonyl carbon atom (R or R' = aryl in Reaction 4.4).³

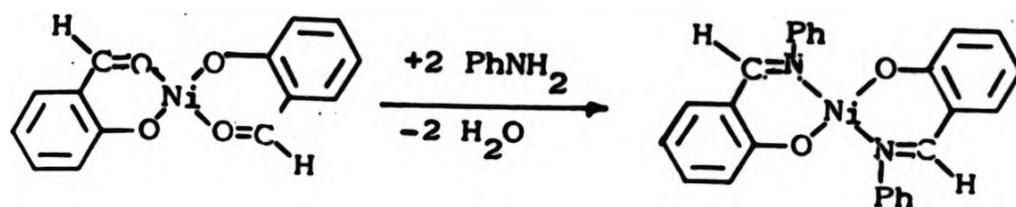


Reaction 4.4.

The condensation of amines with certain carbonyl systems such as salicylaldehyde is also readily accomplished when a metal chelate of the carbonyl compound is employed.⁴ In some cases the products are stabilised by chelation (e.g. Reactions 4.5⁵ and 4.6⁴). Such condensations are often referred to as Schiff base condensations. The reactions of bis(salicylaldehydato) metal(II) complexes with amines and the reaction of salicylaldehyde with amines in the presence of metal salts have been the subjects of extensive studies.^{4,6-9}



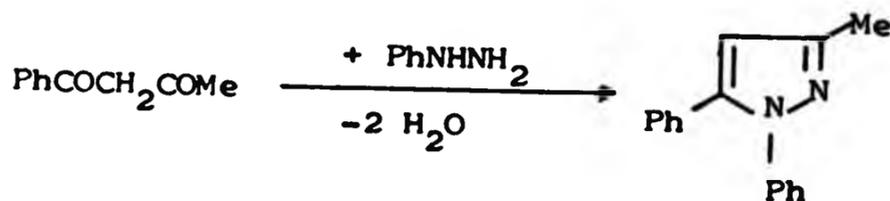
Reaction 4.5.



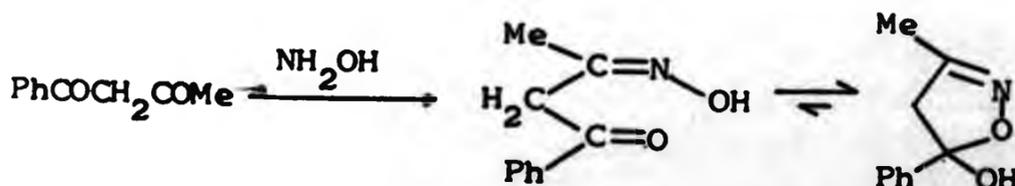
Reaction 4.6.

However, apart from studies carried out in these laboratories,¹⁰⁻¹³ no attention has been given to the condensations of bis(β -diketonato)metal(II) and bis(salicylaldehydato)metal(II) complexes with hydroxylamine.

The behaviour of uncomplexed β -diketones and related species towards compounds of the type ZNH_2 ($\text{Z} = \text{NH}_2$, PhNH and Ph) has received considerable attention (Table 4.1). Such reactions have been extensively utilised for the synthesis of a variety of heterocyclic compounds (e.g. Reactions 4.7 and 4.8).¹⁴



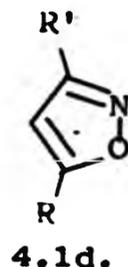
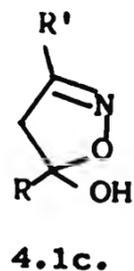
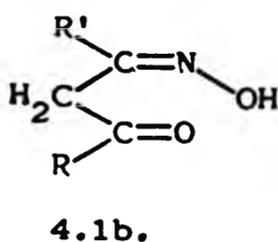
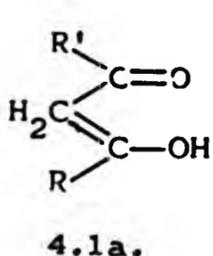
Reaction 4.7.



Reaction 4.8.

4.2. Summary of previous work on the reaction of hydroxylamine with β -diketonato metal complexes.

The work carried out previously in these laboratories has been concerned with the reactions of hydroxylamine with β -diketonato complexes of nickel(II), zinc(II), copper(II) and iron(III). Bennett¹⁰ found that in the bis(β -diketonato)metal(II)-hydroxylamine system (M= Ni, Cu or Zn) the products formed were dependant on the metal, the groups R and R' on the β -diketonato ligand and the reaction conditions.



It was noted that the reaction of bis(acetylacetonato) copper(II) (1 mol) with hydroxylamine (2.5 mol) in methanol gave the monooximate complex $\text{Cu}(\text{acacM})_2$ (acacMH = 2,4-pentanedionemonooxime, 4.1b; R = R' = Me), whilst the bis(acetylacetonato)nickel(II) and bis(acetylacetonato)zinc(II) complexes gave the hydroxylamine adducts, $\text{Ni}(\text{acac})_2(\text{NH}_2\text{OH})_2$ and $\text{Zn}(\text{acac})_2(\text{NH}_2\text{OH})$, respectively. The behaviour of the bis(benzoylacetonato) copper(II) complex was more complex and interesting than that of its acetylacetonato analogue. This complex on treatment with hydroxylamine gave the hydroxy(monooximate)copper(II) complex $[\text{Cu}(\text{bzacM})\text{OH}]$ (bzacMH = 1-phenyl-1,3-butanedione-3-monooxime, 4.1b; R' = Me, R = Ph) and 1-phenyl-1,3-butanedione-1-monooxime

(bzMacH, 4.1b; R' = Ph, R = Me)(Scheme 4.1).

Significantly the latter reaction affords a monooxime complex and a free monooxime in which the condensation had occurred at different carbonyl groups of the β -diketone. Other bis(β -diketonato)metal(II) complexes have also been examined under similar conditions and the results are summarised in Table 4.2.

Table 4.2. Products from the reaction of hydroxylamine (2.5 mol) with bis(β -diketonato)metal(II) (1 mol) in methanol under nitrogen.¹⁰

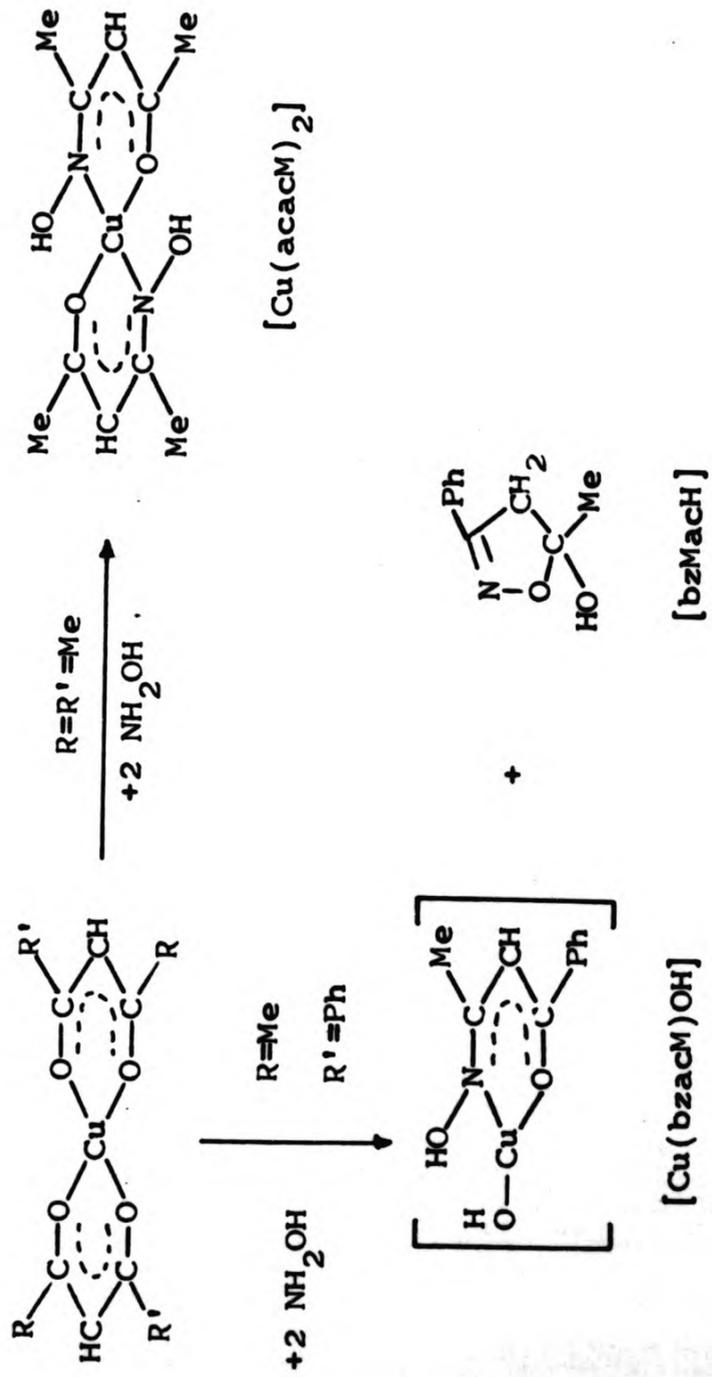
<u>metal</u> <u>diketone</u>	Copper(II)	Nickel(II)	Zinc(II)
acacH	Cu(acacM) ₂	Ni(acac) ₂ (NH ₂ OH) ₂	Zn(acac) ₂ (NH ₂ OH)
bzach	Cu(bzacM)OH + bzMacH	Ni(bzac) ₂ (NH ₂ OH) ₂	Zn(bzac) ₂ (NH ₂ OH) + Zn(bzac) ₂ ^a
bzbzH	No reaction	Ni(bzbz) ₂ (NH ₂ OH) ₂ + Ni(bzbz) ₂ ^a	No reaction
deach	Cu(I) oxide + deacMH	b	b
dpach	Cu(I) oxide + dpacMH	b	b
bdach	Cu(I) oxide + dbacMH	b	b

^aunreacted

^bnot studied

Scheme 4.1.

Reaction of bis(β -diketonato)copper(II) with hydroxylamine in methanol.¹⁰



The previous studies indicated that the products arising from the reaction of a given bis(β -diketonato) metal(II) complex with hydroxylamine were dependant on the solvent, atmosphere and the mole ratio of reactants (Tables 4.3 and 4.4). It was also observed that in the complexes $\text{Cu}(\beta\text{-diketonato})_2$ (β -diketone = 3,5-heptanedione; deach, 4.1a; $R = R' = \text{Et}$, 2,6-dimethyl-3,5-heptanedione; dpach, 4.1a; $R = R' = i\text{Pr}$ and 2,2',6,6'-tetramethyl-3,5-heptanedione; dbach, 4.1a; $R=R'=t\text{Bu}$) reduction of the copper occurred accompanied by the formation of the respective β -ketooxime (Reaction 4.9).

Table 4.3. The effect of solvent, atmosphere and mole ratios of reactants on the reaction between $\text{Cu}(\text{acac})_2$ (1 mol) and NH_2OH (2.5 - 10 mol).¹⁰

NH_2OH (mol)	Solvent	Atmosphere	Products (mol) ^a	
			$\text{Cu}(\text{acac})_2$ recovery	$\text{Cu}(\text{acacM})_2$ yield
10	EtOH	air	0	0.07
5	EtOH	air	0	0.57
5	EtOH	N_2	0	0.60
3	EtOH	air	0.52	0
5	MeOH	air	0	0
3	MeOH	N_2	0	0.59
2.5	MeOH	air	0	0.69

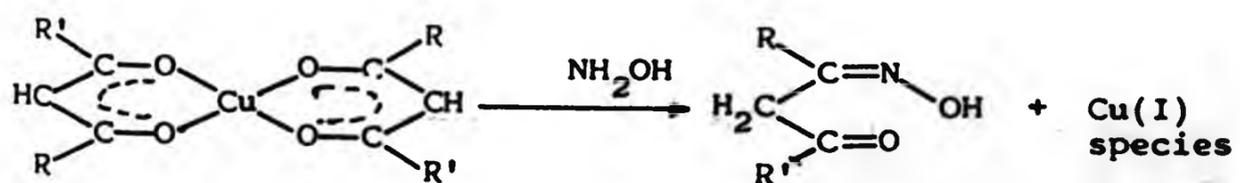
^aill-defined products not included

Table 4.4. The effect of solvent, atmosphere and mole ratios of reactants on the reaction between $\text{Cu}(\text{bzac})_2$ (1 mol) and NH_2OH (2.5 - 8 mol).¹⁰

NH_2OH (mol)	Solvent	Atmosphere	Products (mol) ^a		
			$\text{Cu}(\text{bzac})_2$ recovery	$[\text{Cu}(\text{bzacM})\text{OH}]$ yield	bzMacH yield
8	EtOH	air	0	0.88	0.83
6	EtOH	air	0	0.48	b
6	EtOH	N_2	0	0.51	0.50
2.5	EtOH	air	b	b	0.20
6	MeOH	air	0	0.71	0.70
2.5	MeOH	air	0	0.82	0.75
2.5	MeOH	N_2	0	0.84	0.73

^a ill-defined products not included

^b Mixture of $[\text{Cu}(\text{bzacM})\text{OH}]$ with $\text{Cu}(\text{bzac})_2$



$\text{R} = \text{R}' = \text{Et}, \text{}^i\text{Pr} \text{ or } \text{}^t\text{Bu}$

Reaction 4.9.

The observations noted above suggest that the reaction between the bis(β -diketonato)copper(II) complexes and hydroxylamine may involve internal redox behaviour. As discussed in Chapter 1 such behaviour involves the loss of one of the ligands as a radical from the complex undergoing the reaction and reduction of the metal. In all cases examined loss of one of the ligands from bis(β -diketonato)copper(II) complexes is apparent, except for the bis(acetylacetonato)copper(II)-hydroxylamine system. Furthermore, when loss of the ligand is observed, this is also accompanied by the formation of a copper(I) species. The isolation of a copper(II) product from the bis(benzoylacetonato)copper(II)-hydroxylamine system is not, at first sight, in accord with the suggested internal redox behaviour. However, in view of the facile oxidation of copper(I) compounds the formation of $[\text{Cu}(\text{bzacM})\text{OH}]$ is most probably a consequence of reoxidation of an initially formed copper(I) species. In previous studies of bis(β -diketonato)copper(II)-hydroxylamine systems the occurrence of some form of redox behaviour was noted but neither explained nor mechanistically rationalised.

In all earlier studies of bis(β -diketonato)metal(II)-hydroxylamine systems problems were encountered regarding the reproducibility of the reaction. It was found that the yields and often the nature of the products were not satisfactorily reproducible.¹⁰⁻¹³ Attempts were made to account for the non-reproducibility of these reactions and to improve the yields. In particular the effect of solvent, atmosphere and mole ratios of reactants were studied without success.^{10,11}

4.3. Aims of the present investigation.

From the previous work it can be concluded
a) that the system bis(β -diketonato)copper(II)-hydroxylamine possibly exhibits an interesting redox behaviour of considerable synthetic value, and b) that the factors affecting the reproducibility of the experimental aspects associated with such systems are rather unclear.

This being the case the present study was undertaken with the following aims:

- (i) To investigate the reproducibility of the reaction between bis(β -diketonato)metal(II) complexes and hydroxylamine.
- (ii) To extend the studies to β -diketonato systems which have previously received no attention e.g. bis(trifluoroacetylacetonato)copper(II).
- (iii) To attempt the preparation of bis(monooximato)nickel(II) and bis(monooximato)zinc(II) complexes.
- (iv) To investigate the suspected internal redox behaviour of the bis(β -diketonato)copper(II) complexes.

4.4. Reexamination of the reaction of hydroxylamine with $M(\text{acac})_2$ and $M(\text{bzac})_2$ ($M = \text{Ni, Cu and Zn}$).

In this study the initial attempts to investigate the reaction of bis(β -diketonato)metal(II) with hydroxylamine involved the preparation of a methanolic solution of hydroxylamine from hydroxylamine hydrochloride and sodium methoxide in methanol at 0 °C. The hydroxylamine solution was then mixed and stirred with a suspension of bis(β -diketonato)metal(II) at

room temperature. Under these conditions the yields of the adducts or the monooximate complexes were generally poor and their formation was accompanied by the evolution of ammonia (Table 4.5). It was further observed, qualitatively, that the more pronounced the evolution of ammonia the lower the yield of the metal containing product.

The formation of ammonia suggested that the synthetic problems may relate to the decomposition of hydroxylamine. Hydroxylamine is known to be decomposed by a variety of catalysts^{20,21} and it also undergoes autooxidation.²² Furthermore, hydroxylamine decomposes rapidly at room temperature.²³

As a consequence it was thought that by keeping the temperature at 0 °C during the preparation of the hydroxylamine solution and during the subsequent reaction with the suspension of the bis(β -diketonato)metal(II) complex the yields of the desired products would improve and the reproducibility problem might be eliminated or at least suppressed. Significantly this was found to be the case. In all the reactions carried out at 0 °C the evolution of ammonia was insignificant and the yields of the desired products high.

4.5. Extension of the study to other hydroxylamine-bis(β -diketonato)metal(II) systems.

Using the synthetic route developed for the preparation of $\text{Cu}(\text{acacM})_2$, $[\text{Cu}(\text{bzacM})\text{OH}]$, $\text{Ni}(\text{acac})_2(\text{NH}_2\text{OH})_2$, $\text{Ni}(\text{bzac})_2(\text{NH}_2\text{OH})_2$, $\text{Zn}(\text{acac})_2(\text{NH}_2\text{OH})$ and $\text{Zn}(\text{bzac})_2(\text{NH}_2\text{OH})$ the study of the reaction of hydroxylamine with

Table 4.5. Reaction of NH_2OH (2.5 mol) with ML_2
(LH= acacH, bzacH; M= Ni, Cu, Zn)
(1.0 mol) in methanol at 0 and 25 °C.

ML_2	Product ^a	Reaction temperature/ °C	
		25	0
		Yield (%)	Yield (%)
$\text{Cu}(\text{acac})_2$	$\text{Cu}(\text{acacM})_2$	40	75
$\text{Cu}(\text{bzac})_2$	$[\text{Cu}(\text{bzacM})\text{OH}]$ + bzMacH	38 ^b	84 ^b
$\text{Ni}(\text{acac})_2$	$\text{Ni}(\text{acac})_2(\text{NH}_2\text{OH})_2$	41	90
$\text{Ni}(\text{bzac})_2$	$\text{Ni}(\text{bzac})_2(\text{NH}_2\text{OH})_2$	40	89
$\text{Zn}(\text{acac})_2$	$\text{Zn}(\text{acac})_2(\text{NH}_2\text{OH})$	20	70
$\text{Zn}(\text{bzac})_2$	$\text{Zn}(\text{bzac})_2(\text{NH}_2\text{OH})$	c	69

^a ML_2 was recovered from all reactions

^bYield of metal containing product

^cNo reaction

bis(β -diketonato)metal(II) complexes was extended to other systems. Thus the reactions of hydroxylamine with the complexes ML_2 ($M = Ni$, $LH = tfacH$; $M = Cu$, $LH = tfacH$ or $eaahH$; $M = Co$, $LH = eaahH$) at $0^\circ C$ were examined. The results of these studies are summarised in Table 4.6.

Table 4.6. Reaction of NH_2OH (2.5 mol) with ML_2 ($LH = acach, tfacH, eaahH$) (1 mol) in methanol at $0^\circ C$.

ML_2	Product	Yield (%)
$Ni(tfac)_2$	$Ni(tfac)_2(NH_2OH)_2$	85
$Ni(eaa)_2$	a	
$Cu(tfac)_2$	$Cu(tfacM)OH$ + $tfMach^b$	78
$Cu(eaa)_2$	a	
$Co(eaa)_2$	a	

^aill-defined products

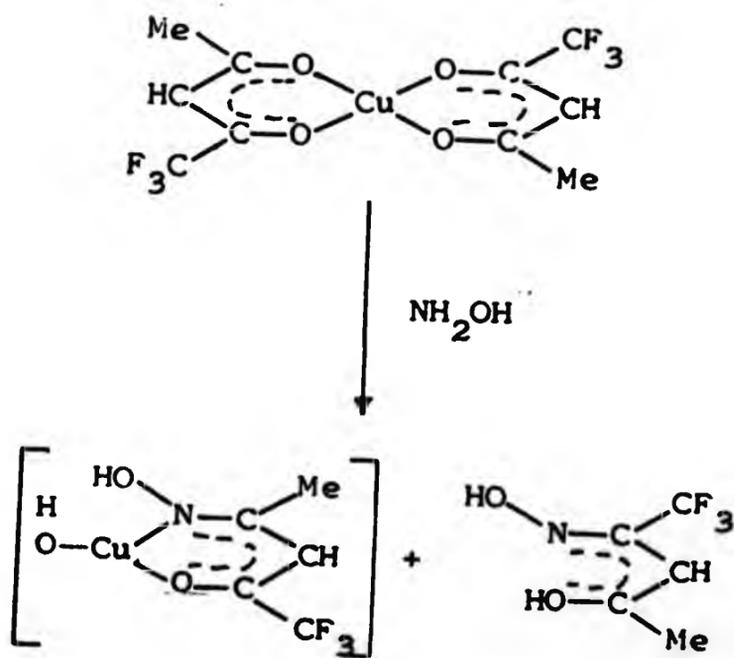
^b1-trifluoromethyl-1,3-butanedione-1-monooxime

The $Ni(tfac)_2$ complex behaved in the same way towards hydroxylamine as $Ni(acac)_2$ and $Ni(bzac)_2$, i.e. the adduct $Ni(tfac)_2(NH_2OH)_2$ was formed. The formulation of the adduct is based on elemental analysis and infrared spectroscopy. The infrared spectrum of the adduct has bands in the region $3500-3000\text{ cm}^{-1}$ assignable to the $\nu(NH)$ and $\nu(OH)$ of the

coordinated hydroxylamine. Furthermore, the adduct gives $\text{Ni}(\text{tfac})_2(\text{py})_2$ on treatment with pyridine.

As noted earlier reaction of hydroxylamine with $\text{Zn}(\text{bzac})_2$ and $\text{Zn}(\text{acac})_2$ at 0°C gave the monohydroxylamine adducts $\text{Zn}(\text{bzac})_2(\text{NH}_2\text{OH})$ and $\text{Zn}(\text{acac})_2(\text{NH}_2\text{OH})$ respectively. These were characterised by elemental analysis and i.r. spectroscopy. Further evidence for the formation of the adducts are again provided by their behaviour towards pyridine which leads to the formation of $\text{Zn}(\text{bzac})_2(\text{py})$ and $\text{Zn}(\text{acac})_2(\text{py})$.

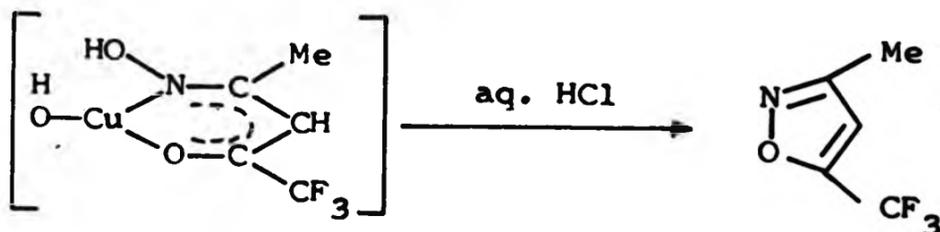
The reaction of $\text{Cu}(\text{tfac})_2$ with hydroxylamine gave 1-trifluoromethyl-1,3-butanedione-3-monooxime, (tfMach) and hydroxy(1-trifluoromethyl-1,3-butanedione-3-monooximato)copper(II), $[\text{Cu}(\text{tfacM})\text{OH}]$ (Reaction 4.10).



Reaction 4.10.

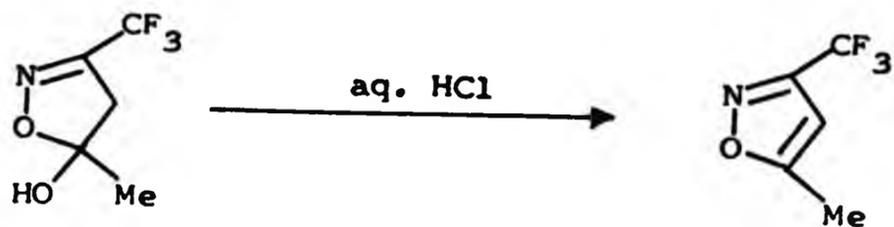
In this reaction a mixture of monooxime moieties is obtained in which the complexed monooxime and the free monooxime have been formed from condensations at the carbonyl group adjacent to the methyl and the trifluoromethyl groups respectively. This behaviour is analogous to that of the bis(benzoylacetonato) copper(II)-hydroxylamine system.

The formulation of $[\text{Cu}(\text{tfacM})\text{OH}]$ is based on elemental analysis and infrared spectroscopy. Further support is provided by the decomposition with dilute hydrochloric acid and the isolation of 1 mole of 3-methyl-5-trifluoromethylisoxazole per mol of complex (Reaction 4.11).



Reaction 4.11.

The compound 1-trifluoromethyl-1,3-butanedione-3-monooxime was characterised by elemental analysis, mass spectrometry, infrared and n.m.r. spectroscopy (the structure and properties of this compound are discussed in Section 4.12). Its formulation was confirmed by decomposition with dilute hydrochloric acid and the isolation of 1 mol of 3-trifluoromethyl-5-methylisoxazole per mol of the starting material (Reaction 4.12).

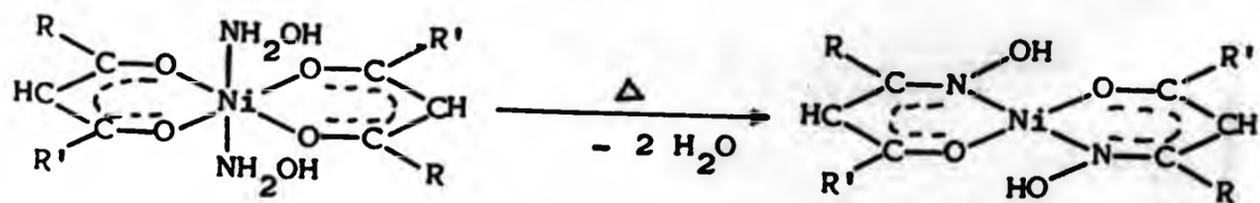


Reaction 4.12.

The complexes $\text{Cu}(\text{eaa})_2$ and $\text{Ni}(\text{eaa})_2$ reacted readily with hydroxylamine and afforded intractable solids. Elemental analysis indicated the presence of nitrogen in these products but the results did not correspond to any reasonable formulation. Furthermore, their infrared spectra exhibited very broad unresolved bands.

4.6. Effect of heating $\text{M}(\beta\text{-diket})_2(\text{NH}_2\text{OH})_n$ in toluene at 115°C ($\beta\text{-diketH} = \text{acacH}$ or bzacH ; $\text{M} = \text{Ni}$, $n = 2$; $\text{M} = \text{Zn}$, $n = 1$, $\beta\text{-diketH} = \text{tfacH}$, $\text{M} = \text{Ni}$, $n = 2$). Formation of bis(monooximato)nickel(II) complexes.

When toluene suspensions of the bis(β -diketonato)nickel(II)-hydroxylamine adducts were heated under conditions allowing the azeotropic removal of water (Dean-Stark apparatus) the bis(monooximato) chelates resulted (Reaction 4.13). In contrast the zinc adducts



$\text{R} = \text{Me}$, $\text{R}' = \text{Me}, \text{Ph}, \text{CF}_3$

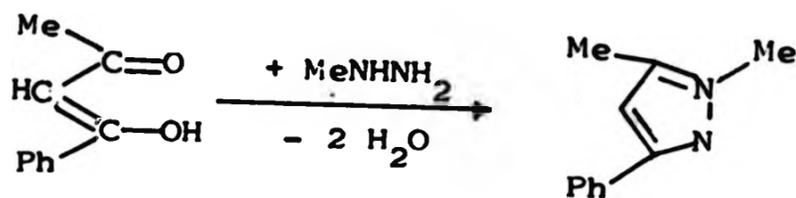
Reaction 4.13.

underwent dissociation to give, in high yields, the β -diketonato complexes which were characterised by elemental analysis, infrared spectroscopy and conversion to the respective pyridine adducts (Table 4.7).

Table 4.7. The effect of heating bis(β -diketonato) metal(II)- NH_2OH adducts in toluene at 115°C .

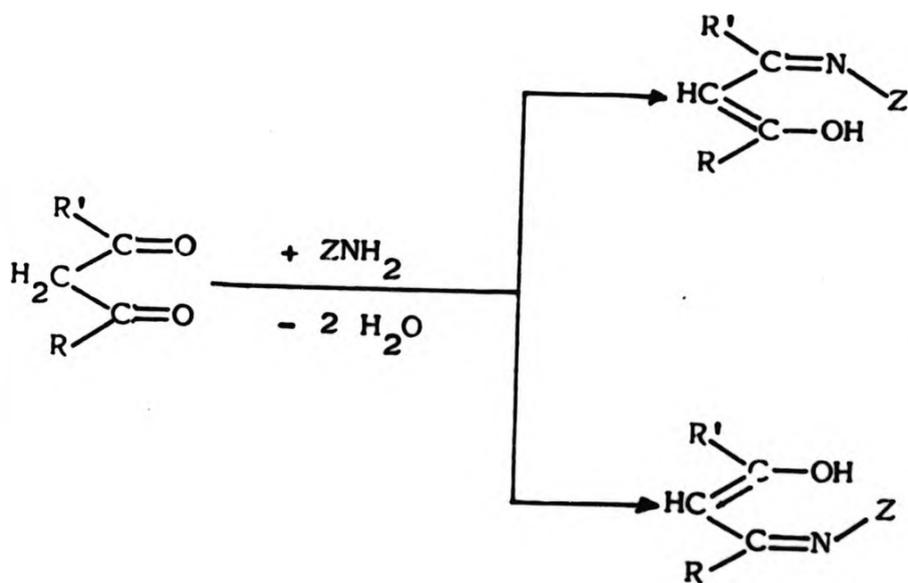
Adduct	Product	Yield (%)
$\text{Ni}(\text{acac})_2(\text{NH}_2\text{OH})_2$	$\text{Ni}(\text{acacM})_2$	95
$\text{Ni}(\text{bzac})_2(\text{NH}_2\text{OH})_2$	$\text{Ni}(\text{bzacM})_2$	97
$\text{Ni}(\text{tfac})_2(\text{NH}_2\text{OH})_2$	$\text{Ni}(\text{tfacM})_2$	95
$\text{Zn}(\text{acac})_2(\text{NH}_2\text{OH})$	$\text{Zn}(\text{acac})_2$	90
$\text{Zn}(\text{bzac})_2(\text{NH}_2\text{OH})$	$\text{Zn}(\text{bzac})_2$	92

The formulation of the nickel monooximato complexes, $\text{Ni}(\text{acacM})_2$, $\text{Ni}(\text{bzacM})_2$ and $\text{Ni}(\text{tfacM})_2$ is based on elemental analysis, infrared spectroscopy and decomposition with dilute hydrochloric acid. The isoxazoles formed from the effect of hydrochloric acid on the complexes were isolated and characterised. Thus $\text{Ni}(\text{acacM})_2$ afforded ca. 2 mole of 2,4-dimethylisoxazole (4.1d; $\text{R} = \text{R}' = \text{Me}$), $\text{Ni}(\text{bzac})_2$ gave ca. 2 mole of 3-methyl-5-phenylisoxazole (4.1d; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) and $\text{Ni}(\text{tfacM})_2$ yielded ca. 2 mole of 3-methyl-5-trifluoromethylisoxazole (4.1d; $\text{R} = \text{CF}_3$, $\text{R}' = \text{Me}$) for every mole of metal complex used.



Reaction 4.15.

The reaction of unsymmetrical β -diketones with amines and hydrazines could, in principle, lead to two isomeric products. One isomer could arise from the condensation of ZNH_2 with the $\text{R}'\text{CO}$ group, the other from the condensation with the RCO group (Scheme 4.2).



Scheme 4.2.

In some of the early studies of the condensation of amines with unsymmetrical β -diketones it was assumed that the condensation could occur at either carbonyl group and that both of the isomers are formed. In other studies it was suggested that only one of the carbonyl groups was involved in the condensation. In these cases the suggested position of condensation was arbitrarily chosen and the structures

Table 4.8. Metal complexes of Schiff bases derived from the reaction of amines with metal β -diketonato complexes.

Metal complex	Amine	Product	Reference
$\text{Cu}(\text{acac})_2$	en	$\text{Cu}(\text{enac})_2^{\text{a}}$	5
$\text{Be}(\text{acac})_2$	Hbg ^b	$\text{Be}(\text{bg}_2\text{ac})^{\text{c}}$	26
$\text{Be}(\text{acac})_2$	Haiu ^d	$\text{Be}(\text{aiuac})_2^{\text{e}}$	26
$\text{Mg}(\text{acac})_2$	Hbg	$\text{Mg}(\text{bgac}_2)(\text{H}_2\text{O})_2^{\text{f}}$	26
$\text{Mg}(\text{acac})_2$	Haiu	$\text{Mg}(\text{Haiuac})_2$	26
$\text{Eu}(\text{bzac})_3$	ama ^g	h	27
$\text{Eu}(\text{bzbz})_3$	ama	h	27

^a see Reaction 4.5.

^b biguanide = $(\text{NH}_2)_2\text{CH}=\text{C}(\text{NH}_2)_2$

^c $\text{H}_2\text{bg}_2\text{ac} = \text{H}_2\overset{*}{\text{N}}\text{C}(\text{NH}_2)=\text{NC}(\text{NH})\overset{*}{\text{N}}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\overset{*}{\text{N}}=\text{C}(\text{NH}_2)\text{N}=\text{C}(\text{NH}_2)\overset{*}{\text{N}}\text{H}_2$
 (* indicates site of coordination to the metal)

^d N' -amidinoisourea = $\text{H}_2\text{NC}(\text{NH})\text{N}=\text{C}(\text{OH})\text{NH}_2$

^e $\text{H}_2\text{aiuac} = \overset{*}{\text{O}}=\text{C}(\text{NH}_2)\text{N}=\text{C}(\text{NH}_2)\overset{*}{\text{N}}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\overset{*}{\text{O}}\text{H}$

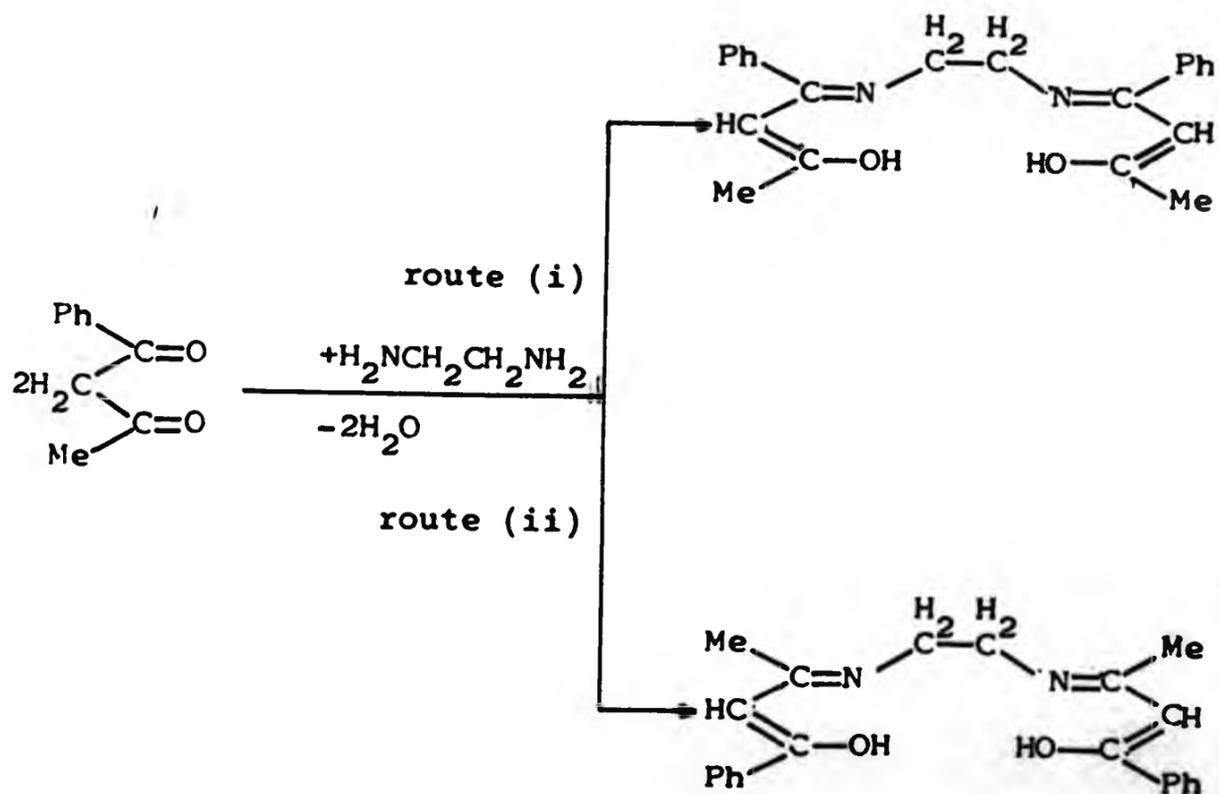
^f $\text{H}_2\text{bgac}_2 = \overset{*}{\text{H}}\text{OC}(\text{Me})=\text{CHC}(\text{Me})=\overset{*}{\text{N}}\text{C}(\text{NH}_2)=\text{NC}(\text{NH})\overset{*}{\text{N}}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\overset{*}{\text{O}}\text{H}$

^g aminoalcohols, phenylglycinol, phenylalaninol and 2-amino-1-phenyl-1,3-propandiol

^h Schiff base formed but structure not established

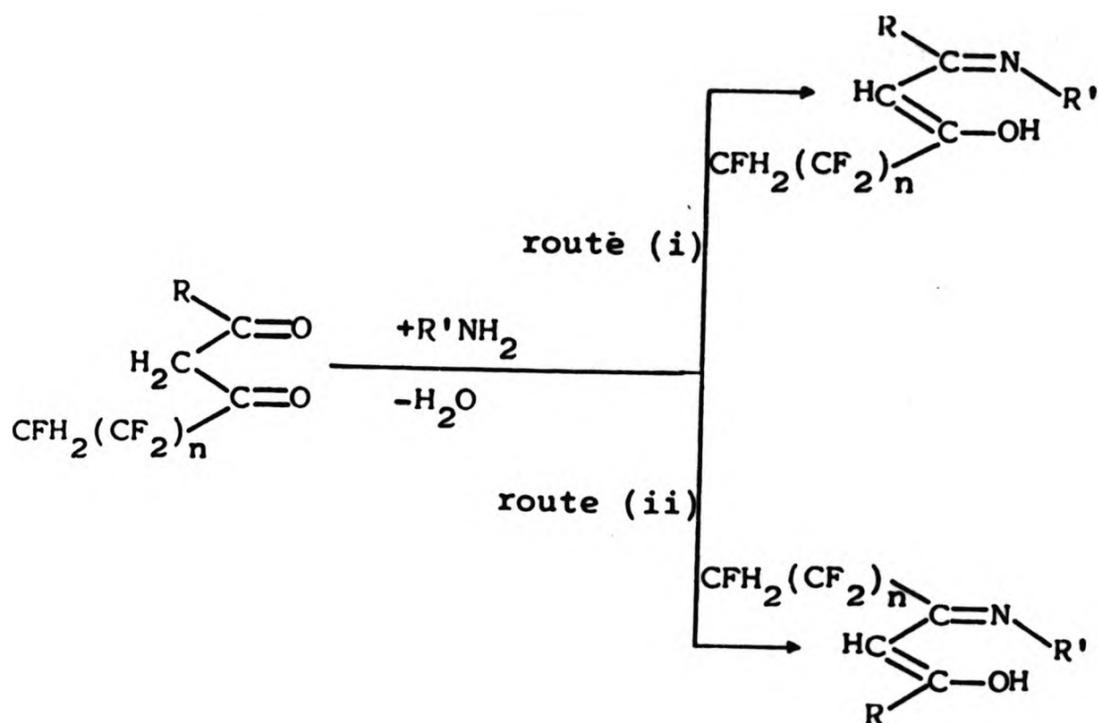
of the products of the reaction were not established. An example of conflicting proposals can be found for the reaction of 1,2-diaminoethane with benzoylacetone (Reaction 4.16).

Originally it was reported that condensation occurs at the carbonyl adjacent to the phenyl group (route i).²⁴ However, a later report states that condensation occurs at the carbonyl adjacent to the methyl group (route ii).²⁶ The latter suggestion was shown to be the correct one by establishing the structures of the Schiff bases formed using n.m.r. and mass spectrometric techniques.



Reaction 4.16.

Another example of this type of contradiction can be found with the condensation of ammonia and primary amines with unsymmetrical polyfluorinated β -diketones (Reaction 4.17).



$n=2$, $\text{R}=\text{Me}$, ^nBu , ^tBu , Ph ; $n=4$, $\text{R}=\text{Me}$; $\text{R}'=\text{H}$, Me and Ph .

Reaction 4.17

For these systems it was reported that the carbonyl adjacent to the R group underwent condensation (route i).^{29,30} However, a counter proposal was reported for the addition of amines in related systems i.e. that it was the carbonyl adjacent to the fluorinated substituent that underwent condensation (route ii).³¹ In an extensive study involving unsymmetrical polyfluorinated β -diketones $\text{CFH}_2(\text{CF}_2)_n\text{COCH}_2\text{COR}$ ($n = 2$, $\text{R} = \text{Me}$, ^nBu , ^tBu and Ph ; $n = 4$, $\text{R} = \text{Me}$) it was established that in every case investigated the condensation occurs at the carbonyl adjacent to the R group.¹⁵

In the case of the reaction of benzoylacetone with hydrazines it has been established that the condensation occurs at the carbonyl adjacent to the methyl group.¹⁴ This is in contrast to previous assumptions that

condensation with hydrazine occurs at either of the carbonyl groups of benzoylacetone. The site of condensation has been established through the characterisation of the resultant pyrazole. The condensation behaviour of benzoylacetone towards hydrazines, which involves nucleophilic attack of the hydrazine on the carbonyl, has been rationalised in terms of the comparative stability of one of the tautomeric forms of the diketone (Fig. 4.2). The phenyl group can conjugate with the adjacent carbonyl group far more so than the methyl group.

Consequently, condensation of the hydrazine with the carbonyl group adjacent to the phenyl is hindered, and nucleophilic attack by the hydrazine occurs at the carbonyl group adjacent to the methyl as represented in Scheme 4.3.

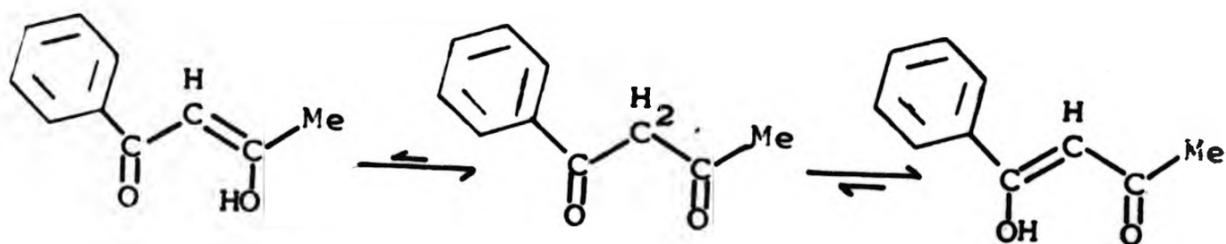
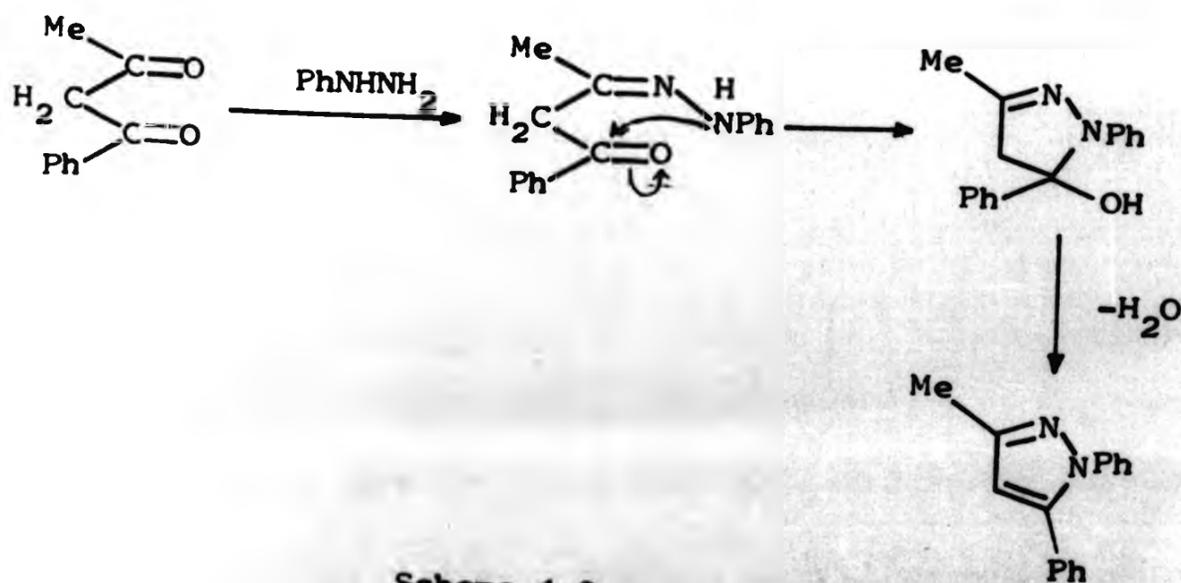


Fig. 4.2.



Scheme 4.3.

Steric effects can also be invoked to account for the nature of the products arising from the reaction of ZNH_2 with $MeCOCH_2COR_f$ (Reaction 4.17) and of hydroxylamine with trifluoroacetylacetone. In both cases the electronic factor favours condensation at the R_fCO , as the electron withdrawing effect of the fluorine atoms renders the carbonyl group adjacent to the fluoroalkyl substituent more electropositive. In contrast the steric factor favours condensation at the $MeCO$ and indeed dominates the reaction, thus accounting for the formation of the products.

From the information presented in this section it can be concluded that,

- a) the mode of condensation of $ROCH_2COR'$ with ZNH_2 is determined by steric and electronic factors. The steric factor has the major influence.
- b) The condensation of benzoylacetone and trifluoroacetylacetone with hydroxylamine should occur at the $MeCO$.
- c) The condensation of the chelated benzoylacetone and trifluoroacetylacetone anions should also occur at the $MeCO$ because chelation does not alter the relative steric and electronic parameters of the carbonyl groups on the β -diketone anion.

The results from this and previous work on the bis(β -diketonato)nickel(II)-hydroxylamine system¹⁰ confirm the conclusions outlined in (b) and (c). Conclusion (c) is also supported by the reactions of hydroxylamine with either $Ni(bzac)_2$ or $Ni(tfac)_2$ which

ultimately give $\text{Ni}(\text{bzacM})_2$ or $\text{Ni}(\text{tfacM})_2$, respectively. In both of these complexes condensation of the hydroxylamine has occurred at the MeCO group.

The behaviour of the bis(β -diketonato)copper(II) complexes towards hydroxylamine, which is rationalised in the following section, is more complex but also supports the above conclusions.

4.8. Mechanistic rationalisation of the behaviour of copper(II) β -diketonates towards hydroxylamine.

4.8.1. The behaviour of $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ towards hydroxylamine.

The reactions of hydroxylamine with either $\text{Cu}(\text{bzac})_2$ or $\text{Cu}(\text{tfac})_2$ in methanol affords a free ketoxime, a $[\text{Cu}(\text{monooximato})(\text{OH})]$ complex and some unidentified products in small yields. In each case the two monooxime moieties formed are different with regard to the position of condensation. This difference can be rationalised as shown in Scheme 4.4 (Mechanism A). An alternative but less plausible mechanism is outlined in Scheme 4.7 (Mechanism B).

Mechanism A.

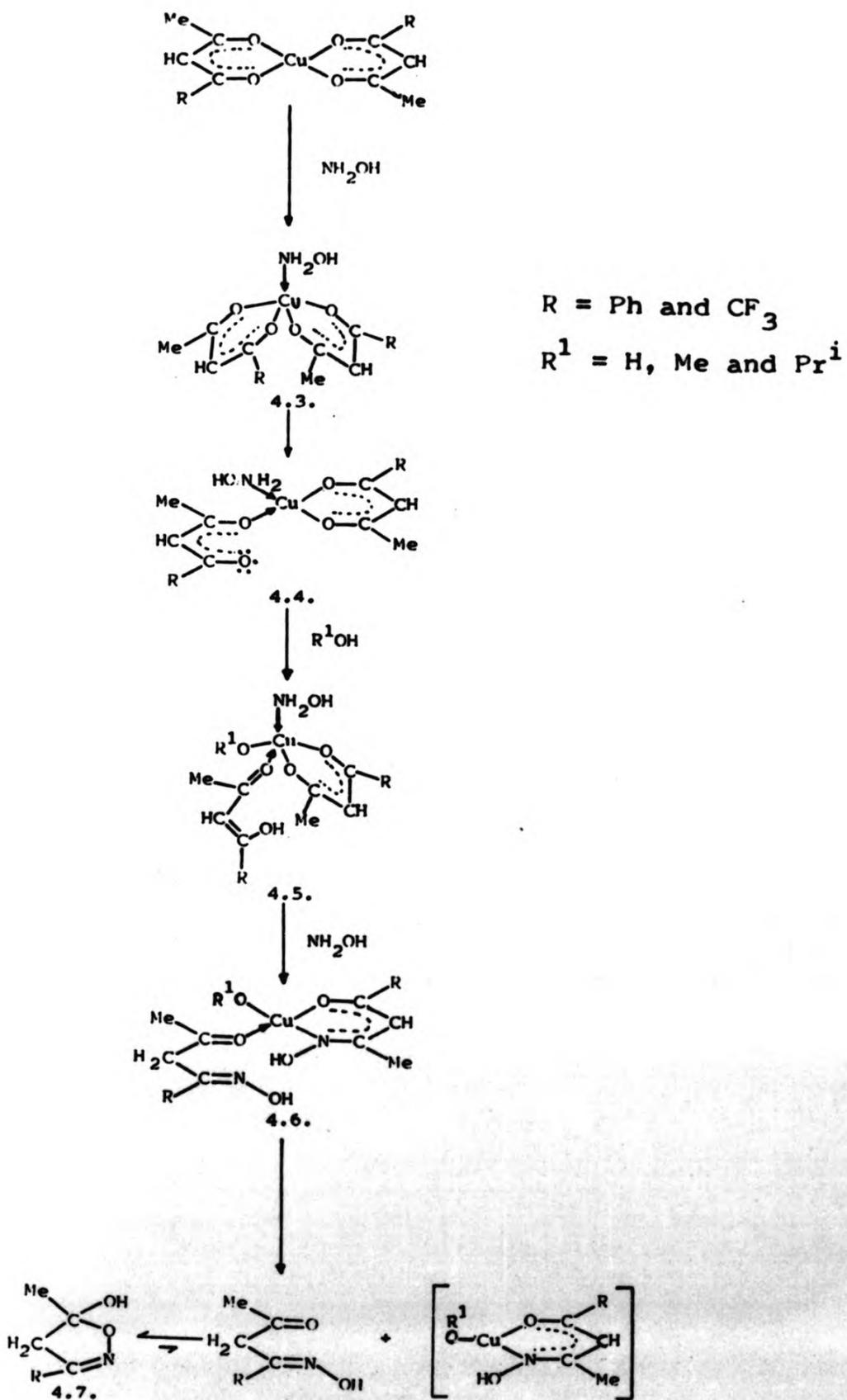
This mechanistic proposal involves several stages which will be referred to as the internal redox, hydrogen abstraction/reoxidation, oximation and redistribution stages.

a) Internal redox stage.

The internal redox reaction is induced by coordination

Scheme 4.4. Mechanism A

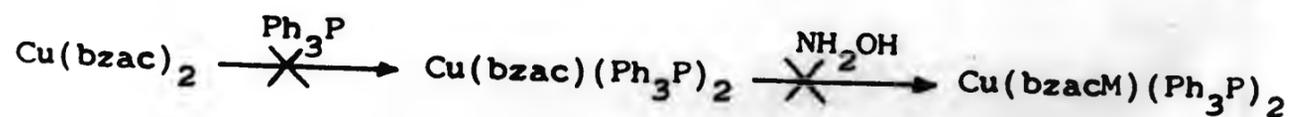
Proposed mechanism for the reaction of $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ with NH_2OH .



of hydroxylamine to the metal. This gives the copper(I) complex 4.4 which contains a β -diketone radical coordinated in a monodentate fashion to the metal, as well as, a chelated β -diketone anion.

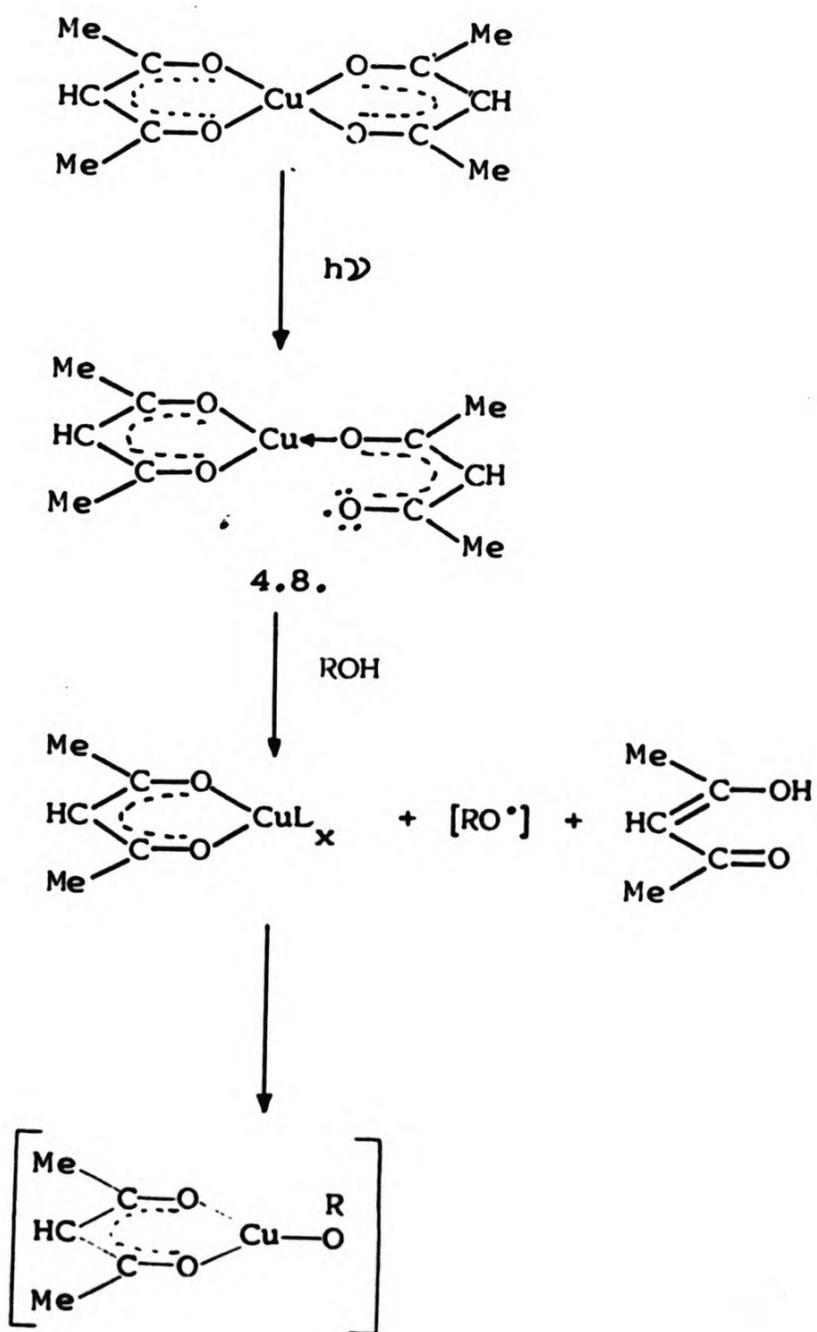
Previously, a species 4.8 similar to 4.4 had been suggested as an intermediate in the photodecomposition of $\text{Cu}(\text{acac})_2$ (Scheme 4.5).³² Supporting evidence for the involvement of this species was obtained by carrying out the reaction in the presence of triphenylphosphine. This resulted in the isolation of $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$.

In the present study evidence for the involvement of a copper(I) intermediate species was also obtained by following the above approach. Thus, when the reaction between $\text{Cu}(\text{bzac})_2$ and hydroxylamine in methanol was carried out in the presence of triphenylphosphine, the copper(I) intermediate was trapped and isolated as $\text{Cu}(\text{bzacM})(\text{Ph}_3\text{P})_2$. The possibility that the complex $\text{Cu}(\text{bzacM})(\text{Ph}_3\text{P})_2$ arises by reduction of the $\text{Cu}(\text{bzac})_2$ complex by triphenylphosphine, followed by oximation (Reaction 4.18) can be discounted by the observation that $\text{Cu}(\text{bzac})_2$ was recovered (>95 %) after being heated in refluxing methanol for 20 days with triphenylphosphine.



Reaction 4.18.

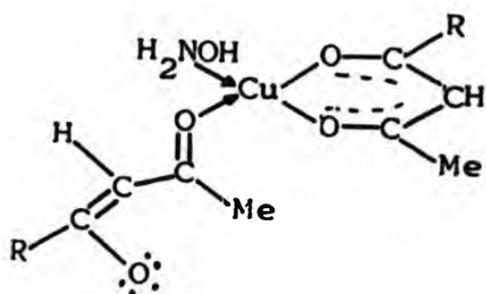
Scheme 4.5. Mechanistic rationalisation for the photochemically induced internal redox reaction of bis(acetylacetonato)copper(II).



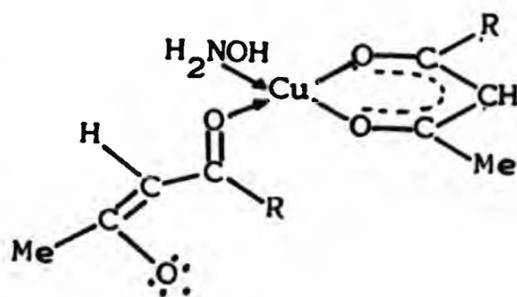
R = Me, Et and Pr^i

L = ligand derived from the solvent

In the intermediate copper(I) species 4.4, the ligand radical is assumed to be coordinated to the metal through the carbonyl adjacent to the methyl group as shown in 4.9, rather than through the carbonyl adjacent to the group R (Ph or CF_3) as shown in 4.10. This is because structure 4.9 is more sterically favoured than 4.10, i.e. in 4.9 there is less crowding around the copper coordination centre due to the smaller size of the Me group relative to Ph or CF_3 . Furthermore, the radical site in 4.9, may be stabilised through conjugation when R = Ph or because of electron withdrawing effects when R = CF_3 , whereas the methyl group cannot stabilise the alternative species 4.10 in either of these ways.



4.9.



4.10.

b) Hydrogen abstraction and reoxidation of the metal.

The subsequent stage involves H-abstraction by the coordinated ligand radical and reoxidation of the metal in 4.4 to give 4.5.

A stoichiometrically attractive explanation for this process is the reaction of 4.4 with water present in the solvent. Thus, H-abstraction from water produces

OH[•] radicals which combine with and reoxidise the metal. This explanation however, is unlikely because of statistical considerations (the solvent used contained very small amount of water) and the fact that water is a poor hydrogen atom donating solvent.³²

The most probable source of the abstracted hydrogen is the solvent. The solvent used was methanol which is capable of donating H[•] from the methyl group.³² This would give rise to CH₂OH[•] radicals which could give OH[•] through further reactions with another species present in the reaction mixture. The nature of this species cannot be defined at this stage on the basis of the observed results. Evidence for the involvement of the solvent in the reaction is provided by the following observation. When the reaction between hydroxylamine and Cu(bzac)₂ or Cu(tfac)₂ was carried out in propan-2-ol the copper containing products were Cu(bzacM)(OPrⁱ) and Cu(tfacM)(OPrⁱ) rather than the corresponding hydroxy(monooximate)copper(II) complex. Significantly when Cu(bzacM)(OH) was stirred in propan-2-ol no exchange of the OH group for the OPrⁱ group occurred.

c) The oximation stage.

Species 4.5 contains two different types of β-diketone moieties. One is anionic and chelated to the metal whilst the other is neutral and coordinated in a monodentate fashion. These react in different ways with hydroxylamine.

Coordination of the hydroxylamine with the chelated species occurs at the carbonyl adjacent to the methyl group for reasons noted earlier (Section 4.7).

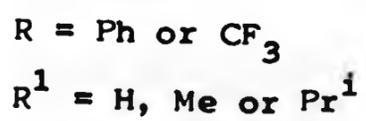
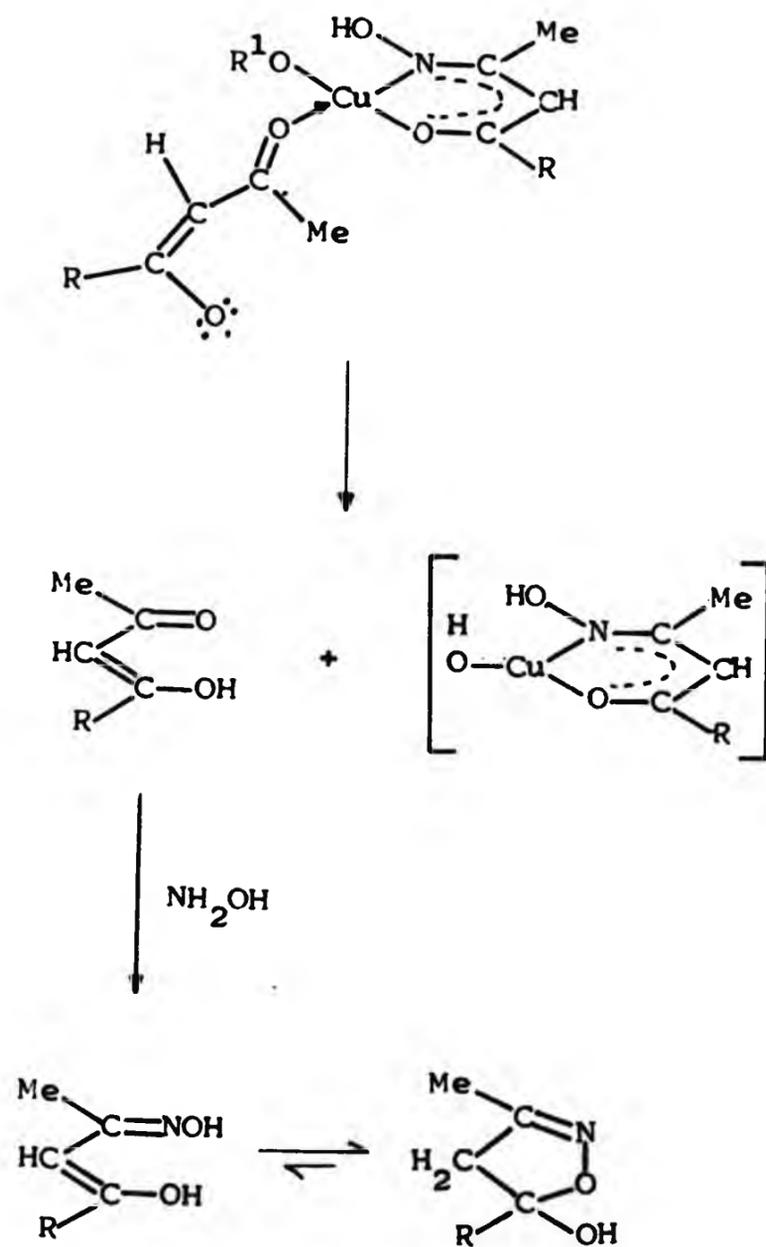
In contrast condensation of hydroxylamine with the neutral β -diketone which is coordinated to the metal occurs at the carbon atom adjacent to the R (Ph or CF_3) group. The reason for this is that attack at the carbon atom adjacent to the methyl group would be highly hindered by the Cu(chelate) species onto which it is bonded.

The possibility that oximation of the neutral β -diketone occurs via the route indicated in Scheme 4.6, i.e. by oximation of the non-coordinated neutral β -diketone moiety, is precluded because such species is expected to undergo oximation at the carbonyl adjacent to the methyl group (cf Section 4.7).

d) The redistribution of species 4.6.

The final stage of the reaction is assumed to involve the redistribution of the oximated species 4.6 to give the products isolated from the reaction, i.e. isoxazoline and hydroxy- or alkoxy- (monooximato) copper(II). This redistribution could occur due to the tendency of monooximes to cyclise (cf. Section 4.12) coupled with the poorer donor properties of the resulting isoxazoline and the insolubility of the resulting copper(II) species which reflects its associated nature (cf. Section 4.10).

Scheme 4.6. Mechanistic proposal for the liberation and oximation of a neutral β -diketone in the reaction of bis(benzoylacetonato) copper(II) and bis(trifluoroacetylacetonato) copper(II) with hydroxylamine.



Mechanism B.

This mechanistic proposal assumes that the hydroxylamine initially attacks the methyl carbonyl group of one of the chelated ligands as illustrated in Scheme 4.7. This reaction affords species 4.11 which then undergoes a Lewis base induced internal redox reaction to give the copper(I) species 4.12 and 4.14.

Species 4.12 arises by homolytic cleavage of the copper- β -diketonato bond and reacts further in a fashion analogous to that described in Scheme 4.4 for species 4.4. This would lead to two different monooxime moieties, one coordinated and oximated at the MeCO and the other free and oximated at the RCO. Species 4.14 arises by homolytic cleavage of the copper-monooximato bond and would lead to two monooxime moieties both oximated at the MeCO.

On the basis of the above the reaction between hydroxylamine and $\text{Cu}(\text{bzac})_2$ or $\text{Cu}(\text{tfac})_2$ is expected to give a mixture of the compounds illustrated in Figs 4.16-4.18. However, only two products are formed and thus this mechanistic proposal can be discounted.

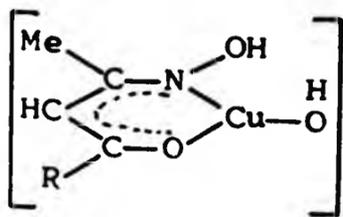


Fig. 4.16

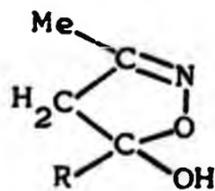


Fig. 4.17

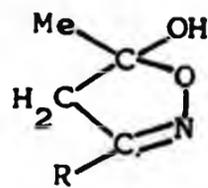
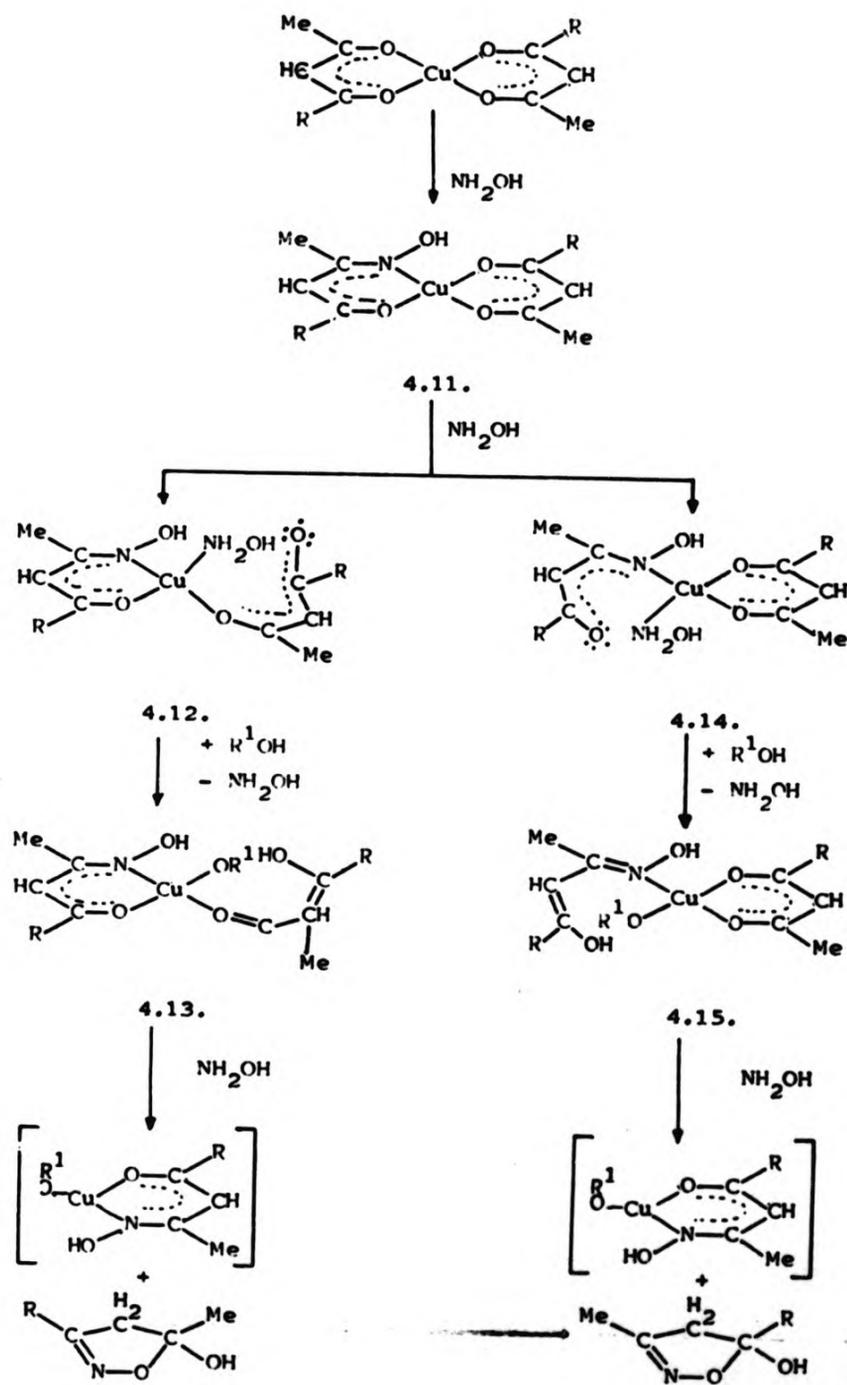


Fig. 4.18.

(R = Ph or CF_3)

Scheme 4.7. Mechanism B.

Alternative mechanism for the reaction of $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ with NH_2OH .



$R = \text{Ph}$ and CF_3

$R^1 = \text{H}, \text{Me}$ and Pr^i

4.8.2. The behaviour of $\text{Cu}(\text{acac})_2$ towards hydroxylamine

The reaction of hydroxylamine with $\text{Cu}(\text{acac})_2$ in methanol affords the copper(II) complex $\text{Cu}(\text{acacM})_2$. The reaction appears to be a straightforward oximation of both chelated acetylacetonato groups which does not involve reduction of the metal. However, in view of the reduction of the copper in $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ by hydroxylamine it was decided to examine the system involving $\text{Cu}(\text{acac})_2$ and hydroxylamine further. Thus the reaction was carried out (i) in the presence of triphenylphosphine in methanol and (ii) using propan-2-ol as the solvent.

When the reaction was performed in the presence of triphenylphosphine the copper(I) complex $\text{Cu}(\text{acacM})(\text{Ph}_3\text{P})_2$ resulted. This complex does not arise from the reaction of $\text{Cu}(\text{acacM})_2$ with triphenylphosphine. This was established by a control experiment. Thus, when $\text{Cu}(\text{acacM})_2$ and triphenylphosphine were heated together in refluxing methanol, $\text{Cu}(\text{acacM})_2$ (>95 %) was recovered after 72 hours. Furthermore, it is known that $\text{Cu}(\text{acac})_2$ reacts very slowly with triphenylphosphine in refluxing methanol.^{33,34} During this study it has also been established that $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$ does not react with hydroxylamine. When $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$ and hydroxylamine were stirred together at 0 °C in anhydrous methanol, $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$ (>95 %) was recovered after 24 hours. The above suggests that the formation of $\text{Cu}(\text{acacM})(\text{Ph}_3\text{P})_2$ from the reaction of $\text{Cu}(\text{acac})_2$ and hydroxylamine in

the presence of triphenylphosphine involves an internal redox reaction promoted by the hydroxylamine.

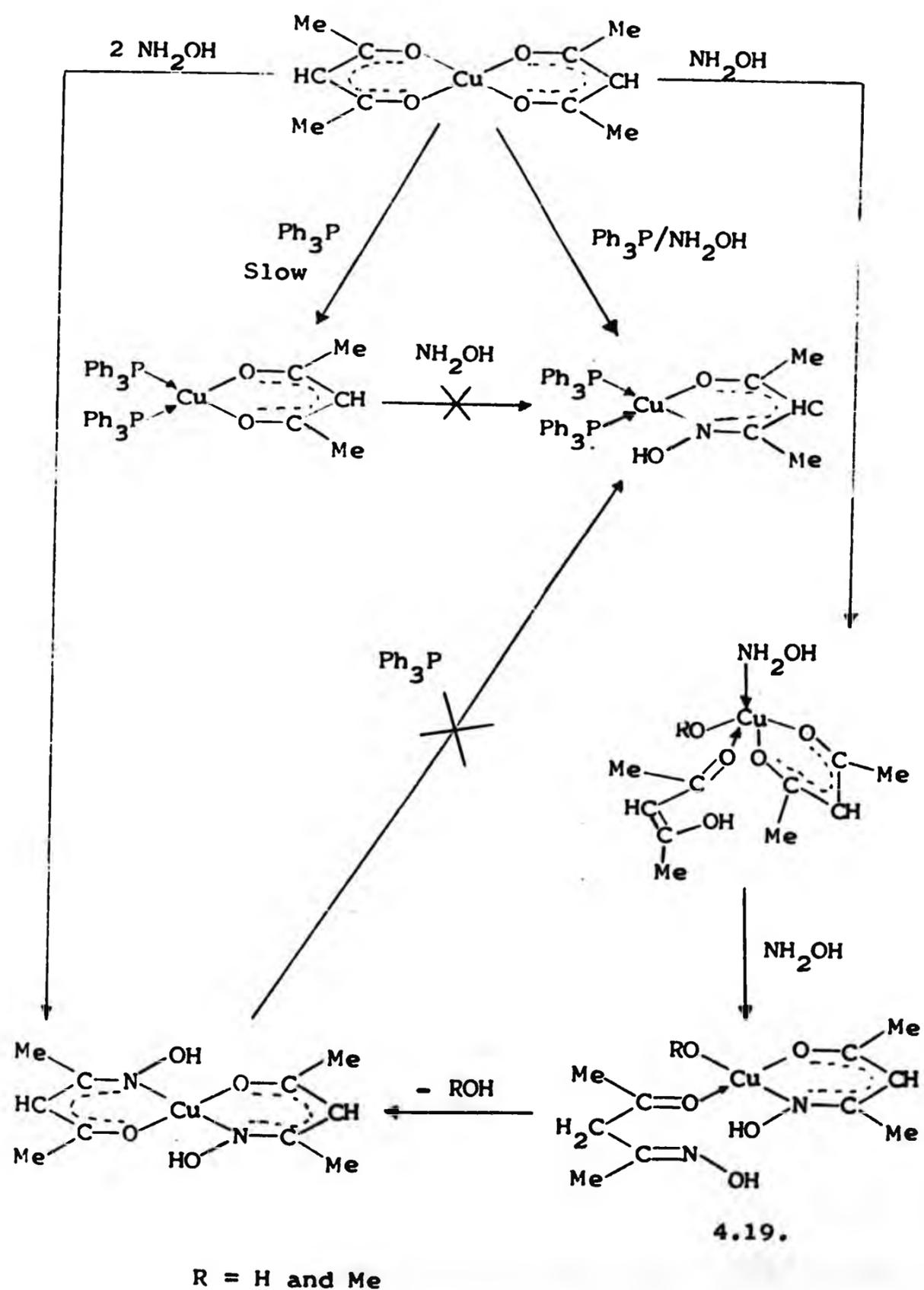
However, the oximated intermediate, 4.19, loses ROH to give $\text{Cu}(\text{acacM})_2$. These reactions are summarised in Scheme 4.8.

When the reaction between $\text{Cu}(\text{acac})_2$ and hydroxylamine is carried out in propan-2-ol the alkoxy copper(II) complex, $\text{Cu}(\text{acacM})(\text{OPr}^i)$, results together with the monooxime, acacMH. The formation of these products is analogous to the behaviour of $\text{Cu}(\text{bzac})_2$ and $\text{Cu}(\text{tfac})_2$ towards hydroxylamine and can be accounted for as indicated in Scheme 4.4.

4.8.3. Conclusions.

In the study outlined above it can be seen that the reactions of hydroxylamine with β -diketones and bis(β -diketonato)metal(II) complexes are interesting and synthetically useful. The novel condensation behaviour exhibited by the bis(β -diketonato)copper(II) complexes involves the regiospecific formation of β -ketooximes. This is a route to previously unattainable isomers of β -ketooximes. Synthetic problems involving the interaction of hydroxylamine with bis(β -diketonato)metal(II) complexes have also been overcome. As a consequence the reactions are now repeatable and the results reproducible. The bis(monooximato)nickel(II) complexes of bzach and tfach have also been prepared along with the elucidation of the internal redox mechanism in the reaction of hydroxylamine with bis(β -diketonato)copper(II) complexes. Also the site of condensation

Scheme 4.8. Proposed mechanism for the reaction of bis(acetylacetonato)copper(II), $\text{Cu}(\text{acac})_2$, with hydroxylamine.



of hydroxylamine on β -diketone moieties, both chelated and free, has been determined. This is useful as it has, for some time, been a contentious point.

4.9. The structure and properties of bis(monooximato) nickel(II) complexes and their pyridine adducts.

Some properties of $\text{Ni}(\text{acacM})_2$, $\text{Ni}(\text{bzacM})_2$, $\text{Ni}(\text{tfacM})_2$ and their respective pyridine adducts are summarised in Table 4.9.

The bis(monooximato)nickel(II) complexes are diamagnetic, suggesting a square planar geometry (Fig. 4.20). However, this does not indicate whether there is association between molecules in adjacent planes. Significantly, relative molecular mass measurements also indicate that there is no association and in the vapour phase there are no ions with m/z values greater than $[\text{Ni}(\text{monooximato})_2]^+$.

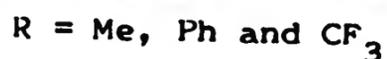
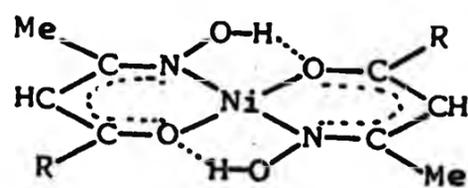


Fig. 4.20.

Comparison of the properties of bis(monooximato) nickel(II) complexes with the properties of related bis(dialkylglyoximato)nickel(II) complexes (Fig. 4.21) allows structural clarification.

Table 4.9. Some properties of bis(monooximate)nickel(II) and dipyridinebis(monooximate)nickel(II) complexes.

Complex	μ_{eff} (B.M. 20 °C)	M.s. data ([M] ⁺ m/z)	M _r ^a Found	Acid decomp. product
Ni(acacM) ₂	b	[Ni(acacM) ₂] ⁺ =287	280	2,4-dimethylisoxazole
Ni(bzacM) ₂	b	[Ni(bzacM) ₂] ⁺ =411	402	3-methyl-5-phenyl isoxazole
Ni(tfacM) ₂	b	[Ni(tfacM) ₂] ⁺ =395	381	3-methyl-5-trifluoro methylisoxazole
Ni(acacM) ₂ (py) ₂	3.11	c	430	c
Ni(bzacM) ₂ (py) ₂	3.09	c	551	c
Ni(tfacM) ₂ (py) ₂	3.05	c	530	545 c

^adetermined in chloroform solution

^bdiamagnetic

^cnot studied

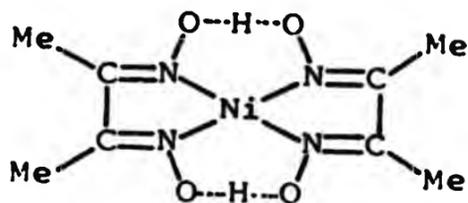


Fig. 4.21.

The facile reactions of bis(monooximato)nickel(II) complexes with pyridine to form the dipyridine adducts and their solubility in various solvents implies that these complexes are not associated in the solid state. This is in contrast to the behaviour of bis(dialkylglyoximato)nickel(II) complexes. Bis(dialkylglyoximato)nickel(II) complexes do not react with pyridine and are very insoluble in all common solvents.³⁵ The bis(dialkylglyoximato)nickel(II) units have a square planar structure and stack one above another, alternative units being twisted through 90° so that the nickel atoms form a chain with a nickel-nickel distance of 3.25 \AA .³⁶ The strength of this association is such that it cannot be disrupted by Lewis bases and thus interaction with pyridine molecules does not occur as the site of coordination is blocked. Hence, the properties of bis(monooximato)nickel(II) complexes indicate the absence of strong interaction between the bis(monooximato)nickel(II) units.

Another related complex whose structure has been determined is bis(salicylaldoximato)nickel(II), $\text{Ni}(\text{sal})_2$ (Fig. 4.22). This has been shown to be monomeric in solution and in the vapour phase with

little, or no, interaction between nickel atoms in adjacent planes.³⁷ As with bis(monooximato)nickel(II) complexes, bis(salicylaldoximato)nickel(II) reacts with pyridine to give the octahedral di-pyridine adduct, $\text{Ni}(\text{sal})_2(\text{py})_2$.³⁷ Hence, this is further evidence for the lack of association in bis(monooximato)nickel(II) complexes.

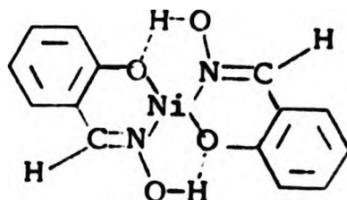


Fig. 4.22.

The infrared spectra of the bis(monooximato)nickel(II) complexes have broad absorption bands in the region of 3100 cm^{-1} . This is indicative of intramolecular hydrogen bonding similar to that found in bis(salicylaldoximato)nickel(II) and bis(dialkylglyoximato)nickel(II) complexes.³⁸ Each bis(dialkylglyoximato)nickel(II) molecule contains very strong intramolecular hydrogen bonds. The infrared spectrum exhibits OH as a broad band in the region $2300\text{-}2900 \text{ cm}^{-1}$.³⁹ An absorption in this region can also be found in the infrared spectrum of bis(salicylaldoximato)nickel(II).³⁷ The infrared spectra of bis(monooximato)nickel(II) complexes also contain bands at 1630 and 1550 cm^{-1} . These bands can be attributed to the coupled vibrations of the chelate ring.¹⁰ The bands for the O-H stretching vibration of the oxime

group can be found in the region 3250 and 3100 cm^{-1} .¹⁰

The Ni(monooximato)₂ complexes gave poorly defined u.v./visible spectra. The room temperature magnetic moments of the pyridine adducts are in the range usually found for octahedral nickel(II) complexes ($\mu_{\text{eff}} = 3.0 - 3.3$ B.M.).

4.10. The structure and properties of Cu(acacM)(Ph₃P)₂, Cu(bzacM)(Ph₃P)₂ and [Cu(tfacM)OH].

Both Cu(acacM)(Ph₃P)₂ and Cu(bzacM)(Ph₃P)₂ are white diamagnetic solids. The infrared spectra of these two complexes contain bands at 1640, 1555, 3260 and 3100 cm^{-1} . Similar absorbances are found in the infrared spectra of bis(monooximato)nickel(II) complexes and have been attributed to vibrations of the chelate ring and the oxime group.¹⁰

The infrared spectrum of [Cu(tfacM)OH] exhibits bands at 3250, 3200 and 3100 cm^{-1} which are assigned to the O-H stretching vibration of the bridging hydroxyl and of the stretching vibration of the O-H of the oxime group.¹⁰

Further support for the structural formulation of [Cu(tfacM)OH] is provided by decomposition with dilute hydrochloric acid and the isolation of 1 mole of 3-methyl-5-trifluoromethyl isoxazole per mole of complex.

The insolubility of [Cu(tfacM)OH] in common solvents

prevented the u.v./visible spectrum of the complex from being obtained. Even when u.v./visible cells with a path length of 10 cm were used the low solubility of the complex was such that a spectrum was still unobtainable.

[Cu(tfacM)OH] exhibits a subnormal room temperature magnetic moment of 0.91 B.M. at 20 °C. Previous work on [Cu(bzacM)OR] and [Cu(acac)OR] (R = H, Me, Et and ⁿC₃H₇), which also have low μ_{eff} at room temperature, indicates that the subnormal moment can be accounted for if the complex contains alkoxy bridges of the type illustrated in Fig. 4.23.^{10,42-44} The structures indicated in Figs. 4.24 and 4.25 were earlier suggested for the complexes [Cu(acac)OR].³²

In the case of [Cu(tfacM)OH] the structure shown in Fig. 4.24 can be discounted due to the copper-copper bond. If the complex were to have the structure illustrated in Fig. 4.24 it would be diamagnetic due to the coupling of the single unpaired electrons on each of the copper atoms. As the complex was found to be paramagnetic this interaction cannot be present and therefore this structure can be ruled out.

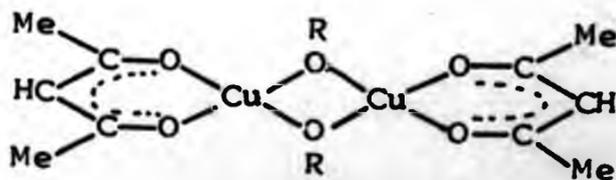


Fig. 4.23

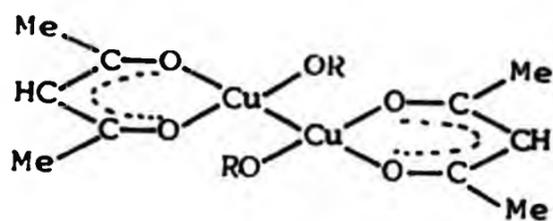


Fig. 4.24.

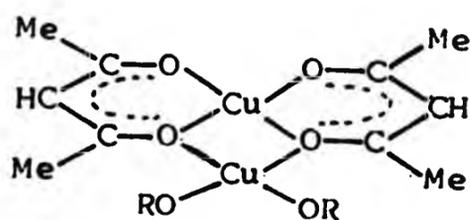


Fig. 4.25.

4.11. The structure and properties of $Zn(bzac)_2(NH_2OH)$.

$Zn(bzac)_2(NH_2OH)$ is a white solid and as expected it is diamagnetic. The formulation is based on infrared spectroscopy and elemental analysis. The infrared spectrum of $Zn(bzac)_2(NH_2OH)$ has bands in the $3500-3000\text{ cm}^{-1}$ region assignable to the $\nu(NH)$ and $\nu(OH)$ vibrations of the coordinated hydroxylamine.¹⁰ Similar bands appear in the infrared spectrum of the previously reported $Zn(acac)_2(NH_2OH)$ ¹⁰ and are also present in the spectrum of $Ni(acac)_2(NH_2OH)_2$, $Ni(bzac)_2(NH_2OH)_2$ and $Ni(tfac)_2(NH_2OH)_2$.

4.12. The structure and properties of 3-trifluoromethyl-5-methylisoxazoline.

3-Trifluoromethyl-5-methylisoxazole is a viscous liquid. On treatment with dilute hydrochloric acid it

afforded 3-trifluoromethyl-5-methylisoxazole (Reaction 4.12).

The mass spectrum shows a peak at $m/z = 169$, corresponding to the isoxazoline. There is also a major peak at $[P-18]^+$, corresponding to the isoxazole ion. The most important point is the loss of CH_3^\bullet followed by the loss of CO from $[P-18]^+$ and the absence of the $[CF_3CO]^+$ and $[CH_3CNO]^+$ ions. If the parent isoxazole had a nitrogen bonded adjacent to the methyl group and an oxygen adjacent to the trifluoromethyl group then these ions would be present in the mass spectrum. Their absence provides some evidence that the parent isoxazole has a nitrogen atom bonded to the carbon atom adjacent to the CF_3 group and not to the carbon atom adjacent to the Me group.

The 1H n.m.r. spectrum shows three resonances. The $-CH_3$ resonance is a singlet at $\delta = 1.75$ p.p.m. The $-CH_2-$ resonance is a doublet at $\delta = 2.79$ and 2.83 p.p.m. The resonance for the hydroxy proton is a broad peak centered at $\delta = 3.61$ p.p.m. The infrared spectrum of the isoxazoline has a weak $\nu(CN)$ band at 1600 cm^{-1} and no bands at ca. 1650 cm^{-1} ($\nu(CO)$ region). This is in accord with previous literature on the infrared spectra of isoxazolines.^{10,17,18} All of the evidence is consistent with the structure of the isoxazoline being that illustrated in Fig. 4.26.

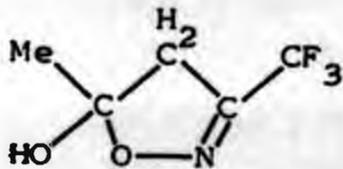


Fig. 4.26.

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CHAPTER FIVE

Reactions of bis(1,2-quinonemonooximate)metal(II) complexes with amines and the rationalisation of the mechanisms of these reactions.

5.1. Introduction.

The tendency of the monooximes of 1,2-quinones to form metal complexes has been the subject of considerable attention.¹⁻⁵ Furthermore, such behaviour has found importance in analysis and in industry. For instance, 1,2-naphthoquinone-2-monooxime is used widely for the gravimetric determination of nickel⁶ and also in the separation of cobalt from its crude ore.⁷ In the early stages of these studies there was an emphasis on the preparation and characterisation of these complexes.^{2,3,8-10} More recently these studies have been concerned predominantly with the potential of these well-studied complexes in synthesis.^{11,12}

In sections 5.2 and 5.3 of this chapter a brief review of the chemistry of the metal complexes of 1,2-quinonemonooximes is presented with respect to (i) their preparation and structures and (ii) their reactions.

5.2. The preparation and studies of metal complexes of 1,2-quinonemonooximes.

5.2.1. Preparation of metal complexes of 1,2-quinone-monooximes.

There are two main methods for the preparation of the

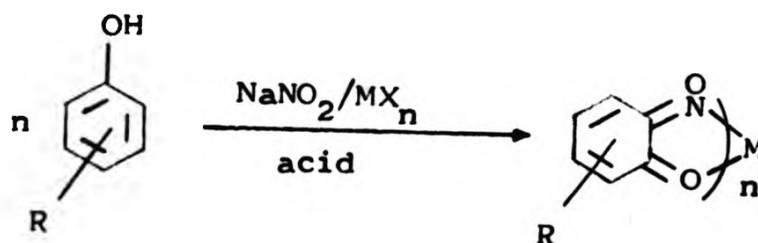
metal complexes of 1,2-quinonemonooximes. These are;

(i) The direct interaction of the 1,2-quinonemonooxime with the desired metal salt in a suitable solvent (Reaction 5.1). This procedure is severely limited by the availability of relatively few 1,2-quinonemonooximes. They are usually prepared by the nitrosation of the appropriate phenol; however, in most cases this reaction results mainly in the 1,4-quinonemonooxime isomer.¹³



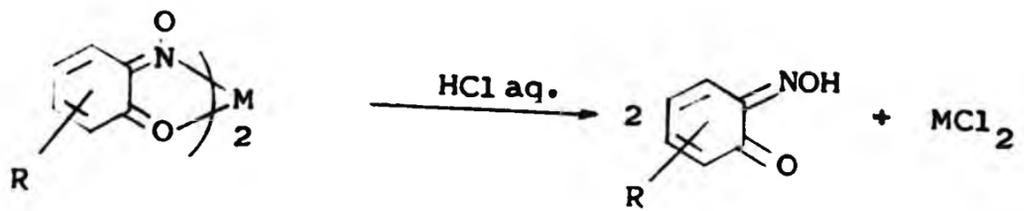
Reaction 5.1.

(ii) The nitrosation of a phenol or naphthol in the presence of a metal salt (Reaction 5.2).



Reaction 5.2.

This method has been used in the preparation of a variety of metal complexes. It is also a convenient route to 1,2-quinonemonooximes since acid hydrolysis of the metal complex yields the potential ligand (e.g. Reaction 5.3). The nitrosation method is however, restricted to the synthesis of complexes of transition metals.



Reaction 5.3.

5.2.2. Structure of metal complexes of 1,2-quinone-monooximes.

The ligand in these complexes can bond to the metal in one of several ways. These are:

- (i) bonding through the nitrogen and ring oxygen atoms (Fig. 5.1).

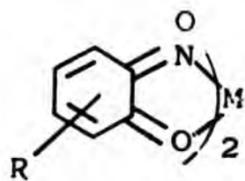


Fig. 5.1.

- (ii) bonding through the oxygen atoms (Fig. 5.2).

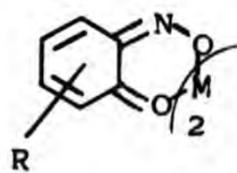


Fig. 5.2.

- (iii) a side-on donor bond (Figure 5.3).

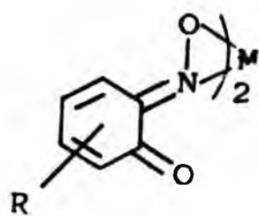


Fig. 5.3.

(iv) Monodentate bonding (Figs. 5.4-5.7).

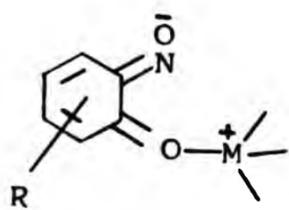


Fig. 5.4.

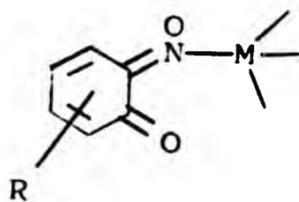


Fig. 5.5.

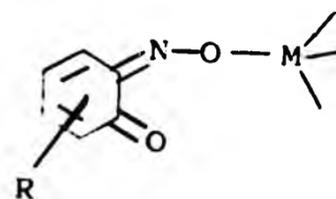


Fig. 5.6

1,2-Quinonemonooximes, besides having the capacity to form several types of bonds to the metal, can, in the complexes, be represented in either a quinonemonooximate (e.g. Fig. 5.7) or nitrosonaphtholato (e.g. Fig. 5.8) form.

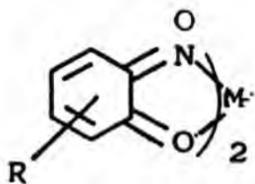


Fig. 5.7.

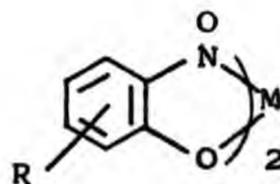


Fig. 5.8.

Previous crystallographic, infrared and mass spectrometry studies of first row transition metal complexes of quinonemonooximes have shown that all

those examined involve bonding through the nitrogen and the ring oxygen atoms. The X-ray structure determinations of these complexes have also shown the CO, CN and NO bond lengths (Table 5.2) to be intermediate between the expected bond lengths for single and double CO, CN and NO bonds (Table 5.1). Therefore the ligands in these complexes can best be described in valence bond terms as resonance hybrids of the two canonical forms illustrated in Figs. 5.7 and 5.8.

Table 5.1. Average bond lengths of C-N, N-O and C-O bonds

Bond type	Bond length.	Reference
C-N	1.47	22
C=N	1.25	22
N-O	1.41	23
N=O	1.21	23
C-O	1.43	23
C=O	1.23	23

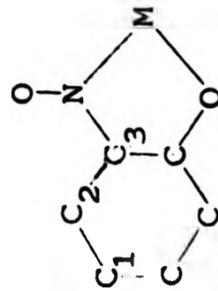
Recent studies of uranium complexes containing 1,2-naphthoquinone-2-monooximate ligands show that in these complexes coordination of the ligand is not as in the above cases. The uranium complex,

$\text{UO}_2(2\text{-nqo})_2(\text{H}_2\text{O})_2 \cdot 2\text{CHCl}_3$, was obtained as a precipitate by the addition of a methanolic solution of 1,2-naphthoquinone-2-monooxime to an aqueous solution of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ and was recrystallised from chloroform.²⁴ The structure of the complex is

Table 5.2. Mean bond lengths (Å) of coordinated quinoneoxime ligands and their metal complexes.

Compound	C ₁ -C ₂ ^a	C ₂ -C ₃ ^a	C-O	C-N	N-O	Reference
Feroverdin ^b	1.38	1.42	1.30	1.42	1.25	14-16
Bis(4-methylbenzo-1-quinone-2-oximato) copper(II), pyridine	1.36	1.43	1.27	1.35	1.25	17
Potassium tris(4-chlorobenzo-1-quinone-2-oximato) nickelate(II), acetone	1.37	1.43	1.25	1.33	1.27	18
Bis(naphtho-2-quinone-1-oximato) copper(II), bisacetone	1.39	1.43	1.30	1.35	1.26	19
Bis(naphtho-1-quinone-2-oximato) copper(II), monohydrate	1.39	1.42	1.28	1.35	1.26	20
Bisquo(4-sulphonatonaphtho-1-quinone-2-oximato) copper(II), trihydrate	1.37	1.44	1.26	1.35	1.25	21

^a atomic numbering in the ligand is;



^b K[Fe(qo)₃], acetone (qoH = 4-hydroxy-3-nitrosobenzoic acid)

illustrated in Fig. 5.9.

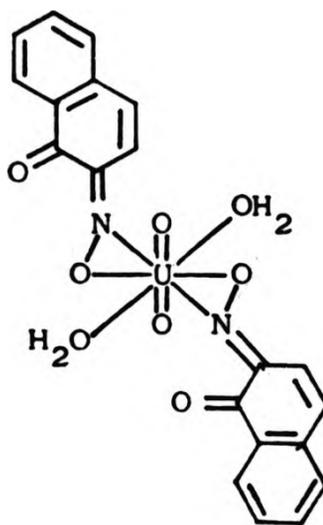
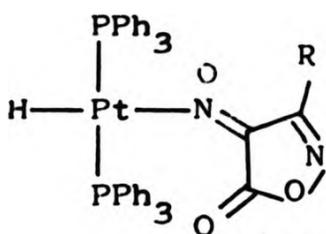


Fig. 5.9.

In this complex the quinoneoximate and water ligands lie in the equatorial plane of the $O=U=O$ group. This type of uranyl complex is not unknown. Previous studies have shown that uranyl complexes can have 4,5 or 6 ligand atoms bonded to the uranium in the equatorial plane of the $O=U=O$ group.²⁵ However, planar 5 and 6 coordination is the most common and appears to give a geometry more stable than the puckered hexagonal configurations.²⁵ In the complex illustrated in Fig. 5.9 steric hindrance prevents the 1,2-naphthoquinoneoximate ligands from chelating via the nitrogen and ring oxygen atoms. The 1,2-naphthoquinoneoximate ligands bond via the nitrogen and oxygen of the NO group as a result of the favoured coordination number of 6 in the equatorial plane of the $O=U=O$ group.

Studies on platinum and gold complexes derived

from 4-isonitroso-3(R)-isoxazol-5-one show that the bonding in the nitroso ligand is through the nitrogen of the NO group only (Figs. 5.10 and 5.11).²⁶



R = CH₃ or Ph

Fig. 5.10.

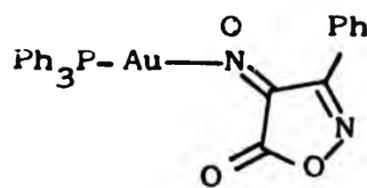


Fig. 5.11.

This type of coordination occurs so that the most stable geometry for each of the complexes is attained i.e. 4-coordinate square-planar geometry for the platinum(II) complex and linear geometry for the gold(I) complex.

5.3. The behaviour of metal complexes derived from the monooximes of 1,2-quinones towards Lewis bases and dienophiles.

In recent years the synthetic potential of metal complexes derived from 1,2-quinonemonooximes has been recognised. These complexes can react with many types of reagents to yield a variety of products. For instance, the ability of these complexes to act as dienes in Diels-Alder reactions has been demonstrated.¹¹ Thus dimethylacetylene dicarboxylate (D.M.A.D.) reacts with quinonemonooximato complexes of copper, e.g.

$\text{Cu}(1\text{-nqo})_2(\text{H}_2\text{O})$, $\text{Cu}(2\text{-nqo})_2(\text{H}_2\text{O})$ and $\text{Cu}(5\text{-MeOqo})_2(\text{H}_2\text{O})$ to yield as major product, in each case, the corresponding benzoxazine (Fig. 5.12).¹¹ This benzoxazine arises by the cycloaddition of the D.M.A.D. across the heterodiene system of the quinonemonooximate ligand.

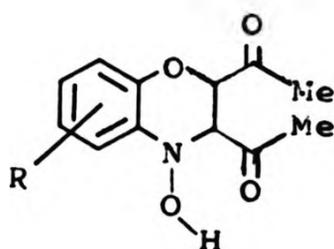


Fig. 5.12.

Interestingly the reactions of D.M.A.D. with 5-MeOqoH, 2-nqoH and 1-nqoH as well as the corresponding methyl esters failed to give the corresponding benzoxazine.¹¹ It was suggested that the reason why the copper complexes, but not the parent ligands, reacted in this way was partly due to the polarisation of the ligand by the copper ion. The ligand was polarised in such a way as to facilitate a reaction. It was also postulated that the copper ion could exert a template effect by weak π -bonding with the triple bond of the acetylene whilst providing a suitable alignment for the cycloaddition.

Another mode of behaviour of the complexes involve their reactions with Lewis bases. The products arising from these reactions depend on the complex used and the Lewis base as discussed in Chapter one.

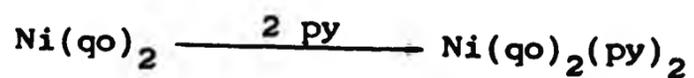
With triphenylphosphine reduction of the metal occurs if a lower oxidation state is available to the metal. In such cases products arising from a deoxygenated ligand radical are also formed.^{12,27} In the case of the nickel(II) and the zinc(II) complexes, where reduction of the metal is not favoured, iminophosphorane complexes are formed (Fig. 5.13).²⁸



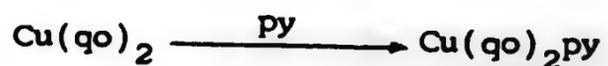
Fig. 5.13.

With amines quinoneoximato complexes undergo a variety of reactions. The type of reaction that occurs depends on both the metal complex and the type of amine (primary, secondary or tertiary) being used.

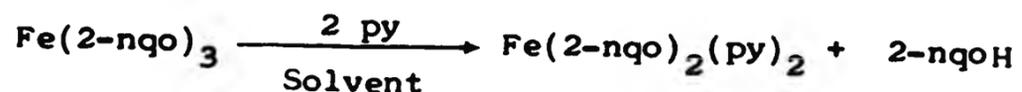
With pyridine the complexes may undergo adduct formation (Reactions 5.4 and 5.5) or internal redox behaviour may result (Reaction 5.6) depending on the nature of the metal.



Reaction 5.4.²⁹



Reaction 5.5.³

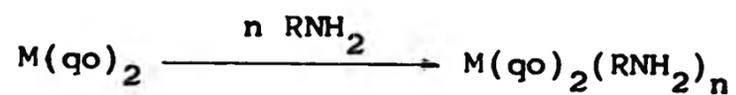


Reaction 5.6.³⁰

When primary amines are used the reactions that can occur are more complex as there is the possibility of deoxygenation of the ligand by the amine. Possible reactions with primary amines are summarised in Scheme 5.1. As the Scheme shows these reactions can be subdivided into the following categories: (i) adduct formation, (ii) internal redox, (iii) Schiff base condensation, (iv) attack on the ligand aromatic ring system and (v) condensation with the NO group.

(i) Adduct formation.

This type of reaction (e.g. Reaction 5.7) is similar to the reactions of the metal complexes with pyridine.



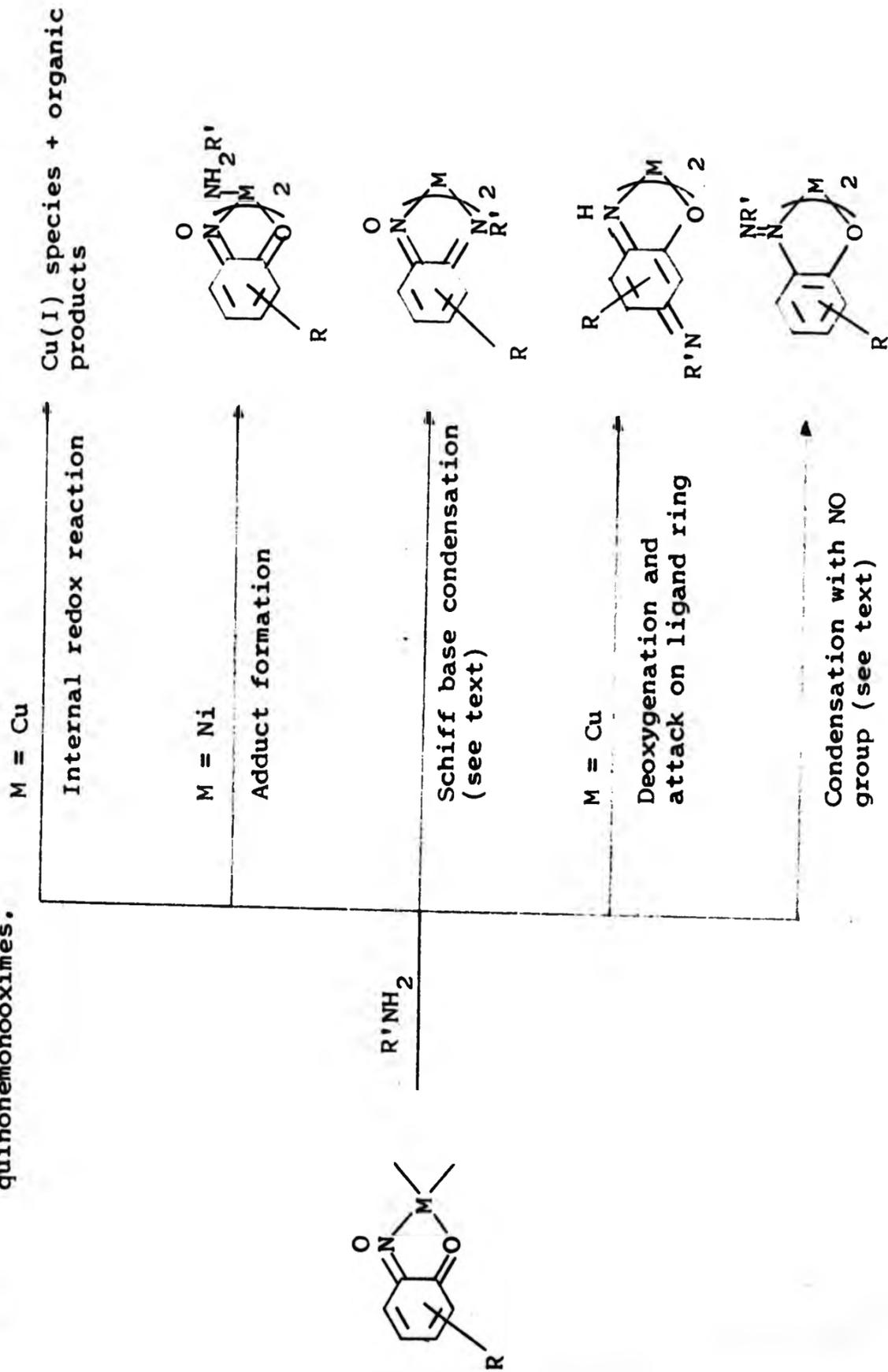
(M = Ni; n = 2, M = Cu; n = 1)

Reaction 5.7.³¹

(ii) Internal redox reaction.

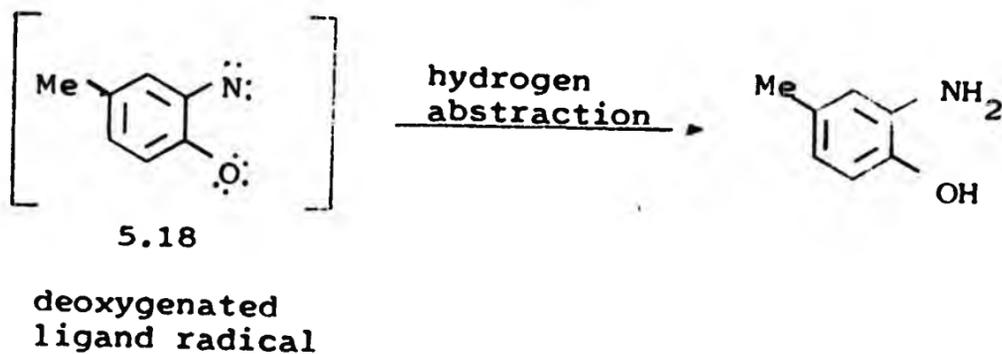
The reaction of an amine with 1,2-quinone-monooximate complexes derived from a metal capable of undergoing reduction can induce an internal redox reaction especially if forcing conditions are used (e.g. refluxing in toluene). The reactions involving 1,2-diaminoethane and copper(II) complexes give ill-

Scheme 5.1. Possible reactions of primary amines with metal complexes derived from quinonemonooximes.

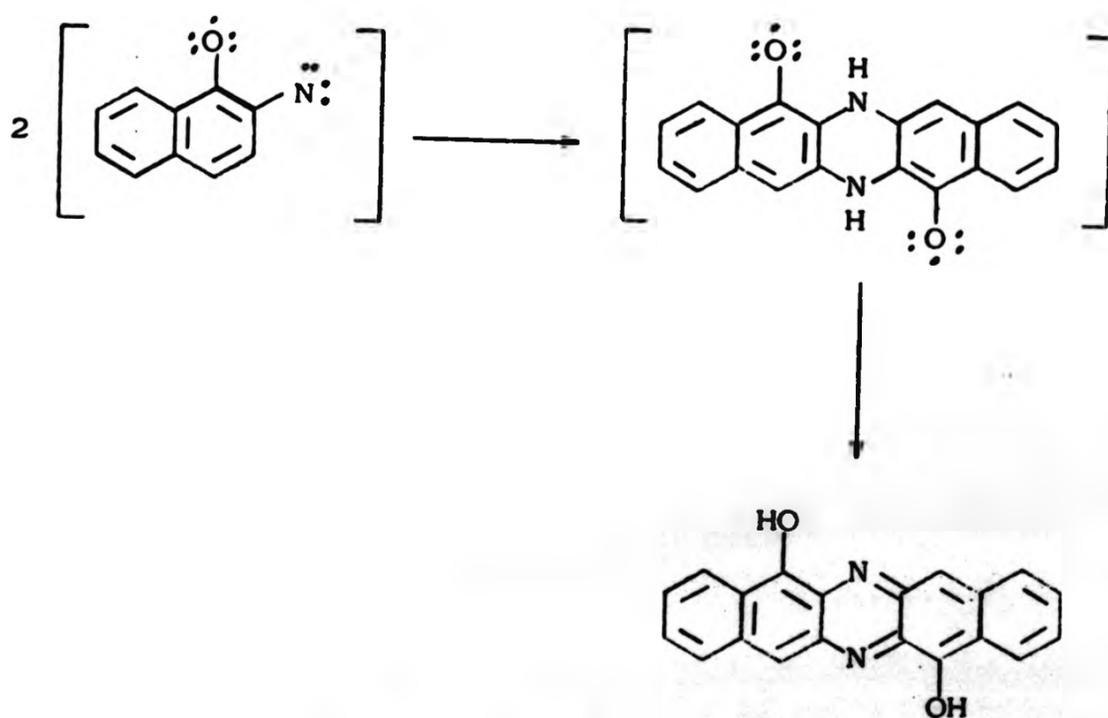


defined copper(I) solids and several organic products (e.g. benzophenazines from $\text{Cu}(1\text{-mqo})_2$). These reactions were rationalised as indicated in Scheme 5.2.³²

It is assumed that the reaction of the copper(II) complex with 1,2-diaminoethane leads to a quinoneimine complex, 5.14 and the nitrene, 5.15. The quinoneimine complex then undergoes an internal redox reaction and yields a copper(I) product and the deoxygenated ligand radical, 5.16. Further reactions of this ligand radical (e.g. Reactions 5.8 and 5.9) and of the nitrene 5.15 leads to the organic products.³³

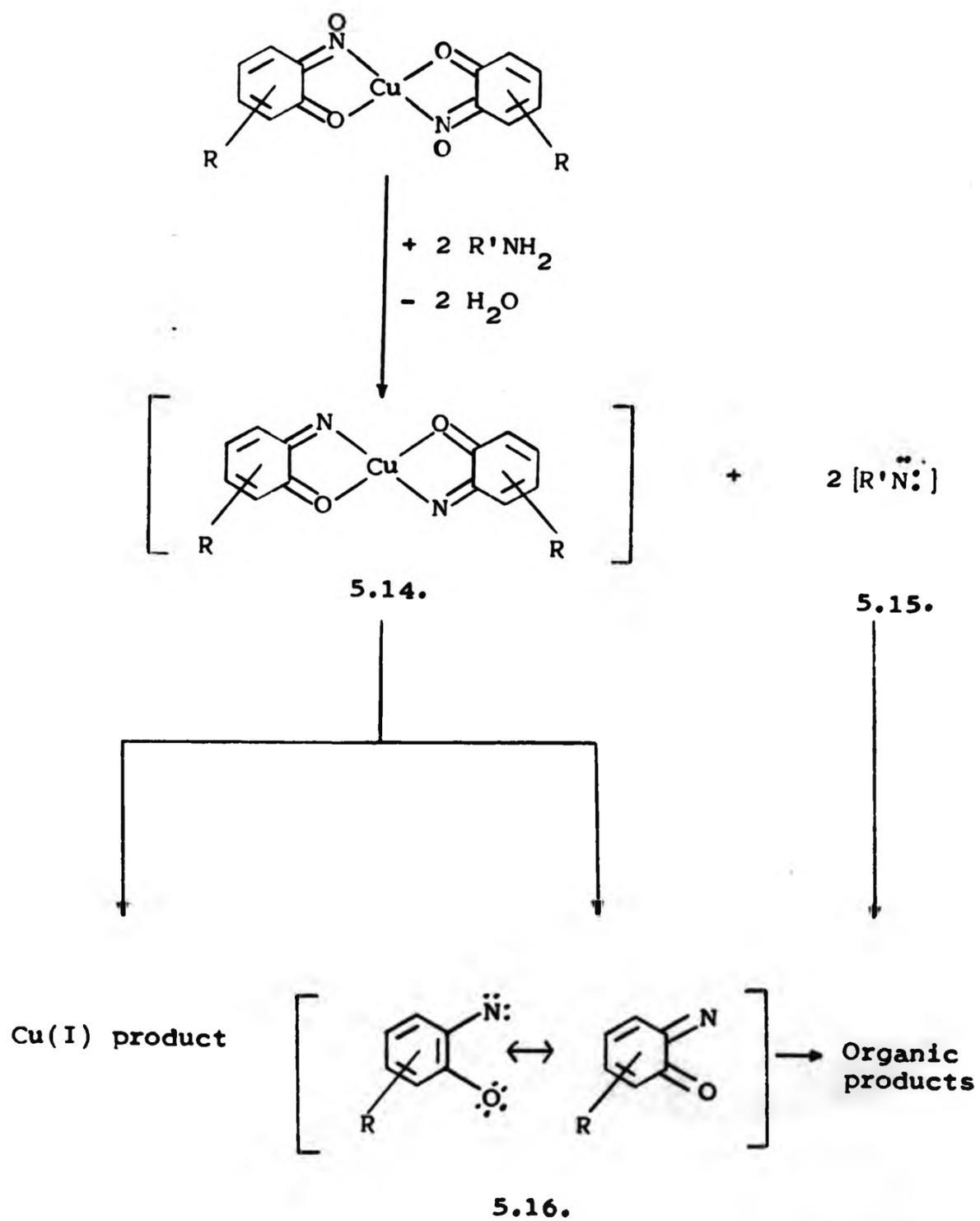


Reaction 5.8.



Reaction 5.9.

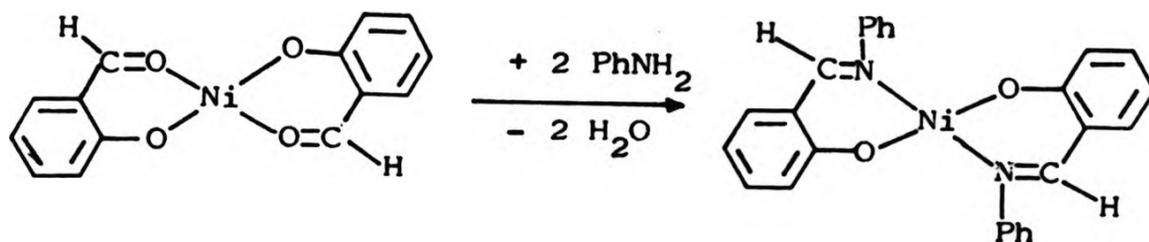
Scheme 5.2. Mechanistic rationalisation for the reaction of 1,2-diaminoethane with copper(II) complexes derived from 1,2-quinonemonooximes.



The suggested formulation of the ill-defined solid obtained from the reaction as a copper(I) product is in accord with its diamagnetic character. The proposed redox reaction parallels the behaviour of other copper(II) complexes.^{12,34} This also corresponds to the behaviour of bis(β -diketonato)copper(II) complexes towards hydroxylamine reported in Chapter 4.

(iii) Schiff base condensation.

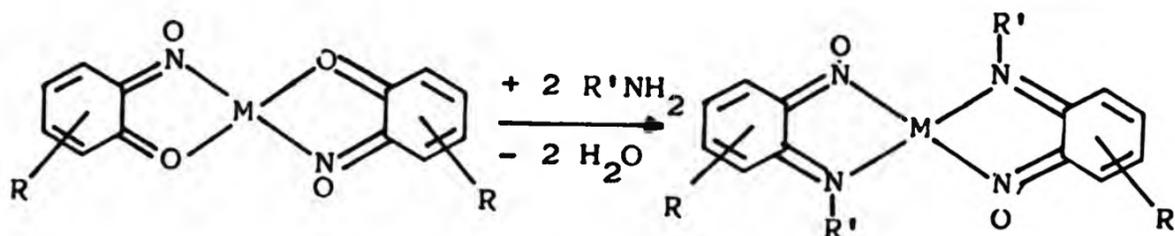
As discussed in Chapter 4, metal complexes of carbonyl compounds undergo Schiff base condensation reactions with amines as shown in Reaction 5.10.³⁵



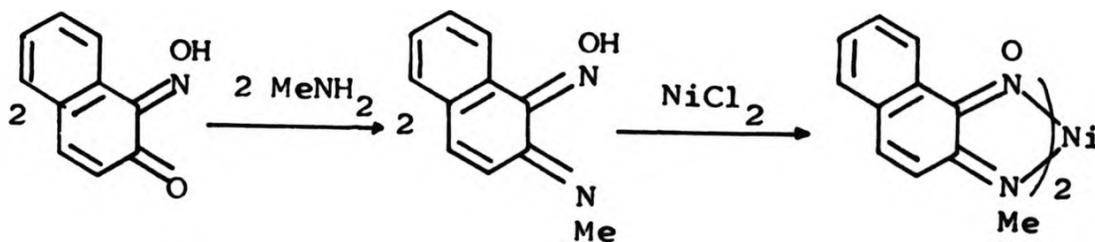
Reaction 5.10.

Such condensations are aided by the presence of the metal coordination site. This is due to the decrease of electron density on the carbon atom of the carbonyl group as a result of its coordination to the metal and hence its increased susceptibility to nucleophilic attack by the amine lone pair.³⁶ Because of the quinoneoximic character of the complexes the amine might condense with the quinone C=O to give a Schiff base type complex (Reaction 5.11). So far this type of reaction has not been observed. However, a Schiff complex of the type shown in Reaction 5.11 has

been prepared by an indirect method.³⁷ This involves the interaction of methylamine with 1,2-naphthoquinone-1-oxime and is followed by complexation of the methylamine derivative with nickel(II) chloride (Reaction 5.12).



Reaction 5.11.

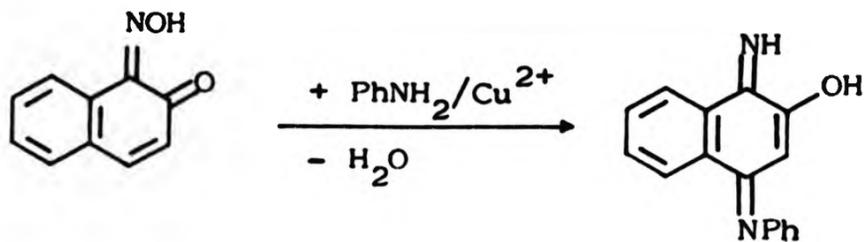


Reaction 5.12.

(iv) Attack on the ligand aromatic ring system.

A few cases are known in which a primary amine attacks a free position on the aromatic ring system of a quinoneoximic ligand coordinated to a metal.^{32,33} Prior to these it was observed that 1-nqoH reacts with aniline to give (N)1-imino-2-hydroxy-(N)4-phenylimino-1,4-naphthoquinone.³⁸ Significantly it was noted that this reaction was catalysed by copper(II) (Reaction 5.13).³⁹

Other workers found that $\text{Cu}(1\text{-nqo})_2$ reacts with aniline to give the complex illustrated in Fig. 5.17³²



Reaction 5.11.

Analogous iron complexes have been obtained from the reaction of $\text{Fe}(\text{CO})_5$ with 1-nqoH or 2-nqoH in the presence of aniline.³³

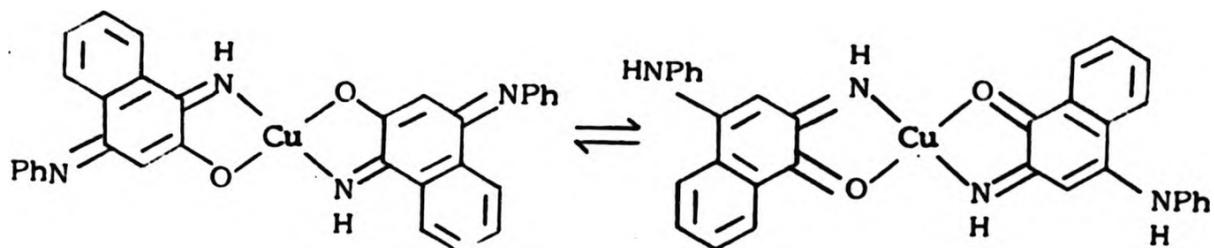
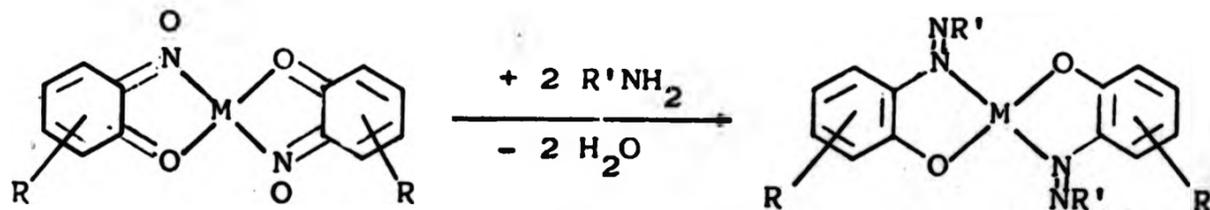


Fig. 5.17.

(v) Condensation of the amine with the NO group.

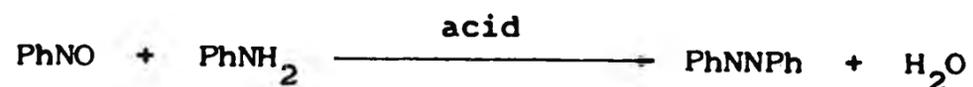
A condensation reaction between a metal complex of a quinoneminoxime and a primary amine would lead to an azo complex (e.g. Reaction 5.13).



Reaction 5.13.

Although the acid catalysed condensation of nitrobenzene with primary aromatic amines is well

known (Reaction 5.14)^{38,40,41} no such reaction has been reported for a quinoneoximato complex.



Reaction 5.14.

The wide range of behaviour of these metal complexes is clearly illustrated by the five categories of reaction described above. In the majority of cases the products identified from the reactions of metal quinonemonooximates with amines suggest that more than one of the reactions described above occur, either simultaneously and/or consecutively. As a consequence the separation of the reaction products are, as a rule, difficult and the deciphering of the reaction mechanism equally so.

5.4. Reaction of metal(II) complexes of 1,2-quinone-2-monooxime with amines.

In view of the previous results discussed in Sections 5.1-5.3 it was of interest to study the reaction of metal(II) complexes of 1,2-quinonemonooximes with amines. A greater understanding of the behaviour of these systems would provide a better foundation for their use in synthesis.

Preliminary studies on the reaction of phenylethylamine with bis(1,2-naphthoquinone-2-monooximato)copper(II) showed that di(phenylethyl)amine was formed in moderate yield and that this was accompanied by several other products. Further the reaction proceeded with the

evolution of ammonia. This novel behaviour provided the basis for the present study which was undertaken with the following aims;

- i) To investigate the reactions of various bis(quinonemonooximato)metal(II) complexes with a variety of primary amines.
- ii) To examine the reaction between $\text{Cu}(2\text{-nqo})_2$ and phenylethylamine in detail.
- iii) To study the reaction between $\text{Cu}(2\text{-nqo})_2$ with primary diamines.

5.4.1. The general reactions of metal(II) complexes of quinonemonooximes with primary amines.

The interactions of primary amines with metal(II) complexes derived from quinonemonooximes were carried out in pyridine at room temperature. From the results presented in Table 5.3 it can be seen that phenylethylamine reacts with all the bis(quinonemonooximato)copper(II) complexes to give di(phenylethyl)amine. However, when other copper(II) compounds are used (e.g. $\text{Cu}(\text{cup})_2$, CuCl_2 , $\text{Cu}(\text{MeCO}_2)_2$ and $\text{Cu}(\text{acac})_2$) no reaction occurs. Since the bis(quinonemonooximato)copper(II) complexes as well as the bis(cupferronato)copper(II) and bis(acetylacetonato)copper(II) complexes are capable of undergoing Lewis base promoted internal redox reactions, and only quinonemonooximato complexes lead to the secondary amine, the formation of the amine product cannot be accounted for in terms of this process alone. Further, it appears that the quinonemonooximato group

Table 5.3. Interaction of metal(II) complexes with primary amines.

Metal complex	Amine	Product(s)
Cu(2-nqo) ₂	phenylethylamine	di(phenylethyl)amine, dibenzo[b,i]dihydrophenazine-5,12-diol, ammonia
Cu(2-nqo) ₂	benzylamine	di(benzyl)amine ^a
Cu(2-nqo) ₂	o-anisidine	b
Cu(4-Meqo) ₂	phenylethylamine	di(phenylethyl)amine ^a
Fe(2-nqo) ₂	o-anisidine	b
Fe(2-nqo) ₂	phenylethylamine	b
Fe(1-nqo) ₂	o-anisidine	b
Fe(1-nqo) ₂	phenylethylamine	c
Cu(1-nqo) ₂	o-anisidine	b
Cu(1-nqo) ₂	phenylethylamine	di(phenylethyl)amine ^a
Cu(2-nqo) ₂	hydroxylamine	b
Cu(cup) ₂	phenylethylamine	b
Cu(MeCO ₂) ₂	phenylethylamine	b
CuCl ₂	phenylethylamine	b
Cu(acac) ₂	phenylethylamine	b

^aother products not identified

^bsecondary amine not formed

^ccomplex mixture of products

plays a specific role in the formation of the secondary amine. It is unclear what this role is precisely. It may exert an effect on the metal complex, it may provide a site for amine reaction or the radical it generates from the internal redox reaction may be specifically required for the formation of the secondary amine.

It is significant that the reaction of bis(quinone monooximate)iron(II) complexes with phenylethylamine gave a complex mixture of products which did not contain any di(phenylethyl)amine. This indicates that the reactions involving the iron complexes proceed by a different pathway from those involving the copper complexes. It shows, too, that when the secondary amine is formed the ligand (i.e. quinonemonooximate) is not the only important factor but also that the metal in the complex is equally important. Such a difference may be in accord with the fact that bis(quinonemonooximate) iron(II) complexes are known to undergo Lewis base promoted internal redox reactions only under forcing conditions.³⁰

As previously stated the nature of the amine used in the reaction with the metal complexes is also a factor in governing the products formed. For instance, phenylethylamine and benzylamine yield di(phenylethyl)amine and di(benzyl)amine respectively but o-anisidine gave no corresponding secondary amine.

The explanation may be due to the fact that phenylethylamine and benzylamine have a CH_2 group adjacent to the amine group whereas the other amines

do not. If the $-\text{CH}_2\text{NH}_2$ group takes part in the reaction (e.g. by having a hydrogen abstracted to give $-\overset{\cdot}{\text{C}}\text{NH}_2$) then amines lacking a CH_2 group adjacent to the amine group would not react in an analogous fashion to give the respective secondary amine. This is further supported by the reaction of aniline with bis(1,2-naphthoquinone-1-monooximato)copper(II). As already discussed in Section 5.1 this leads to attack on the ligand aromatic system by the amine.³²

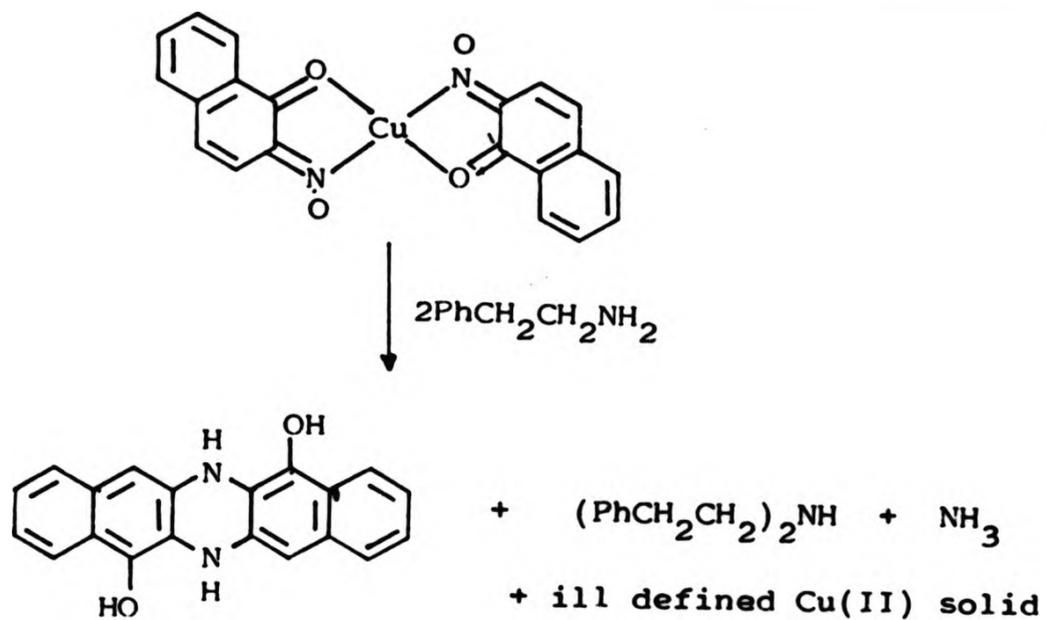
It can be concluded that the products from the reaction of metal(II) complexes with primary amines are dependant on three factors:

- i) the nature of the metal.
- ii) the type of amine (i.e. aliphatic or aromatic).
- iii) the character of the ligand in the complex.

5.4.2. The reaction of bis(1,2-naphthoquinone-2-monooximato)copper(II) with phenylethylamine.

In the previous Section it was noted that the reaction of bis(1,2-naphthoquinone-2-monooximato)copper(II) with phenylethylamine at room temperature leads to di(phenylethyl)amine. In this Section this reaction is discussed in greater detail. The product, di(phenylethyl)amine, was accompanied by the formation of an ill-defined copper(II) solid, dibenzo[b,i]dihydrophenazine-5,12-diol and ammonia (Reaction 5.15). When the reaction was carried out at 90°C a complex mixture of products was formed. This mixture could not be resolved due to its complexity but chromatographic examination showed

the absence of di(phenylethyl)amine.



Reaction 5.15.

The evolution of ammonia was indicated by connecting the reaction vessel to a 'U' tube containing a solution of phenolphthalein. After the reaction was complete the phenolphthalein had changed colour to purple. However, this colour change could result from a reaction of the phenolphthalein solution with other basic components present in the reaction system (e.g. pyridine or phenylethylamine). Because of this a control was set up. This control consisted of a solution of phenylethylamine in pyridine. After 24 hours of stirring the control the phenolphthalein had not changed colour indicating that the colour change in the initial reaction was due to the evolution of ammonia.

The copper containing solid from the reaction at room temperature shows a high proportion of copper (49.9%).

Its infrared spectrum is poorly defined with broad peaks centred at 3440, 2920, 1630, 1450 and 1390 cm^{-1} . It failed to give a mass spectrum due to its involatility. The copper in the solid is in oxidation state (II) since magnetic susceptibility measurements show that it is paramagnetic.

The system bis(1,2-naphthoquinone-2-monooximate)copper(II)-phenylethylamine was also studied in a variety of solvents (diethylether, trichlorotrifluoroethane and propan-2-ol) in order to determine the effect of solvent on the system. It was found that no reaction occurred in these solvents. This may be in part due to the poor solubility of the bis(1,2-naphthoquinone-2-monooximate)copper(II) in these solvents. In pyridine bis(1,2-naphthoquinone-2-monooximate)copper(II) is very soluble but in the other solvents the solubility is greatly reduced.

5.4.3. Reaction of bis(1,2-naphthoquinone-2-monooximate)copper(II) with diamines.

The reactions of bis(1,2-naphthoquinone-2-monooximate)copper(II) with diamines which were investigated during this study are summarised in Table 5.4. The cyclic amines were obtained by extraction and were identified by g.l.c. comparison with authentic samples. Comparative t.l.c. indicated that dibenzo[b,i]dihydrophenazine-5,12-diol was also produced. A solution of phenolphthalein in a 'U' tube connected to the apparatus changed colour indicating that ammonia was evolved.

Table 5.4. Interaction of bis(1,2-naphthoquinone-2-monooximate)copper(II) with diamines.

Diamine	Products
1,2-diaminoethane	a
1,3-diaminopropane	a
1,4-diaminobutane	pyrrolidine ^b
1,5-diaminopentane	piperidine ^b
1,8-diaminooctane	a

^aNo reaction

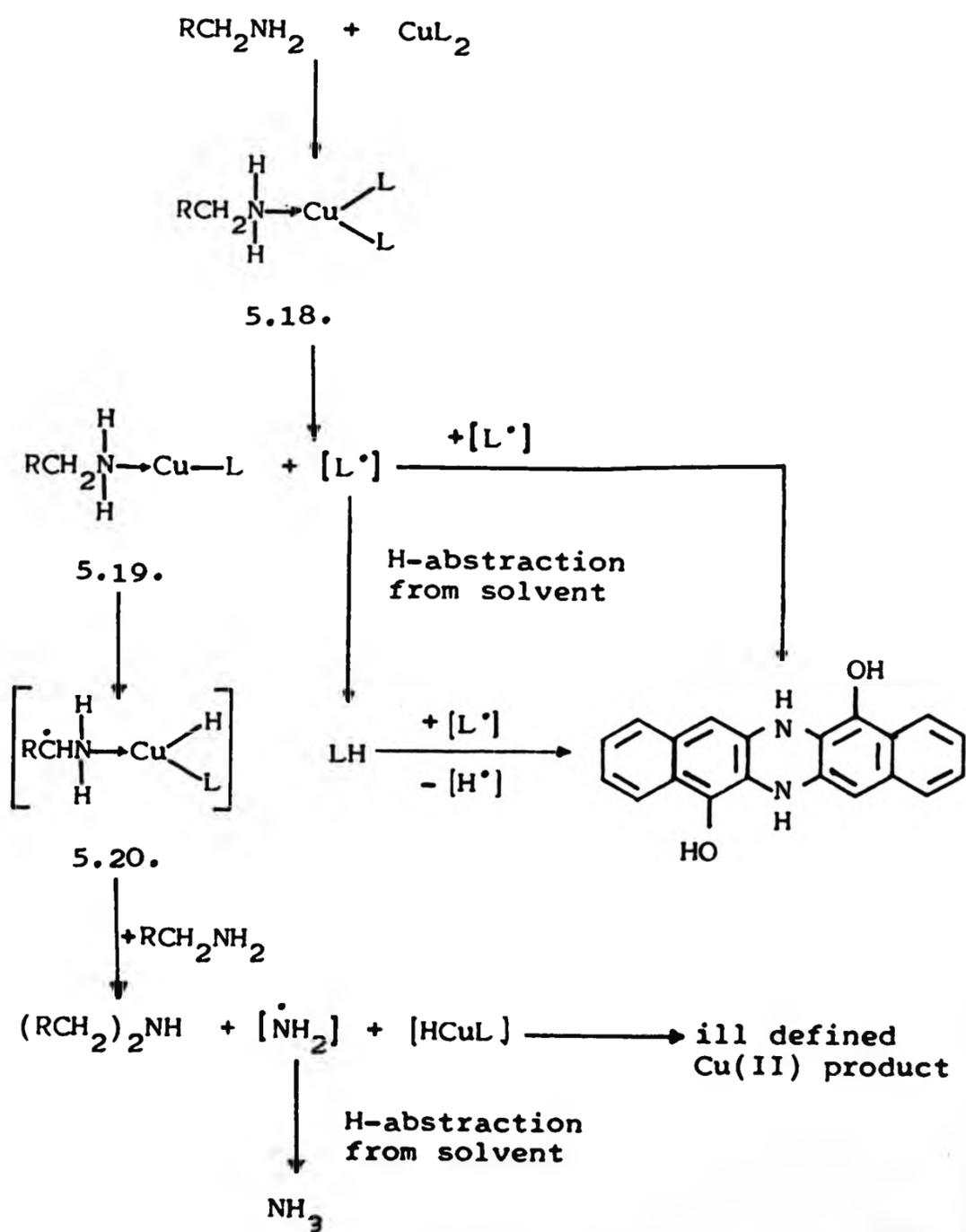
^bdibenzo[b,i]dihydrophenazine-5,12-diol
and ammonia also produced

It can be seen that cyclisation of the diamine only occurs if a 5- or 6-membered heterocyclic ring results. 1,2-Diaminoethane, 1,3-diaminopropane and 1,8-diaminooctane would give 3-, 4- and 9-membered rings respectively. It is well known that rings of this size are very difficult to produce because of ring strain.⁴³

5.5. A mechanistic rationalisation for the reactions of bis(1,2-naphthoquinone-2-monooximate)copper(II) with phenylethylamine and with diamines.

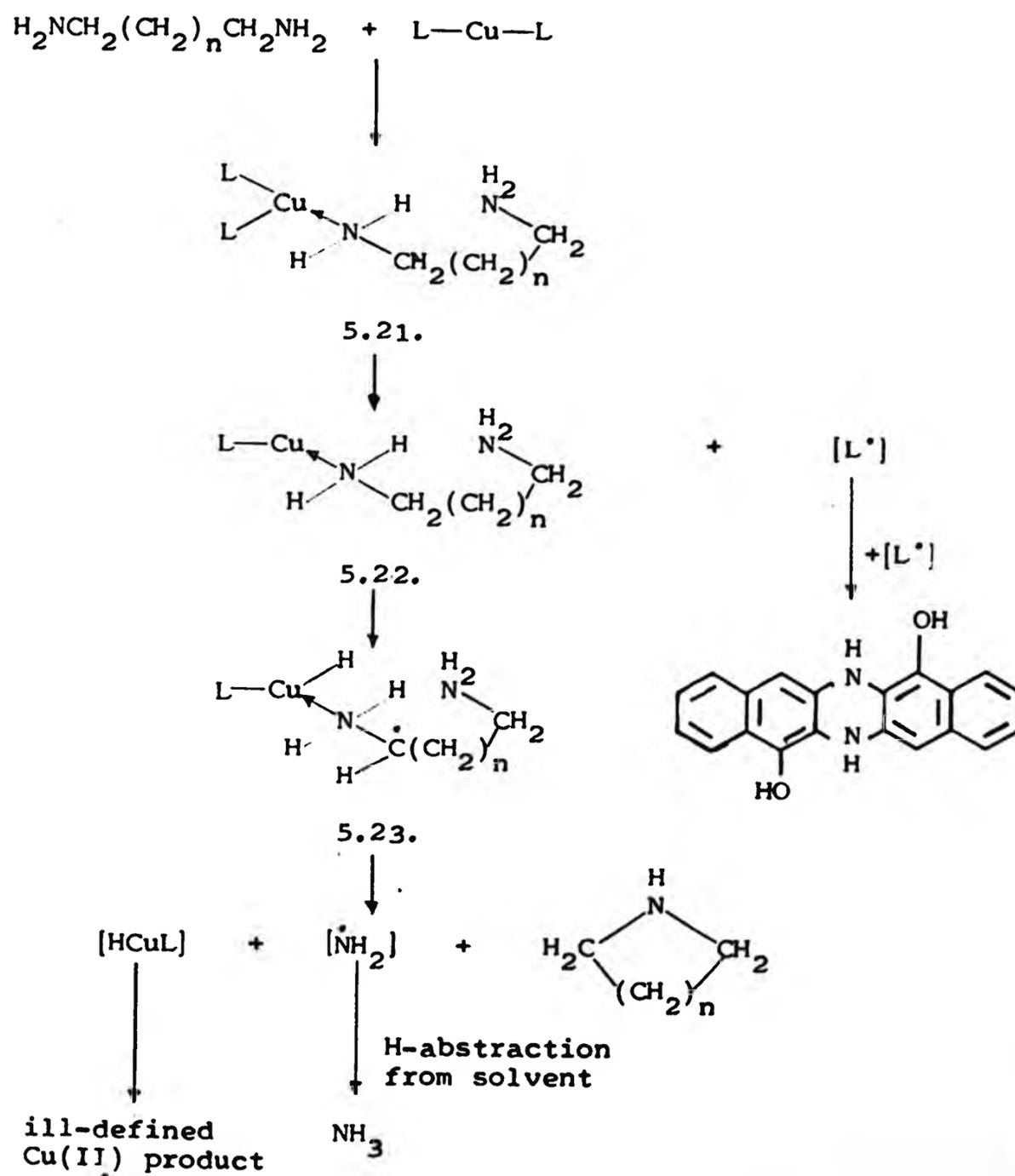
The mechanisms postulated for the reactions of bis(1,2-naphthoquinone-2-monooximate)copper(II) with phenylethylamine and with diamines are outlined in Schemes 5.3 and 5.4 respectively. In each case the

Scheme 5.3. Possible mechanistic pathways for the reaction of bis(1,2-naphthoquinone-2-monooximato)copper(II) with phenylethylamine.



R = PhCH₂, LH = 1,2-naphthoquinone-2-monooxime.
 For clarity, in formulae 5.18 - 5.20 the ligand is depicted as monodentate.

Scheme 5.4. Possible mechanistic pathways for the reaction of bis(1,2-naphthoquinone-2-monooximato)copper(II) with diamines.



LH = 1,2-naphthoquinone-2-monooxime, $n = 2, 3$.

For clarity, in formulae 5.21 - 5.23 the ligand is depicted as monodentate.

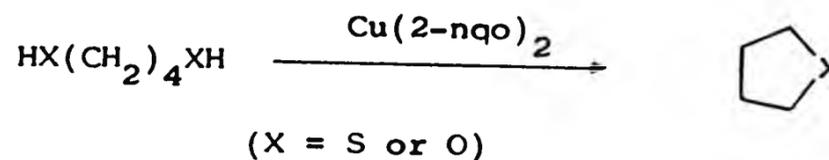
initial step involves adduct formation (5.18 and 5.21). This is followed by Lewis base promoted internal redox reactions to give the copper(I) species 5.19 and 5.22 along with the ligand radical L^\cdot . The ligand radical can either abstract hydrogen from the solvent to form LH, which is attacked by further L^\cdot to give dibenzo[b,i] dihydrophenazine-5,12-diol or, but less likely, two L^\cdot radicals could couple to give this compound.

The next step involves hydrogen atom migration from the α - CH_2 group of the amine to the copper. The copper is thus reoxidised to copper(II) (5.20 and 5.23) The copper(II) species 5.20, now reacts with another molecule of phenylethylamine to give di(phenylethyl)amine, $\dot{N}H_2$ and the copper-containing species $HCuL$. The species 5.23 undergoes an intramolecular reaction which results in the heterocycle, $HCuL$ and $\dot{N}H_2$. In both systems the radical $\dot{N}H_2$ abstracts hydrogen from the solvent to give ammonia. The ill-defined copper(II) product may arise from the reaction of $HCuL$ with other species present.

5.6. Conclusion.

The reaction of bis(quinonemonooximato)copper(II) complexes with amines shows some interesting and potentially useful chemistry. With primary amines having a CH_2 group adjacent to the amino group the reaction leads to secondary amines and with diamines the reaction can lead to cyclic amines if the ring is not strained. The reactions occur readily. Yields are

moderate but no optimisation of yields has been attempted. The detection of dibenzo[b,i]dihydrophenazine-5,12-diol as a product from the reactions is indicative of internal redox behaviour. The nature of the copper-containing moieties arising from these reactions is unclear and further studies would be needed to determine this. This work could be extended to compounds that contain groups other than NH_2 e.g. SH or OH. If these compounds reacted in an analogous fashion (e.g. Reaction 5.16) then the reaction would have much synthetic potential and could be useful in the synthesis of a variety of substituted heterocyclic compounds.



Reaction 5.16

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CHAPTER SIX

6.1. General.

The reagents and solvents used were generally of GPR or 'AnalaR' grade and were used without further purification.

The kinetic experiments were carried out in 'AnalaR' pyridine which was used as supplied.

Silica gel absorbent used in column chromatography was of 70-230 mesh and supplied by B.D.H. Chemicals Ltd. Pre-coated silica plates of 0.25 mm thickness were used for thin layer chromatography.

6.2. Analytical techniques.

Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services at the Polytechnic of North London.

Metal analyses were carried out by atomic absorption spectroscopy on a Pye Unicam SP9 machine at the Polytechnic of North London. Wet oxidation was achieved by heating a small amount (ca. 0.1g) of the material in a mixture of concentrated nitric/sulphuric acid (1:1) (10 cm³), plus a few drops of 100 volume hydrogen peroxide.

6.3. Physical techniques:

Infrared spectroscopy.

Infrared spectra over the region 600-4000 cm⁻¹ were recorded on a Pye Unicam SP3-200 spectrophotometer. The spectra were recorded as KBr discs.

Electronic spectroscopy.

Ultra violet and visible spectra in the region 200-900 nm were recorded on a Varian DMS90 programmable spectrophotometer.

Nuclear magnetic resonance spectroscopy.

^1H nuclear magnetic resonance spectra were obtained using a Perkin Elmer R12B 60 MHz spectrometer and a Bruker WP80 MHz Fourier transform spectrometer at the Polytechnic of North London. Tetramethylsilane was used as the standard reference.

Mass spectrometry.

Mass spectra were recorded using a modified AEI MS9 double focussing spectrometer at the Polytechnic of North London.

Gas liquid chromatography.

Gas liquid chromatograms were obtained using Pye Unicam instruments at the Polytechnic of North London. A stainless steel column 1.8 m long and 2.2 mm internal diameter packed with 5% Apiazon L on Chromosorb was used. 0.5 μl Of sample was injected for each chromatogram with an injection temperature of 190 $^{\circ}\text{C}$ and a column temperature of 155 $^{\circ}\text{C}$. Nitrogen was used as the carrier gas with flame ionisation detection.

Relative molecular mass measurements.

Determination of the relative molecular masses were carried out using an $\mu\text{billometer}$ calibrated with benzil in chloroform.

Variable temperature susceptibility measurements.

Variable temperature susceptibility measurements were recorded on a Newport Instrument variable temperature Gouy balance.

6.4. Metal complexes of N-nitrosophenylhydroxylamine.

6.4.1. Reaction of ammonium N-nitrosophenylhydroxylamine with metal(II) sulphates (M= Zn, Cu, Mn, Co, Ni and Fe).

The hydrated metal(II) sulphate (ca. 2.5 g, 1 mol equiv.) was stirred with ammonium N-nitrosophenylhydroxylamine (2 mol equiv.) in water (300 cm³) for 4 h.¹ Bis(cupferronato)metal(II) was filtered off, washed with water and dried in vacuo. See Tables 6.1 and 6.2 for analyses, yields and other data.

6.4.2. Reaction of ammonium N-nitrosophenylhydroxylamine with metal(III) sulphates and/or chlorides (M = Fe, Cr and V).

The hydrated metal(III) sulphate and/or chloride (ca. 2.5 g, 1 mol equiv.) was stirred with ammonium N-nitrosophenylhydroxylamine (3 mol equiv.) in water (300 cm³) for 4 h.² The solid product was filtered off, washed with water and dried in vacuo. The solids had ill-defined infrared spectra and elemental analyses

Table 6.1. Analytical data for bis(cupferronato)metal(II) complexes and tris(cupferronato)iron(III) complex.

Complex	Yield (%)	Found (%)				Calc. (%)			
		C	H	N	M	C	H	N	M
Fe(cup) ₂	99	43.9	3.1	16.5	16.4	43.6	3.0	17.0	17.0
Zn(cup) ₂	76	42.2	3.3	16.4	19.4	42.5	2.9	16.5	19.2
Ni(cup) ₂	97	41.3	3.3	15.7	16.8	43.3	3.0	16.8	17.6
Cu(cup) ₂	98	42.9	3.0	16.6	18.7	42.7	3.0	16.6	18.8
Mn(cup) ₂	94	43.3	3.1	16.9	16.7	43.8	3.0	17.0	16.7
Co(cup) ₂	62	43.6	3.2	16.3	17.6	43.2	3.0	16.8	17.7
Fe(cup) ₃	93	46.4	3.0	18.1	12.0	46.2	3.2	18.0	12.0
Cu(cup) ₂ (py) ^a	65	48.8	3.4	16.8	15.2	48.9	3.6	16.8	15.2
Ni(cup) ₂ (py) ₂ ^a	60	53.5	4.4	17.4	12.2	53.8	4.1	17.1	12.0
Co(cup) ₂ (py) ₂ ^a	71	49.6	4.0	16.4	14.0	49.5	3.6	17.0	14.3

^aComplexes that have not been reported previously

Table 6.1 (continued).

Complex	Yield (%)	Found (%)			Calc. (%)		
		C	H	N	C	H	N
Mn(cup) ₂ (py) ₂ ^a	68	52.5	5.1	16.8	52.1	4.0	16.6
Fe(cup) ₂ (py) ₂ ^a	59	56.1	3.7	16.2	56.2	3.9	16.4
Cr(cup) ₃	-	61.2	3.5	9.6	55.0	3.3	9.2
V(cup) ₃	-	62.0	3.6	9.9	55.3	3.3	9.2

^aComplexes that have not been reported previously

Table 6.2. Physical properties of bis(cupferronato) metal(II) complexes and tris(cupferronato) iron(III) complex.

Complex	$\mu_{\text{eff}}/\text{B.M.}$ (20 °C)	Reflectance spectra $\lambda_{\text{max}}/\text{nm}$	M_r^a	
			Found	Calc.
Fe(cup) ₂	5.11	b	319	330
Zn(cup) ₂	c	-	330	339
Ni(cup) ₂	2.83	660,460	331	333
Cu(cup) ₂	1.82	550,769	342	337
Mn(cup) ₂	6.19	b	321	329
Co(cup) ₂	3.46	460,550,650	321	333
Fe(cup) ₃	5.92	b	455	467
Ni(cup) ₂ (py) ₂	2.72	400,600,880,1075	473	491
Co(cup) ₂ (py)	4.01	350,460,500,550	394	412
Mn(cup) ₂ (py) ₂	6.10	b	473	487
Fe(cup) ₂ (py) ₂	5.09	b	455	488
Cu(cup) ₂ (py)	1.80	360,570,750	401	416

^adetermined in chloroform solution

^bill-defined

^cdiamagnetic

were not consistent with a $M(\text{cup})_3$ formulation, except for $\text{Fe}(\text{cup})_3$. See Tables 6.1 and 6.2 for analysis, yields and other data on $\text{Fe}(\text{cup})_3$.

6.4.3. Reaction of bis(cupferronato)metal(II) complexes with pyridine.

$M(\text{cup})_2$ ($M = \text{Cu, Mn, Co, Ni and Fe}$) (ca. 1.0 g) and pyridine (25 cm^3) were stirred for 5 h. Light petroleum (b.p. $60-80^\circ\text{C}$) (50 cm^3) was added and the resulting mixture filtered, to give the adduct. This was washed with light petroleum and dried in vacuo. See Tables 6.1 and 6.2 for analyses, yields and other data.

When $M = \text{Zn}$ unchanged $\text{Zn}(\text{cup})_2$ (>95 % recovery) was obtained on filtration.

6.4.4. Reaction of tris(cupferronato)iron(III) with pyridine.

$\text{Fe}(\text{cup})_3$ (2.0 g) and pyridine (25 cm^3) were stirred for 5 h. Light petroleum (b.p. $60-80^\circ\text{C}$) (50 cm^3) was added and the resulting mixture filtered, to give $\text{Fe}(\text{cup})_2(\text{py})_2$. This was washed with light petroleum and dried in vacuo. See Tables 6.1 and 6.2 for analysis, yields and other data.

G.l.c of the filtrate gave benzene (0.14 g, 41 %) and aniline (0.16 g, 42 %) (identified and estimated by comparison with authentic samples). Chromatography of the filtrate (silica gel) gave, with light petroleum (b.p. $60-80^\circ\text{C}$)-toluene, 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (Found: C, 80.0;

H, 5.3; N, 11.6. Calc. for $C_{24}H_{19}N_3O$: C, 78.9; H, 5.2; N, 11.5 %) (confirmed by m.s. and t.l.c. comparison with authentic sample, m.pt. $203^{\circ}C$, lit. m.pt.³ $204-205^{\circ}C$).

6.4.5. Reaction of bis(cupferronato)metal(II) complexes with triphenylphosphine.

$M(cup)_2$ ($M = Zn, Mn, Co, Ni$ and Fe) (2.5 g, 1 mol equiv.) was added to a solution of triphenylphosphine (8.0 g, 4 mol equiv.) in acetone (200 cm^3). After 12 h unchanged $M(cup)_2$ (>95 % recovery) was filtered off.

6.4.6. Reaction of bis(cupferronato)copper(II) complex with triphenylphosphine in various solvents.

Triphenylphosphine (8.0g, 4 mol equiv.) was added to a suspension of bis(cupferronato)copper(II) (2.5 g, 1 mol equiv.) in different solvents, S. (S= acetone, pyridine, trichlorotrifluoroethane and propan-2-ol.) After 12 h yellow diamagnetic cupferronatobis(triphenylphosphine)copper(I) (see Table 6.3 for typical analysis) was filtered off, washed with the solvent and dried in vacuo.

Using acetone, pyridine and propan-2-ol as solvents, g.l.c. of the filtrate indicated the presence of benzene and aniline (identified and estimated by comparison with authentic samples). Chromatography of the filtrate (silica gel) using light petroleum (b.p $60-80^{\circ}C$) as eluant gave unchanged triphenylphosphine (identified by t.l.c.).

Elution with light petroleum (b.p. 60-80 °C)-toluene gave, when S = acetone and pyridine only, 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (Found: C, 78.8; H, 5.3; N, 11.4. Calc. for $C_{24}H_{19}N_3O$: C, 78.9; H, 5.2; N, 11.5 %) (confirmed by m.s. and t.l.c. comparison with authentic sample, m.pt. 204 °C, lit. m.pt.³ 204-205 °C). Elution with toluene gave triphenylphosphine oxide (identified by t.l.c.).

When S = trichlorotrifluoroethane chromatography of the filtrate (silica gel) gave, with light petroleum (b.p. 60-80 °C) as eluant unchanged triphenylphosphine (identified by t.l.c.). Elution with toluene gave triphenylphosphine oxide (identified by t.l.c.).

Elution with toluene-ethyl acetate gave N-phenyltriphenylimidophosphorane (Found: C, 81.8; H, 5.6; N, 3.9; P, 8.7. Calc. for $C_{24}H_{20}NP$: C, 81.6; H, 5.7; N, 4.0; P, 8.8 %) (confirmed by t.l.c. comparison with authentic sample, m.pt. 129 °C, lit. m.pt.⁴ 129-130 °C). See Table 6.3 for yields and other data.

6.4.7. Reaction of tris(cupferronato)iron(III) complex with triphenylphosphine.

Triphenylphosphine (4.00 g, 4 mol equiv.) was added to a suspension of tris(cupferronato)iron(III) (1.90 g, 1 mol equiv.) in acetone (200 cm³). After 28 days orange bis(cupferronato)di(triphenylphosphine)iron(II) (0.90 g, 22 %) (Found: C, 67.5; H, 4.5; N, 6.5; P, 7.5; Fe, 6.6. $C_{48}H_{40}N_4O_4P_2Fe$ requires : C, 67.4; H, 4.7; N, 6.6; P, 7.3; Fe, 6.6 %) was filtered off, washed with

acetone and dried in vacuo. G.l.c. of the filtrate indicated the presence of benzene (0.13 g, 41%) and aniline (0.15 g, 42 %) (identified and estimated by comparison with authentic samples). Chromatography of the filtrate (silica gel) gave, with light petroleum (b.p. 60-80 °C as eluant, unchanged triphenylphosphine (3.70 g, 92 %) (identified by t.l.c.). Elution with light petroleum (b.p. 60-80 °C)-toluene gave 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (0.02 g, 14 %) (Found: C, 78.6; H, 5.4; N, 11.5. Calc for $C_{24}H_{19}N_3O$: C, 78.9; H, 5.2; N, 11.5 %) (confirmed by m.s. and t.l.c. comparison with authentic sample, m.pt. 204 °C, lit. m.pt.³ 204-205 °C). Elution with toluene gave unreacted tris (cupferronato)iron(III) (1.60 g, 84 %) (identified by t.l.c.) and triphenylphosphine oxide (0.30 g, 7 %) (identified by t.l.c.).

6.4.8. Decomposition of N-nitrosophenylhydroxylamine in pyridine.

N-nitrosophenylhydroxylamine (2.0 g) was stirred in pyridine (50 cm³) at 20 °C. After 48 h chromatographic work up of the mixture gave benzene (0.48 g, 42 %) aniline (0.56 g, 41 %) and 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (0.16 g, 12 %) (confirmed by t.l.c. and g.l.c. comparison to authentic samples).

6.4.9. Reaction of N-nitrosophenylhydroxylamine with triphenylphosphine in various solvents.

Triphenylphosphine (5.0 g, 1 mol equiv.) was added to a solution of N-nitrosophenylhydroxylamine (2.0 g,

1 mol equiv.) in different solvents, S. (S = acetone, trichlorotrifluoroethane and propan-2-ol), at 20 °C.

Using acetone and propan-2-ol as solvents, g.l.c. of the filtrate indicated the presence of benzene and aniline (identified and estimated by comparison with authentic samples, see Table 6.3 for yields). Chromatography of the solution (silica gel) using light petroleum (b.p. 60-80 °C) as eluant gave unchanged triphenylphosphine (identified by t.l.c.). Elution with light petroleum (b.p. 60-80 °C)-toluene gave, when S = acetone only, 2-hydroxy-5-phenylamino-2,4-diphenylimino-1,4-benzoquinone (Found : C, 78.9; H, 5.4; N, 11.6. Calc. for $C_{24}H_{19}N_3O$: C, 78.8; H, 5.2; N, 11.5 %) (confirmed by m.s. and t.l.c. comparison with authentic sample, m.pt. 204 °C, lit. m.pt.³ 204-205 °C). Elution with toluene gave triphenylphosphine oxide (identified by t.l.c.).

When S = trichlorotrifluoroethane chromatography of the solution gave, with light petroleum (b.p. 60-80 °C) as eluant unchanged triphenylphosphine (identified by t.l.c.). Elution with toluene gave triphenylphosphine oxide (identified by t.l.c.). Elution with toluene-ethyl acetate gave N-phenyltriphenylimidophosphorane (Found: C, 81.7; H, 5.8; N, 4.0; P, 8.9. Calc. for $C_{24}H_{20}NP$: C, 81.6; H, 5.7; N, 4.0; P, 8.8 %) (confirmed by t.l.c. comparison with authentic sample, m.pt. 129 °C, lit. m.pt.⁴ 129-130 °C). See Table 6.3 for yields and other data.

Table 6.3. Yield of products from the reactions of $\text{Cu}(\text{cup})_2$ (2.5 g) with Ph_3P (8.0 g) and cupH (2.0 g) with Ph_3P (5.0 g).

Solvent	Products wt. in g (% yield)						
	$\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2^a$	PhNH_2	PhH	(3)	$\text{PhN}=\text{PPh}_3$	Ph_3PO	Ph_3P
acetone ^b	5.30(98)	0.28(40)	0.24(42)	0.08(11)	-	4.00(47)	0.20(3)
pyridine ^b	5.20(97)	0.30(43)	0.24(42)	0.08(11)	-	3.80(45)	0.60(8)
acetone/ aniline (50:1) ^b	4.00(75)	0.33(47)	0.13(22)	0.14(20)	-	4.20(49)	1.00(13)
$\text{CCl}_3\text{CF}_3^b$	5.20(97)	-	-	-	2.48(95)	1.20(15)	1.08(14)
propan-2-ol ^b	5.20(97)	0.34(49)	0.28(48)	-	-	3.10(37)	1.10(14)
acetone ^c	-	0.55(41)	0.49(43)	0.14(10)	-	1.41(26)	3.50(70)
$\text{CCl}_3\text{CF}_3^c$	-	-	-	-	4.86(95)	0.85(16)	0.59(12)
propan-2-ol ^c	-	0.67(50)	0.55(49)	-	-	3.98(74)	1.25(25)

^a typical analysis, Found: C, 70.8; H, 4.8; Cu, 8.7; N, 4.2; P, 8.5.

$\text{C}_{42}\text{H}_{35}\text{CuN}_2\text{O}_2\text{P}_2$ requires: C, 69.6; H, 4.8; Cu, 8.8; N, 3.9; P, 8.5%

^b for the reaction of $\text{Cu}(\text{cup})_2$ with Ph_3P

^c for the reaction of cupH with Ph_3P

6.4.10. Reaction of bis(cupferronato)copper(II) with hydroxylamine.

Hydroxylamine (1.0 g, 2.5 mol equiv.) in methanol (50 cm³) was added to a stirred suspension of bis(cupferronato)copper(II) (4.0 g, 1 mol equiv.) in methanol (150 cm³). After 6 h pale green hydroxylaminebis(cupferronato)copper(II) (3.9 g, 89 %) (Found : C, 39.2; H, 3.2; Cu, 17.0; N, 18.7. C₁₂H₁₃CuN₅O₅ requires : C, 38.9; H, 3.5; Cu, 17.1; N, 18.9 %) was filtered off, washed with methanol and dried in vacuo.

6.5. Reactions of hydroxylamine with bis(β -diketonato) metal(II) complexes.

6.5.1. Reagents

Bis(β -diketonato)copper(II) complexes were prepared by established techniques^{5,6} from the reaction of copper(II) acetate with the β -diketone in a basic alcoholic medium. The bis(β -diketonato) complexes of zinc(II), cobalt(II) and nickel(II) were also prepared by standard methods.⁷⁻¹⁰ The characterisation of the prepared complexes is summarised in Table 6.4.

3,5-Dimethylisoxazole was obtained from B.D.H. 3-Methyl-5-phenylisoxazole and 3-methyl-5-trifluoromethyl isoxazole were prepared by the action of hydroxylamine on benzoylacetone and 1,1,1-trifluoroacetylacetone respectively.¹¹

6.5.2. Preparation of hydroxylamine solution.

Hydroxylamine hydrochloride (1.74 g, 25 mmol) was dissolved in dry methanol (50 cm³) at 0 °C. While maintaining the temperature at 0 °C sodium metal (0.70 g, 30 mmol) was added slowly to the solution. After complete addition of the sodium the precipitated sodium chloride was removed by filtration to yield a clear solution of hydroxylamine.

6.5.3. Action of hydroxylamine on bis(β -diketonato) metal(II) complexes at 20 °C (M = Cu, Ni and Zn).

Hydroxylamine (ca. 0.83 g, 2.5 mol equiv.) in

Table 6.4. Analysis of bis(β -diketonato)metal(II) complexes.

Complex	Found (%)			Calc. (%)		
	C	H	M	C	H	M
Cu(acac) ₂	45.8	5.3	24.3	45.9	5.4	24.3
Cu(bzac) ₂	65.0	4.9	16.4	65.2	4.7	16.5
Cu(tfac) ₂	32.8	2.6	17.1	32.5	2.2	17.2
Cu(eaa) ₂	44.8	5.7	20.1	44.8	5.6	19.7
Ni(acac) ₂ (H ₂ O) ₂	41.1	6.4	20.2	41.0	6.2	20.0
Ni(bzac) ₂ (H ₂ O) ₂	57.4	5.0	14.0	57.6	5.3	14.1
Ni(tfac) ₂ (H ₂ O) ₂	28.1	3.0	13.9	27.8	2.8	13.4
Ni(eaa) ₂ (H ₂ O) ₂	41.0	6.2	16.6	40.9	6.3	16.5
Zn(acac) ₂ (H ₂ O)	42.7	5.9	23.0	42.7	5.7	23.1
Zn(bzac) ₂ (H ₂ O)	59.0	5.3	16.3	59.2	5.0	16.0
Co(acac) ₂	47.0	5.5	22.0	46.7	5.4	22.9

dry methanol (50 cm^3) at 0°C was added slowly to a suspension of bis(β -diketonato)metal(II) hydrate (ca. 3.0 g, 1 mol equiv.) in dry methanol (100 cm^3) at 20°C . Immediately ammonia was liberated. After 24 h the adduct or monooximate in poor yield was filtered off, washed with methanol ($3 \times 15 \text{ cm}^3$) and dried in vacuo. See Table 6.5 for analyses, yields and other data.

6.5.4. Action of hydroxylamine on bis(β -diketonato) metal(II) complexes at 0°C (M = Cu, Ni and Zn).

Hydroxylamine (ca. 0.83 g, 2.5 mol equiv.) in dry methanol (50 cm^3) at 0°C was added slowly to a suspension of bis(β -diketonato)metal(II) hydrate (ca. 3.0 g, 1 mol equiv.) in dry methanol (100 cm^3) at 0°C . After 24 h the adduct or monooximate was filtered off, washed with methanol ($3 \times 15 \text{ cm}^3$) and dried in vacuo. Analyses, yields and other data are given in Table 6.6.

M=Cu. The filtrate and washings were taken to dryness at $20^\circ\text{C}/20 \text{ mmHg}$ and the residue extracted with chloroform (100 cm^3). Concentration of the chloroform solution to 20 cm^3 followed by addition of diethyl ether (150 cm^3) afforded the isoxazole. Analyses, yields and other data are given in Table 6.7.

Hydroxylamine (ca. 0.83 g, 2.5 mol equiv.) in dry methanol (50 cm^3) at 0°C was added slowly to a suspension of bis(2,4-pentanedionato)cobalt(II) (ca. 3.0 g, 1 mol equiv.) in dry methanol (100 cm^3) at 0°C . After 24 h unreacted bis(2,4-pentanedionato)cobalt(II) was recovered (>95 %).

Table 6.5. Analytical and other data for bis(β -diketonato)metal(II)-hydroxylamine adducts and (monooximate)metal complexes obtained from the reaction of hydroxylamine with bis(β -diketonato)metal(II) complexes at 20 °C

Complex	Yield (%)	Found (%)			Requires (%)			μ_{eff} (B.M.) (20 °C)	
		C	H	N	C	H	N		
Ni(acac) ₂ (NH ₂ OH) ₂	41	37.3	6.0	9.1	18.0	6.2	8.7	18.2	2.70
Ni(bzac) ₂ (NH ₂ OH) ₂	40	53.5	5.0	6.1	13.2	5.4	6.3	13.1	2.71
Zn(acac) ₂ (NH ₂ OH) ₂	20	40.5	5.2	4.4	30.0	5.8	4.7	21.9	a
Cu(acacM) ₂	40	45.5	5.0	9.0	20.0	5.1	8.9	20.1	1.83
Cu(bzacM)OH	38	42.5	5.0	5.1	24.7	4.8	5.6	25.2	1.87

^a diamagnetic.

Table 6.6. Analytical and other data for bis(β -diketonato)metal(II)-hydroxylamine adducts and (monooximate)metal complexes obtained from the reaction of hydroxylamine with bis(β -diketonato)metal(II) complexes at 0 °C.

Complex	Yield (%)	Found (%)			Requires (%)			μ_{eff} (B.M.) (20 °C)		
		C	H	N	M	C	H		N	M
Ni(acac) ₂ (NH ₂ OH) ₂	90	37.7	6.0	9.0	18.1	37.2	6.2	8.7	18.2	2.74
Ni(bzac) ₂ (NH ₂ OH) ₂	89	53.5	5.2	6.5	13.0	53.7	5.4	6.3	13.1	2.69
Ni(tfac) ₂ (NH ₂ OH) ₂	85	28.1	3.0	6.2	13.5	27.9	3.2	6.5	13.5	2.70
Zn(acac) ₂ (NH ₂ OH)	70	40.6	5.2	4.3	21.9	40.5	5.8	4.7	21.9	a
Zn(bzac) ₂ (NH ₂ OH)	69	56.9	5.3	3.0	15.8	57.1	5.0	3.3	15.5	a
Cu(acacM) ₂	75	46.5	5.5	8.4	19.9	45.6	5.1	8.9	20.1	1.81
Cu(bzacM)OH	85	41.3	5.2	5.2	25.0	42.9	4.8	5.6	25.2	1.80
Cu(tfacM)OH	78	23.9	2.6	5.3	26.0	24.1	2.4	5.6	25.5	1.80

^adiamagnetic

Table 6.7. Analytical data for isoxazoles and isoxazolines.

Compound	Yield (%)	Found (%)		Calc. (%)		Other data
		C	H	C	H	
3-phenyl-5-methylisoxazoline.	45	68.0	6.2	67.8	6.2	7.9 a
3-trifluoromethyl-5-methylisoxazoline.	44	35.2	3.1	35.5	3.5	8.3 a
3-phenyl-5-methylisoxazole.	40	76.0	5.2	75.5	5.6	8.8 a,b,c
3-trifluoromethyl-5-methylisoxazole.	46	40.1	2.3	39.7	2.6	9.3 a,b,d

^ai.r. spectroscopy.

^b¹H n.m.r. spectroscopy.

^cm.p. 41-42 °C

^dm.p. 74-75 °C

6.5.6. Action of hydroxylamine on bis(β -diketonato) copper(II) complexes at 0 °C in the presence of triphenylphosphine.

6.5.6a. The reaction of NH_2OH with $\text{Cu}(\text{acac})_2$ in the presence of Ph_3P .

Triphenylphosphine (8.0 g, 30.5 mmol), followed immediately by hydroxylamine (0.6 g, 19.0 mmol) in absolute methanol (50 cm³) at 0 °C was added to a suspension of bis(2,4-pentanedionato)copper(II) (2.0 g, 7.6 mmol) in absolute methanol (100 cm³). After 24 h white di(triphenylphosphine)(2,4-pentanedione-2-monooximato)copper(I) (4.7 g, 88%) (Found: C, 70.2; H, 5.2; Cu, 9.1; N, 2.3; P, 9.0. $\text{C}_{41}\text{H}_{38}\text{CuN}_2\text{OP}_2$ requires C, 70.1; H, 5.4; Cu, 9.0; N, 2.0; P, 8.8 %) was filtered off, washed with methanol (3 x 20 cm³) and dried in vacuo.

6.5.6b. The reaction of NH_2OH with $\text{Cu}(\text{bzac})_2$ in the presence of Ph_3P .

Triphenylphosphine (5.3 g, 20.4 mmol), followed immediately by hydroxylamine (0.43 g, 13.0 mmol) in absolute methanol (50 cm³) at 0 °C was added to a suspension of bis(1-phenyl-1,3-butanedionato)copper(II) (2.0 g, 5.1 mmol) in absolute methanol (100 cm³). After 24 h white di(triphenylphosphine)(1-phenyl-1,3-butanedione-3-monooximato)copper(I) (3.5 g, 90%) (Found: C, 72.3; H, 5.0; Cu, 8.5; N, 2.0; P, 8.0. $\text{C}_{46}\text{H}_{40}\text{CuN}_2\text{OP}_2$ requires C, 72.3; H, 5.2; Cu, 8.3; N, 1.8; P, 8.1 %) was filtered off, washed with methanol (3 x 20 cm³) and dried in vacuo.

6.5.7. Action of hydroxylamine on di(triphenylphosphine) (2,4-pentanedionato)copper(I) at 0 °C.

Hydroxylamine (0.2 g, 6.0 mmol) in dry, absolute methanol (50 cm³) at 0 °C was added slowly to a suspension of freshly prepared bis(triphenylphosphine) (2,4-pentanedionato)copper(I)¹² (2.0 g, 2.8 mmol) in absolute methanol (100 cm³) at 0 °C. After 24 h unreacted bis(triphenylphosphine)(2,4-pentanedionato)copper(I) (95%)(identical i.r. with authentic sample) was recovered by filtration.

6.5.8. Action of triphenylphosphine on bis(1-phenyl-1,3-butanedionato)copper(II).

Triphenylphosphine (8.0 g, 30.5 mmol) was added to a suspension of bis(1-phenyl-1,3-butanedionato)copper(II) (2.9 g, 7.5 mmol) in methanol (300 cm³). After refluxing for 14 days bis(1-phenyl-1,3-butanedionato)copper(II)(95%)(identical i.r. with authentic sample) was recovered by filtration.

6.5.9. Action of triphenylphosphine on bis(2,4-pentanedione-2-oximato)copper(II).

Triphenylphosphine (8.0 g, 30.5 mmol) was added to a suspension of bis(2,4-pentanedione-2-oximato)copper(II) (2.9 g, 7.5 mmol) in toluene (300 cm³). After refluxing for 14 days bis(2,4-pentanedione-2-oximato)copper(II) (95%)(identical i.r. with authentic sample) was recovered by filtration.

6.5.10. Action of hydroxylamine on bis(1-phenyl-1,3-butanedionato)copper(II) at 0 °C in the presence of propan-2-ol.

Hydroxylamine (0.4 g, 12.1 mmol) in absolute methanol (50 cm³) at 0 °C was added slowly to a suspension of bis(1-phenyl-1,3-butanedionato)copper(II) (2.0 g, 5.1 mmol) in dry, absolute methanol/propan-2-ol (100 cm³ 1:1) at 0 °C. After 24 h green/blue (2-propoxy)(1-phenyl-1,3-butanedione-3-monooximato)copper(I) (1.1 g, 76%) (Found : C, 56; H, 6.2; Cu, 22.3; N, 5.4. C₁₃H₁₇CuNO₂ requires C, 55.2; H, 6.0; Cu, 22.5; N, 5.0 %) was filtered off, washed with methanol (3 x 20 cm³) and dried in vacuo.

The combined filtrate and washings were dried at 20 °C/20 mmHg and the residue extracted with chloroform (100 cm³). Concentration of the chloroform solution to 20 cm³ followed by addition of diethyl ether (150 cm³) afforded 3-phenyl-5-methylisoxazoline (0.8 g, 44%) (Found: C, 68.1; H, 6.2; N, 8.0. C₁₀H₁₁NO₂ requires C, 67.8; H, 6.2; N, 7.9%).

6.5.11. Action of propan-2-ol on hydroxy(1-phenyl-1,3-butanedione-3-monooximato)copper(I).

Hydroxy(1-phenyl-1,3-butanedionato-3-monooximato)copper(I) (1.0 g, 4.1 mmol) was stirred in propan-2-ol (100 cm³). After 24 h hydroxy(1-phenyl-1,3-butanedione-3-monooximato)copper(I) (95%) (identical i.r. with authentic sample) was recovered by filtration.

6.5.12. Dehydration of bis(β -diketonato)metal(II)-hydroxylamine adducts.

6.5.12a. Dehydration of Ni(acac)₂(NH₂OH)₂ in toluene under reflux.

A suspension of di(hydroxylamine)bis(2,4-pentanedionato)nickel(II) (2.0 g, 6.1 mmol) in toluene (150 cm³) was heated under reflux in a Dean-Stark water separator for 2 h. Filtration and subsequent recrystallisation of the solid product from dichloromethane (20 cm³) afforded green bis(2,4-pentanedione-2-monooximato)nickel(II) (1.9 g, 95%) (Found: C, 42.0; H, 5.8; Ni, 19.6; N, 10.0. C₁₀H₁₆N₂NiO₄ requires C, 42.2; H, 5.6; Ni, 19.7; N, 9.9%).

6.5.12b. Dehydration of Ni(bzac)₂(NH₂OH)₂ in toluene under reflux.

A suspension of di(hydroxylamine)bis(1-phenyl-1,3-butanedionato)nickel(II) (2.0 g, 4.5 mmol) in toluene (150 cm³) was heated under reflux in a Dean-Stark water separator for 2 h. Filtration and subsequent recrystallisation of the solid product from dichloromethane (20 cm³) afforded light green bis(1-phenyl-1,3-butanedione-3-monooximato)nickel(II) (1.9 g, 97%) (Found: C, 58.6; H, 5.1; Ni, 14.4; N, 6.4. C₂₀H₂₂N₂NiO₄ requires C, 58.4; H, 4.9; Ni, 14.3; N, 6.8%).

6.5.12c. Dehydration of Ni(tfac)₂(NH₂OH)₂ in toluene under reflux.

A suspension of di(hydroxylamine)bis(1-trifluoromethyl-

1,3-butanedionato)nickel(II) (2.0 g, 5.1 mmol) in toluene (150 cm³) was heated under reflux in a Dean-Stark water separator for 2 h. Filtration and subsequent recrystallisation of the solid product from dichloromethane (25 cm³) afforded bis(1-trifluoromethyl-1,3-butanedione-3-monooximato)nickel(II) (1.9 g, 95%) (Found: C, 30.7; H, 2.3; Ni, 14.5; N, 7.0. C₁₀H₁₀F₆N₂NiO₄ requires C, 30.5; H, 2.5; Ni, 14.7; N, 7.1%).

6.5.12d. Effect of heating Zn(acac)₂(NH₂OH) and Zn(bzac)₂(NH₂OH) in toluene under reflux.

A suspension of the adduct (ca. 2.0 g) in toluene (100 cm³) was heated under reflux in a Dean-Stark water separator for 24 h. Filtration of the reaction mixture gave the respective bis(β-diketonato)zinc(II) complex (ca. 95%) identified by comparative t.l.c. with authentic sample.

6.5.13. Action of pyridine on bis(β-diketonato)metal(II)-hydroxylamine adducts and bis(monooximato)metal(II) complexes.

The metal complex (ca. 1.5 g, 1.2 mmol) was stirred in pyridine (25 cm³) at 20 °C. After 24 h the resulting solution was transferred to a dropping funnel. The solution was added dropwise to petroleum ether (30-40 °C fraction)(400 cm³) with vigorous stirring. The pyridine adduct was filtered off, washed with petroleum ether (30-40 °C fraction)(2 x 25 cm³) and dried in vacuo. See Table 6.8 for analysis and yields of the products.

Table 6.8. Yields and analytical data for the pyridine adducts of bis(monooximato)metal(II) and bis(β -diketonato)metal(II) complexes.

Complex	Products	Yield (%)	Found (%)			Requires (%)		
			C	H	N	C	H	N
Ni(acacM) ₂	Ni(acacM) ₂ (py) ₂	91	60.0	5.0	12.2	57.8	5.4	11.6
Ni(bzacM) ₂	Ni(bzacM) ₂ (py) ₂	90	63.5	5.1	10.1	63.3	53.9	10.2
Ni(tfacM) ₂	Ni(tfacM) ₂ (py) ₂	92	47.6	3.4	9.1	47.3	3.4	9.5
Ni(tfac) ₂ (NH ₂ OH) ₂	Ni(tfac) ₂ (py) ₂	90	a					
Zn(bzac) ₂ (NH ₂ OH)	Zn(bzac) ₂ (py)	87	a					
Zn(acac) ₂ (NH ₂ OH)	Zn(acac) ₂ (py)	88	a					

^aidentified by comparative t.l.c.with authentic sample.

6.5.14. Action of hydrochloric acid on isoxazolines.

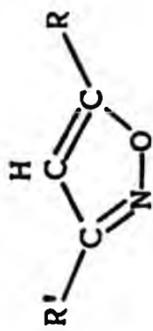
The isoxazoline (ca. 0.5 g, 3.0 mmol) was added to hydrochloric acid (2 mol dm^{-3} , 20 cm^3) with stirring. The resulting solution was diluted to 50 cm^3 with water, neutralised with potassium hydroxide solution (1 mol dm^{-3}) and extracted with diethyl ether ($3 \times 25 \text{ cm}^3$). The ethereal layer was separated. The combined ether extracts were dried with anhydrous magnesium sulphate. Removal of the diethyl ether gave the isoxazole. Analyses, yields and other data are given in Table 6.7.

6.5.15. Action of hydrochloric acid on complexes of the type $\text{Ni}(\text{monooximato})_2$ and $\text{Cu}(\text{monooximato})(\text{OH})$.

The (monooximato)metal complex (ca. 1.5 g, 5 mmol) was added to hydrochloric acid (2 mol dm^{-3} , 20 cm^3) with stirring. The resulting solution was diluted to 50 cm^3 with water, neutralised with potassium hydroxide solution (1 mol dm^{-3}) and extracted with diethyl ether ($3 \times 25 \text{ cm}^3$). The ethereal layer was separated. The combined ether extracts were dried with anhydrous magnesium sulphate. Removal of the diethyl ether gave the isoxazole. See Table 6.9 for analyses, yields and other data.

Table 6.9. Action of hydrochloric acid on (monooximato)metal complexes.

Complex	Formula	Product (isoxazole)						
		Yield (%)	Found (%)			Calc. (%)		
			C	H	N	C	H	N
Ni(acacM) ₂	R=R'=Me	80	61.9	7.8	14.7	61.8	7.3	14.4
Ni(bzacM) ₂	R=Ph, R'=Me ^a	79	76.5	5.8	8.8	75.7	5.7	8.8
Ni(tfacM) ₂	R=CF ₃ , R'=Me ^b	80	34.7	3.3	8.0	35.0	2.9	8.2
Cu(acacM)OH	R=R'=Me	85	61.9	7.6	14.6	61.8	7.3	14.4
Cu(bzacM)OH	R=Ph, R'=Me ^a	90	75.9	5.2	9.1	75.5	5.7	8.8
Cu(tfacM)OH	R=CF ₃ , R'=Me ^b	75	35.2	3.0	8.6	35.0	2.9	8.2



^am.p. 66-67 °C (lit.,¹³ 67 °C).

^bm.p. 81-82 °C

20 cm³) with vigorous stirring. The resulting solution was diluted with water (100 cm³), neutralised with potassium hydroxide solution (1 mol dm⁻³) and extracted with diethyl ether (3 x 20 cm³). The ethereal layer was separated. The combined ether extracts were dried with anhydrous magnesium sulphate. Removal of the diethyl ether gave a yellow solid (0.1 g) with an ill-defined infrared spectrum (Found: C, 67.8; H, 4.2; N, 7.9 %).

6.6. Reaction of amines with bis(quinoneoximato)metal(II) complexes.

6.6.1. Reaction of bis(quinoneoximato)metal(II) complexes with amines in pyridine at room temperature.

Bis(quinoneoximato)metal(II) (1.0 g) and amine (1 cm³) were stirred for 24 h in pyridine (50 cm³) at room temperature. The reaction was monitored using t.l.c. (see Table 6.10. for results). In the cases where reaction had occurred the procedure described below was then followed.

Silica gel (ca. 20 g) was added to the pyridine/amine reaction mixture. The pyridine was allowed to evaporate off. The dry silica gel/impure products mixture was transferred to an extraction thimble. This was placed in a Soxhlet extraction apparatus. The solid was extracted in turn with light petroleum

Table 6.10. Interaction of bis(quinoneoximato)metal(II) complexes with amines in pyridine at room temperature.

Metal complex	Amine	Product (%)
Cu(2-nqo) ₂	phenylethylamine	di(phenylethyl)amine (23%) ^a
Cu(2-nqo) ₂	1,4-diaminobutane	pyrrolidine (25%) ^a
Cu(2-nqo) ₂	1,5-diaminopentane	piperidine (25%) ^a
Cu(2-nqo) ₂	1,2-diaminoethane	b
Cu(2-nqo) ₂	1,3-diaminopropane	b
Cu(2-nqo) ₂	diethylamine	c
Cu(2-nqo) ₂	hydroxylamine	b
Cu(2-nqo) ₂	1,8-diaminooctane	b
Cu(2-nqo) ₂	benzylamine	di(benzyl)amine (19%) ^a
Cu(2-nqo) ₂	o-anisidine	b
Cu(4-Meqo) ₂	phenylethylamine	di(phenylethyl)amine (20%) ^a
Fe(2-nqo) ₂	o-anisidine	b
Fe(2-nqo) ₂	phenylethylamine	d
Fe(1-nqo) ₂	o-anisidine	b
Fe(1-nqo) ₂	phenylethylamine	d
Cu(1-nqo) ₂	o-anisidine	b
Cu(1-nqo) ₂	phenylethylamine	di(phenylethyl)amine (15%) ^a

^a A gas evolved changes the colour of neutral phenolphthalein solution to pink

^b No reaction

^c Amine adduct formed

^d Complex mixture of products

(b.p. 60-80 °C), toluene, acetone and methanol.

G.l.c. analysis of the light petroleum extract gave unreacted primary amine and the secondary amine (Identified and estimated by comparison with authentic samples)(see Table 6.10 for yields and other data).

Using bis(1,2-naphthoquinone-2-oximato)copper(II) and phenylethylamine ($\text{PhCH}_2\text{CH}_2\text{NH}_2$), chromatography of the toluene extract (silica gel) gave with toluene as elutant 1,2-dihydroxyphenazine (0.9 g)(identified by t.l.c.). Elution with chloroform and methanol gave trace amounts of an organic, ill defined, brown solid (0.05 g).

6.6.2. Reaction of bis(1,2-naphthoquinone-2-oximato) copper(II) with phenylethylamine, 1,5-diaminopentane and benzylamine in pyridine at 90 °C.

Bis(1,2-naphthoquinone-2-oximato)copper(II) (1.0 g) and the amine (1 cm^{-3}) were stirred for 24 h in pyridine (50 cm^3) at 90 °C. A mixture of products resulted (multi-component by t.l.c.).

6.6.3. Examination of the effect of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{cup})_2$ on phenylethylamine at room temperature.

The metal compound (1.0 g) and phenylethylamine (1 cm^3) were stirred for 24 h in pyridine (50 cm^3) at room temperature. T.l.c. examination indicated that no reaction had occurred.

6.6.4. Interaction of bis(1,2-naphthoquinone-2-oximato) copper(II) with phenylethylamine in diethyl ether, trichlorotrifluoroethane or propan-2-ol at room temperature.

Bis(1,2-naphthoquinone-2-oximato)copper(II) (1.0 g) and phenylethylamine (1 cm³) were stirred for 24 h in diethyl ether , trichlorotrifluoroethane or propan-2-ol at room temperature. In all cases t.l.c. indicated that no reaction had occurred.

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APPENDIX ONE

Appendix 1

Crystal data and details of structure determination
for cupferronatobis(triphenylphosphine)copper(I).

Molecular formulae : $C_{42}H_{35}CuN_2O_2P_2$

Relative molecular mass = 724.5 g mol^{-1}

Colour yellow

Crystal system : triclinic

$a/\text{\AA}$ 10.097(4)

$b/\text{\AA}$ 12.955(4)

$c/\text{\AA}$ 14.740(6)

$\alpha/^\circ$ 88.384(3)

$\beta/^\circ$ 104.438(3)

$\gamma/^\circ$ 103.332(5)

D 1.326 g cm^{-3}

z 2

Number of unique
observed reflections 4642

Table 1. Fractional atomic coordinates and thermal parameters (\AA^2) for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

Atom	x	y	z	U_{iso} or U_{eq}^*
Cu	0.08409(4)	0.16652(3)	-0.23142(3)	0.0410(2)
P(1)	0.11749(9)	0.00329(7)	-0.24551(6)	0.0391(5)
P(2)	0.23315(9)	0.29942(7)	-0.13236(6)	0.0375(5)
O(1)	0.0342(3)	0.2403(2)	-0.3603(2)	0.062(2)
O(2)	-0.1243(3)	0.1744(2)	-0.2506(2)	0.062(2)
N(1)	-0.0920(3)	0.2579(2)	-0.3746(2)	0.047(2)
N(2)	-0.1768(3)	0.2251(3)	-0.3213(2)	0.061(2)
C(1)	-0.1427(5)	0.3153(3)	-0.4557(3)	0.057(2)
C(2)	-0.2736(6)	0.3412(4)	-0.4717(4)	0.097(4)
C(3)	-0.3218(8)	0.3940(5)	-0.5510(4)	0.140(6)
C(4)	-0.2430(9)	0.4223(5)	-0.6141(4)	0.131(6)
C(5)	-0.1129(8)	0.3974(4)	-0.5994(4)	0.103(4)
C(6)	-0.0621(5)	0.3424(3)	-0.5173(3)	0.071(3)
C(111)	-0.0327(4)	-0.0885(3)	-0.3221(2)	0.045(2)
C(112)	-0.0753(5)	-0.1947(3)	-0.3058(3)	0.064(3)
C(113)	-0.1892(6)	-0.2607(4)	-0.3673(4)	0.082(3)
C(114)	-0.2611(5)	-0.2206(5)	-0.4477(4)	0.083(4)
C(115)	-0.2208(5)	-0.1163(5)	-0.4648(3)	0.082(4)
C(116)	-0.1063(4)	-0.0490(3)	-0.4031(3)	0.062(3)
C(121)	0.2654(4)	-0.0050(3)	-0.2921(2)	0.042(2)
C(122)	0.2670(4)	-0.0888(3)	-0.3461(3)	0.069(3)
C(123)	0.3838(6)	-0.0901(4)	-0.3771(4)	0.093(4)
C(124)	0.5038(5)	-0.0074(4)	-0.3528(3)	0.075(3)
C(125)	0.5033(4)	0.0757(3)	-0.2985(3)	0.060(2)
C(126)	0.3861(4)	0.0776(3)	-0.2688(3)	0.051(2)

Table 1 (continued).

C(131)	0.1530(3)	-0.0638(2)	-0.1342(2)	0.038(2)
C(132)	0.0500(4)	-0.0842(3)	-0.0844(3)	0.051(2)
C(133)	0.0797(4)	-0.1221(3)	0.0060(3)	0.058(2)
C(134)	0.2114(5)	-0.1393(3)	0.0486(3)	0.056(2)
C(135)	0.3130(4)	-0.1213(3)	-0.0001(3)	0.052(2)
C(136)	0.2855(4)	-0.0839(3)	-0.0907(3)	0.047(2)
C(211)	0.2932(3)	0.2771(2)	-0.0065(2)	0.038(2)
C(212)	0.3136(4)	0.1771(3)	0.0218(3)	0.049(2)
C(213)	0.3604(4)	0.1559(3)	0.1155(3)	0.058(2)
C(214)	0.3828(5)	0.2335(4)	0.1834(3)	0.066(3)
C(215)	0.3590(5)	0.3314(3)	0.1576(3)	0.067(3)
C(216)	0.3161(4)	0.3532(3)	0.0632(3)	0.053(2)
C(221)	0.3962(3)	0.3371(2)	-0.1702(2)	0.040(2)
C(222)	0.5289(3)	0.3434(3)	-0.1096(3)	0.044(2)
C(223)	0.6474(4)	0.3663(3)	-0.1436(3)	0.054(2)
C(224)	0.6346(4)	0.3840(3)	-0.2377(3)	0.059(3)
C(225)	0.5027(5)	0.3776(3)	-0.2987(3)	0.062(3)
C(226)	0.3831(4)	0.3530(3)	-0.2656(3)	0.049(2)
C(231)	0.1828(3)	0.4269(3)	-0.1333(2)	0.040(2)
C(232)	0.0471(4)	0.4257(3)	-0.1312(3)	0.063(3)
C(233)	0.0106(4)	0.5232(3)	-0.1244(3)	0.071(3)
C(234)	0.1049(5)	0.6181(3)	-0.1238(3)	0.061(3)
C(235)	0.2367(4)	0.6176(3)	-0.1304(3)	0.054(2)
C(236)	0.2767(4)	0.5227(3)	-0.1343(3)	0.048(2)

$$* U_{eq} = \frac{1}{2} \sum_i \sum_j u_{ij} a_i^* a_j^* a_i a_j$$

Table 2. Fractional atomic coordinates for the hydrogen atoms in $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

Atom	x	y	z
H(2)	-0.3369	0.3197	-0.4218
H(3)	-0.4233	0.4133	-0.5631
H(4)	-0.2817	0.4642	-0.6758
H(5)	-0.0504	0.4194	-0.6497
H(6)	0.0391	0.3228	-0.5046
H(124)	0.5958	-0.0094	-0.3769
H(222)	0.5385	0.3304	-0.0357
H(233)	-0.0945	0.5232	-0.1197
H(212)	0.3210	0.1348	-0.0239
H(213)	0.3850	0.0837	0.1347
H(215)	0.3800	0.4021	0.2066
H(216)	0.2871	0.4235	0.0476
H(116)	-0.0794	0.0391	-0.4085
H(114)	-0.3547	-0.2766	-0.5012
H(112)	-0.0361	-0.2258	-0.2413
H(135)	0.4035	-0.1325	0.0316
H(113)	-0.2259	-0.3471	-0.3560
H(232)	-0.0355	0.3623	-0.1385
H(224)	0.7289	0.4066	-0.2572
H(115)	-0.2681	-0.0946	-0.5312
H(214)	0.4068	0.2171	0.2540
H(235)	0.3058	0.6778	-0.1222
H(234)	0.0646	0.6825	-0.1251
H(236)	0.3742	0.5282	-0.1359
H(223)	0.7469	0.3747	-0.0995

Table 2 (continued).

H(225)	0.4962	0.3966	-0.3782
H(226)	0.2822	0.3438	-0.3125
H(132)	-0.0476	-0.0736	-0.1135
H(133)	0.0047	-0.1428	0.0415
H(126)	0.3814	0.1381	-0.2246
H(122)	0.1814	-0.1480	-0.3685
H(136)	0.3730	-0.0635	-0.1212
H(134)	0.2300	-0.1595	0.1213
H(123)	0.3969	-0.1573	-0.4037
H(125)	0.5937	0.1333	-0.2762

Table 3. Anisotropic thermal parameters (\AA^2) for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2^*$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0408(2)	0.0386(2)	0.0436(3)	0.0036(2)	0.0080(2)	0.0122(2)
P(1)	0.040(1)	0.036(1)	0.041(1)	0.001(1)	0.006(1)	0.011(1)
P(2)	0.0373(5)	0.0333(5)	0.0420(5)	0.0001(4)	0.0070(4)	0.0112(4)
O(1)	0.057(2)	0.075(2)	0.053(2)	0.025(1)	0.019(1)	0.025(1)
O(2)	0.046(1)	0.083(2)	0.058(2)	0.018(2)	0.018(1)	0.020(1)
N(1)	0.050(2)	0.049(2)	0.042(2)	0.004(1)	0.006(2)	0.016(1)
N(2)	0.051(2)	0.077(2)	0.054(2)	0.009(2)	0.011(2)	0.027(2)
C(1)	0.083(3)	0.053(2)	0.037(2)	0.000(2)	0.002(2)	0.027(2)
C(2)	0.113(4)	0.114(4)	0.064(3)	0.009(3)	0.011(3)	0.071(4)
C(3)	0.178(7)	0.165(7)	0.076(4)	0.015(4)	-0.008(4)	0.134(6)
C(4)	0.217(9)	0.115(5)	0.061(4)	0.025(4)	0.008(5)	0.099(6)
C(5)	0.166(6)	0.082(4)	0.062(3)	0.017(3)	0.020(4)	0.027(4)
C(6)	0.100(4)	0.060(3)	0.053(3)	0.011(2)	0.016(3)	0.021(2)
C(111)	0.044(2)	0.049(2)	0.042(2)	-0.003(2)	0.009(2)	0.007(2)
C(112)	0.084(3)	0.056(3)	0.053(3)	-0.001(2)	0.003(2)	-0.006(2)
C(113)	0.106(4)	0.065(3)	0.075(3)	-0.014(3)	0.020(3)	-0.025(3)
C(114)	0.071(3)	0.117(5)	0.062(3)	-0.028(3)	0.006(3)	-0.020(3)
C(115)	0.084(4)	0.112(4)	0.051(3)	-0.006(3)	-0.016(3)	0.019(3)
C(116)	0.066(3)	0.069(3)	0.050(2)	0.002(2)	-0.003(2)	0.014(2)
C(121)	0.047(2)	0.037(2)	0.042(2)	0.001(2)	0.009(2)	0.012(2)
C(122)	0.058(3)	0.059(3)	0.088(3)	-0.025(2)	0.021(2)	0.009(2)
C(123)	0.092(4)	0.080(3)	0.106(4)	-0.032(3)	0.036(3)	0.032(3)
C(124)	0.063(3)	0.079(3)	0.084(3)	0.003(3)	0.032(3)	0.029(2)
C(125)	0.045(2)	0.064(3)	0.069(3)	0.003(2)	0.016(2)	0.009(2)
C(126)	0.054(2)	0.048(2)	0.051(2)	-0.001(2)	0.018(2)	0.007(2)

Table 3 (continued).

C(131)	0.041(2)	0.031(2)	0.042(2)	-0.003(1)	0.007(2)	0.007(1)
C(132)	0.047(2)	0.050(2)	0.057(2)	0.000(2)	0.012(2)	0.017(2)
C(133)	0.067(3)	0.053(2)	0.054(2)	0.005(2)	0.027(2)	0.013(2)
C(134)	0.077(3)	0.048(2)	0.043(2)	0.004(2)	0.014(2)	0.017(2)
C(135)	0.052(2)	0.048(2)	0.055(2)	0.008(2)	0.002(2)	0.020(2)
C(136)	0.045(2)	0.046(2)	0.050(2)	0.006(2)	0.013(2)	0.017(2)
C(211)	0.036(2)	0.036(2)	0.043(2)	0.000(2)	0.009(2)	0.008(1)
C(212)	0.054(2)	0.044(2)	0.050(2)	-0.001(2)	0.008(2)	0.015(2)
C(213)	0.064(3)	0.047(2)	0.061(3)	0.011(2)	0.010(2)	0.019(2)
C(214)	0.077(3)	0.076(3)	0.045(2)	0.011(2)	0.011(2)	0.024(2)
C(215)	0.096(3)	0.059(3)	0.047(2)	-0.004(2)	0.018(2)	0.021(2)
C(216)	0.063(2)	0.046(2)	0.051(2)	-0.000(2)	0.012(2)	0.016(2)
C(221)	0.041(2)	0.033(2)	0.045(2)	-0.004(1)	0.010(2)	0.013(1)
C(222)	0.038(2)	0.042(2)	0.053(2)	-0.003(2)	0.009(2)	0.008(2)
C(223)	0.037(2)	0.054(2)	0.071(3)	0.002(2)	0.012(2)	0.012(2)
C(224)	0.047(2)	0.059(2)	0.072(3)	-0.008(2)	0.026(2)	0.009(2)
C(225)	0.068(3)	0.063(3)	0.055(3)	-0.001(2)	0.026(2)	0.012(2)
C(226)	0.046(2)	0.051(2)	0.049(2)	-0.002(2)	0.009(2)	0.011(2)
C(231)	0.039(2)	0.040(2)	0.040(2)	-0.000(2)	0.004(2)	0.013(1)
C(232)	0.043(2)	0.051(2)	0.095(3)	-0.003(2)	0.019(2)	0.013(2)
C(233)	0.052(2)	0.055(3)	0.106(4)	-0.007(2)	0.021(2)	0.024(2)
C(234)	0.079(3)	0.042(2)	0.062(3)	-0.002(2)	0.006(2)	0.034(2)
C(235)	0.069(3)	0.032(2)	0.060(3)	0.002(2)	0.010(2)	0.010(2)
C(236)	0.049(2)	0.040(2)	0.056(2)	0.002(2)	0.014(2)	0.012(2)

* Anisotropic thermal parameters ($\times 10^3$), in the form

$$\exp[-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + u_{12}hka^*b^* + 2u_{13}hka^*c^* + 2u_{23}klb^*c^*)]$$

Table 4. Bond lengths (Å) for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

Cu	-P(1)	2.240(1)	Cu	-P(2)	2.283(1)
Cu	-O(1)	2.102(3)	Cu	-O(2)	2.078(3)
P(1)	-C(111)	1.838(3)	P(1)	-C(121)	1.818(4)
P(1)	-C(131)	1.830(3)	P(2)	-C(211)	1.839(3)
P(2)	-C(221)	1.826(4)	P(2)	-C(231)	1.835(4)
O(1)	-N(1)	1.310(4)	O(2)	-N(2)	1.282(4)
N(1)	-N(2)	1.297(5)	N(1)	-C(1)	1.436(5)
C(1)	-C(2)	1.401(8)	C(1)	-C(6)	1.352(7)
C(2)	-C(3)	1.378(8)	C(3)	-C(4)	1.360(11)
C(4)	-C(5)	1.388(12)	C(5)	-C(6)	1.431(7)
C(111)-C(112)	1.378(5)	C(111)-C(116)	1.392(5)		
C(112)-C(113)	1.394(6)	C(113)-C(114)	1.383(7)		
C(114)-C(115)	1.354(9)	C(115)-C(116)	1.407(6)		
C(121)-C(122)	1.368(6)	C(121)-C(126)	1.400(4)		
C(122)-C(123)	1.372(8)	C(123)-C(124)	1.396(6)		
C(124)-C(125)	1.362(7)	C(125)-C(126)	1.365(6)		
C(131)-C(132)	1.389(6)	C(131)-C(136)	1.411(5)		
C(132)-C(133)	1.393(6)	C(133)-C(134)	1.388(6)		
C(134)-C(135)	1.367(7)	C(135)-C(136)	1.391(5)		
C(211)-C(212)	1.395(5)	C(211)-C(216)	1.384(5)		
C(212)-C(213)	1.386(6)	C(213)-C(214)	1.378(6)		
C(214)-C(215)	1.371(7)	C(215)-C(216)	1.392(6)		
C(221)-C(222)	1.399(4)	C(221)-C(226)	1.393(5)		
C(222)-C(223)	1.377(6)	C(223)-C(224)	1.379(6)		
C(224)-C(225)	1.394(6)	C(225)-C(226)	1.380(6)		
C(231)-C(232)	1.375(6)	C(231)-C(236)	1.379(4)		
C(232)-C(233)	1.409(6)	C(233)-C(234)	1.370(5)		
C(234)-C(235)	1.360(7)	C(235)-C(236)	1.386(6)		

Table 5. Bond angles ($^{\circ}$) for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

P(2) -Cu -P(1)	125.6(1)	O(1) -Cu -P(1)	113.5(1)
O(1) -Cu -P(2)	104.2(1)	O(2) -Cu -P(1)	115.0(1)
O(2) -Cu -P(2)	111.5(1)	O(2) -Cu -O(1)	75.1(1)
C(121)-P(1) -Cu	116.1(1)	C(111)-P(1) -Cu	114.1(1)
C(131)-P(1) -Cu	113.7(1)	C(121)-P(1) -C(111)	103.9(2)
C(131)-P(1) -C(121)	102.6(2)	C(131)-P(1) -C(111)	105.1(2)
C(221)-P(2) -Cu	107.9(1)	C(211)-P(2) -Cu	120.7(1)
C(231)-P(2) -Cu	117.6(1)	C(221)-P(2) -C(211)	103.5(2)
C(231)-P(2) -C(221)	101.8(2)	C(231)-P(2) -C(211)	102.9(2)
N(2) -O(2) -Cu	117.2(2)	N(1) -O(1) -Cu	109.5(2)
N(2) -N(1) -O(1)	124.5(3)	C(1) -N(1) -N(2)	116.9(3)
C(1) -N(1) -O(1)	118.6(3)	N(1) -N(2) -O(2)	113.2(3)
C(2) -C(1) -N(1)	121.0(4)	C(6) -C(1) -N(1)	118.5(4)
C(6) -C(1) -C(2)	120.5(4)	C(3) -C(2) -C(1)	120.1(6)
C(4) -C(3) -C(2)	120.7(7)	C(5) -C(4) -C(3)	120.1(6)
C(6) -C(5) -C(4)	119.6(6)	C(5) -C(6) -C(1)	119.1(5)
C(112)-C(111)-P(1)	124.2(3)	C(116)-C(111)-P(1)	118.1(3)
C(116)-C(111)-C(112)	117.7(3)	C(113)-C(112)-C(111)	121.5(4)
C(114)-C(113)-C(112)	120.3(5)	C(115)-C(114)-C(113)	119.0(4)
C(116)-C(115)-C(114)	121.2(5)	C(115)-C(116)-C(111)	120.3(4)
C(122)-C(121)-P(1)	123.8(3)	C(126)-C(121)-P(1)	117.9(3)
C(126)-C(121)-C(122)	118.3(4)	C(123)-C(122)-C(121)	120.3(4)
C(124)-C(123)-C(122)	120.7(5)	C(125)-C(124)-C(123)	119.2(5)
C(126)-C(125)-C(124)	119.9(4)	C(125)-C(126)-C(121)	121.5(4)
C(132)-C(131)-P(1)	118.3(3)	C(136)-C(131)-P(1)	123.2(3)

Table 5 (continued).

C(136)-C(131)-C(132)	118.0(3)	C(133)-C(132)-C(131)	120.0(4)
C(134)-C(133)-C(132)	121.3(4)	C(135)-C(134)-C(133)	119.3(4)
C(136)-C(135)-C(134)	120.3(4)	C(135)-C(136)-C(131)	121.0(4)
C(212)-C(211)-P(2)	118.9(3)	C(216)-C(211)-P(2)	123.9(3)
C(216)-C(211)-C(212)	117.2(3)	C(213)-C(212)-C(211)	121.5(4)
C(214)-C(213)-C(212)	119.9(4)	C(215)-C(214)-C(213)	119.7(4)
C(216)-C(215)-C(214)	120.1(4)	C(215)-C(216)-C(211)	121.5(4)
C(222)-C(221)-P(2)	123.1(3)	C(226)-C(221)-P(2)	116.6(2)
C(226)-C(221)-C(222)	120.1(4)	C(223)-C(222)-C(221)	120.3(4)
C(224)-C(223)-C(222)	119.6(3)	C(225)-C(224)-C(223)	120.5(4)
C(226)-C(225)-C(224)	120.4(4)	C(225)-C(226)-C(221)	119.1(3)
C(232)-C(231)-P(2)	118.1(3)	C(236)-C(231)-P(2)	122.3(3)
C(236)-C(231)-C(232)	119.5(4)	C(233)-C(232)-C(231)	118.5(3)
C(234)-C(233)-C(232)	121.6(4)	C(235)-C(234)-C(233)	118.9(4)
C(236)-C(235)-C(234)	120.7(3)	C(235)-C(236)-C(231)	120.7(4)

Table 6. Intermolecular distances (Å) for Cu(cup)(Ph₃P)₂^o

C(133)...Cu	4.04	-1	0.0	0.0	0.0
H(133)...Cu	3.13	-1	0.0	0.0	0.0
H(133)...P(2)	3.30	-1	0.0	0.0	0.0
H(125)...O(2)	2.70	1	1.0	0.0	0.0
C(134)...O(2)	3.30	-1	0.0	0.0	0.0
H(134)...O(2)	2.39	-1	0.0	0.0	0.0
H(224)...N(2)	2.99	1	1.0	0.0	0.0
H(125)...N(2)	2.58	1	1.0	0.0	0.0
H(123)...C(2)	2.89	-1	0.0	0.0	-1.0
C(224)...H(2)	2.96	1	1.0	0.0	0.0
C(225)...H(2)	2.93	1	1.0	0.0	0.0
H(123)...C(3)	3.04	-1	0.0	0.0	-1.0
C(226)...H(4)	2.82	-1	0.0	1.0	-1.0
C(236)...H(4)	2.81	-1	0.0	1.0	-1.0
H(122)...C(6)	2.91	-1	0.0	0.0	-1.0
C(113)...H(6)	2.93	-1	0.0	0.0	-1.0
C(114)...H(6)	3.08	-1	0.0	0.0	-1.0
H(115)...C(121)	2.88	-1	0.0	0.0	-1.0
H(115)...C(122)	2.94	-1	0.0	0.0	-1.0
H(115)...C(123)	3.04	-1	0.0	0.0	-1.0
H(115)...C(125)	3.04	-1	0.0	0.0	-1.0
H(115)...C(126)	2.91	-1	0.0	0.0	-1.0
H(133)...C(211)	3.03	-1	0.0	0.0	0.0
H(133)...C(212)	3.04	-1	0.0	0.0	0.0
H(236)...C(215)	2.97	-1	1.0	1.0	0.0

Table 6 (continued).

C(235)...H(222)	2.87	-1	1.0	1.0	0.0
H(233)...C(223)	2.86	1	-1.0	0.0	0.0
H(216)...C(223)	2.96	-1	1.0	1.0	0.0
H(233)...C(224)	3.05	1	-1.0	0.0	0.0
H(215)...C(224)	2.86	-1	1.0	1.0	0.0
H(215)...C(225)	3.04	-1	1.0	1.0	0.0
H(223)...C(233)	3.00	1	1.0	0.0	0.0
H(112)...C(234)	3.00	1	0.0	-1.0	0.0

Table 7. Intramolecular distances (Å) for $\text{Cu}(\text{cup})(\text{Ph}_3\text{P})_2$

C(1) ...Cu	4.22	C(111)...Cu	3.43
C(116)...Cu	3.66	C(121)...Cu	3.45
C(126)...Cu	3.66	C(131)...Cu	3.41
C(132)...Cu	3.85	C(211)...Cu	3.59
C(212)...Cu	3.86	C(221)...Cu	3.33
C(226)...Cu	3.54	C(231)...Cu	3.53
C(232)...Cu	3.84	H(212)...Cu	3.46
H(116)...Cu	3.02	H(232)...Cu	3.49
H(226)...Cu	3.10	H(132)...Cu	3.66
H(126)...Cu	3.09	P(2) ...P(1)	4.02
O(1) ...P(1)	3.63	O(2) ...P(1)	3.64
C(112)...P(1)	2.85	C(116)...P(1)	2.78
C(122)...P(1)	2.82	C(126)...P(1)	2.76
C(132)...P(1)	2.77	C(136)...P(1)	2.86
H(116)...P(1)	2.81	H(112)...P(1)	3.02
H(132)...P(1)	2.88	H(126)...P(1)	2.78
H(122)...P(1)	2.99	H(136)...P(1)	3.06
O(1) ...P(2)	3.46	O(2) ...P(2)	3.61
C(212)...P(2)	2.79	C(216)...P(2)	2.85
C(222)...P(2)	2.84	H(222)...P(2)	3.00
C(226)...P(2)	2.75	C(232)...P(2)	2.76
C(236)...P(2)	2.82	H(212)...P(2)	2.80
H(216)...P(2)	3.01	H(232)...P(2)	2.99
H(236)...P(2)	2.98	H(226)...P(2)	2.84
H(126)...P(2)	3.33	O(2) ...O(1)	2.55
C(113)...C(113)	2.36	C(114)...C(113)	2.75
H(114)...C(113)	2.22	H(112)...C(113)	2.68

Table 7 (continued).

N(2) ...O(1)	2.31	C(1) ...O(1)	2.36
C(6) ...O(1)	2.71	H(6) ...O(1)	2.36
H(116)...O(1)	2.63	H(226)...O(1)	2.49
N(1) ...O(2)	2.15	H(232)...O(2)	2.82
C(2) ...N(1)	2.47	H(2) ...N(1)	2.69
C(6) ...N(1)	2.40	H(6) ...N(1)	2.61
H(116)...N(1)	2.93	C(1) ...N(2)	2.33
C(2) ...N(2)	2.75	H(2) ...N(2)	2.43
H(2) ...C(1)	2.15	C(3) ...C(1)	2.41
C(4) ...C(1)	2.77	C(5) ...C(1)	2.40
H(6) ...C(1)	2.12	H(3) ...C(2)	2.13
C(4) ...C(2)	2.38	C(5) ...C(2)	2.76
C(6) ...C(2)	2.39	C(3) ...H(2)	2.13
H(4) ...C(3)	2.12	C(5) ...C(3)	2.38
C(6) ...C(3)	2.78	C(4) ...H(3)	2.11
H(5) ...C(4)	2.15	C(6) ...C(4)	2.44
C(5) ...H(4)	2.14	H(6) ...C(5)	2.19
C(6) ...H(5)	2.18	C(113)...C(111)	2.42
C(114)...C(111)	2.81	C(115)...C(111)	2.43
C(121)...C(111)	2.88	C(122)...C(111)	3.13
C(131)...C(111)	2.91	C(132)...C(111)	3.39
H(116)...C(111)	2.13	H(112)...C(111)	2.11
H(122)...C(111)	2.70	C(114)...C(112)	2.41
C(115)...C(112)	2.74	C(116)...C(112)	2.37
C(131)...C(112)	3.18	C(132)...C(112)	3.41
H(113)...C(112)	2.21	H(122)...C(112)	2.90
C(115)...C(113)	2.36	C(116)...C(113)	2.75
H(114)...C(113)	2.22	H(112)...C(113)	2.08

Table 7 (continued).

C(116)...C(114)	2.41	H(113)...C(114)	2.13
H(115)...C(114)	2.02	H(116)...C(115)	2.23
H(114)...C(115)	2.20	H(115)...C(116)	2.16
C(123)...C(121)	2.38	C(124)...C(121)	2.78
C(125)...C(121)	2.41	C(131)...C(121)	2.85
C(136)...C(121)	3.09	H(126)...C(121)	2.08
H(122)...C(121)	2.08	H(136)...C(121)	2.65
C(124)...C(122)	2.41	C(125)...C(122)	2.76
C(126)...C(122)	2.38	H(123)...C(122)	2.09
H(124)...C(123)	2.15	C(125)...C(123)	2.38
C(126)...C(123)	2.72	H(122)...C(123)	2.04
C(126)...C(124)	2.36	H(123)...C(124)	2.05
H(125)...C(124)	2.07	C(125)...H(124)	2.12
H(126)...C(125)	2.13	H(136)...C(126)	2.81
H(125)...C(126)	2.08	C(133)...C(131)	2.41
C(134)...C(131)	2.81	C(135)...C(131)	2.44
H(212)...C(131)	3.00	H(112)...C(131)	2.72
H(132)...C(131)	2.10	H(136)...C(131)	2.18
C(134)...C(132)	2.42	C(135)...C(132)	2.78
C(136)...C(132)	2.40	H(112)...C(132)	2.82
H(133)...C(132)	2.10	C(135)...C(133)	2.38
C(136)...C(133)	2.75	H(132)...C(133)	2.08
H(134)...C(133)	2.10	C(136)...C(134)	2.39
H(135)...C(134)	2.00	H(133)...C(134)	2.05
H(136)...C(135)	2.09	H(134)...C(135)	2.16
H(212)...C(136)	2.94	H(135)...C(136)	2.07
C(213)...C(211)	2.43	C(214)...C(211)	2.80
C(215)...C(211)	2.42	C(221)...C(211)	2.88

Table 7 (continued).

C(222)...C(211)	3.08	H(222)...C(211)	2.55
C(231)...C(211)	2.87	H(212)...C(211)	1.96
H(216)...C(211)	2.10	C(214)...C(212)	2.39
C(215)...C(212)	2.75	C(216)...C(212)	2.37
H(222)...C(212)	2.93	H(213)...C(212)	2.11
C(215)...C(213)	2.38	C(216)...C(213)	2.75
H(212)...C(213)	2.01	H(214)...C(213)	2.11
C(216)...C(214)	2.39	H(213)...C(214)	2.09
H(215)...C(214)	2.23	H(216)...C(215)	2.07
H(214)...C(215)	2.08	H(222)...C(216)	3.04
C(231)...C(216)	3.10	H(215)...C(216)	2.12
H(222)...C(221)	2.15	C(223)...C(221)	2.41
C(224)...C(221)	2.76	C(225)...C(221)	2.39
C(231)...C(221)	2.84	C(236)...C(221)	3.04
H(236)...C(221)	2.61	H(226)...C(221)	2.14
H(126)...C(221)	2.68	C(224)...C(222)	2.38
C(225)...C(222)	2.77	C(226)...C(222)	2.42
H(223)...C(222)	2.11	H(126)...C(222)	3.06
C(223)...H(222)	2.13	C(225)...C(223)	2.41
C(226)...C(223)	2.79	H(224)...C(223)	2.05
C(226)...C(224)	2.41	H(223)...C(224)	2.09
H(225)...C(224)	2.22	H(224)...C(225)	2.16
H(226)...C(225)	2.13	C(231)...C(226)	3.43
C(236)...C(226)	3.48	H(236)...C(226)	3.04
H(225)...C(226)	2.23	H(126)...C(226)	2.83
C(233)...C(231)	2.39	C(234)...C(231)	2.78
C(235)...C(231)	2.40	H(216)...C(231)	2.62
H(232)...C(231)	2.15	H(236)...C(231)	2.08

Table 7 (continued).

H(233)...C(232)	2.15	C(234)...C(232)	2.43
C(235)...C(232)	2.76	C(236)...C(232)	2.38
C(235)...C(233)	2.35	C(236)...C(233)	2.73
H(232)...C(233)	2.03	H(234)...C(233)	2.01
C(234)...H(233)	2.12	C(236)...C(234)	2.39
H(235)...C(234)	1.99	H(234)...C(235)	2.12
H(236)...C(235)	2.02	H(216)...C(236)	2.93
H(235)...C(236)	1.97		

APPENDIX TWO

Appendix 2

One of the initial objectives of the work undertaken for this thesis was to investigate the commercial potential of selected complexes prepared during the study as epoxidation catalysts. Circumstances prevented this being done during the time that the bulk of the work described in this thesis was carried out. However, a preliminary study of the potential of the complexes $\text{Cu}(\text{cup})_2$ and $\text{Ni}(\text{acacM})_2$ as epoxidation catalysts for methyl oleate, as well as comparative studies involving the complexes; $[\text{VO}(\text{1-nqo})_2]\text{HSO}_4$, $[\text{VO}(\text{1-nqo})_2]_2\text{SO}_4$, $\text{VO}(\text{1-nqo})_2$, $\text{Fe}(\text{1-nqo})_2$, $\text{Ni}(\text{acac})_2$ and $\text{VO}(\text{acac})_2$ were investigated. These studies were carried out at 65°C at atmospheric pressure.

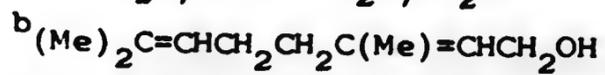
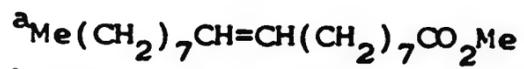
As can be seen from the results presented in Table 1 promising results were obtained for the complexes $[\text{VO}(\text{1-nqo})_2]\text{HSO}_4$ and $[\text{VO}(\text{1-nqo})_2]_2\text{SO}_4$. The behaviour of these complexes was also examined at 20°C (Table 2) and 65°C (Table 3) using various olefins as substrates. Again the results proved to be quite promising and the value of these complexes is now being further explored in these laboratories.

Table 1 Catalytic aerobic oxidation of methyl oleate by various metal complexes at 65 °C (1 week oxidation time).

Catalyst	% Conversion
VO(1-nqo) ₂	87
[VO(1-nqo) ₂] ₂ SO ₄ (2)	85
[VO(1-nqo) ₂]HSO ₄ (1)	87
Fe(1-nqo) ₂	54
Ni(acacM) ₂	41
Ni(acac) ₂	35
Cu(cup) ₂	0
VO(acac) ₂	0

Table 2 Catalytic aerobic oxidation of olefins at 20 °C.

Olefin	Catalyst	Aeration time/weeks	% conversion
Methyl oleate ^a	2	10	44
methyl oleate ^a	1	10	37
Geraniol ^b	2	8	33
Geraniol ^b	1	4	c
Vernol ^d	2	8	35
Vernol ^d	1	8	33
Linalool ^e	2	8	31
Linalool ^e	1	8	27



^c100 % polymerisation

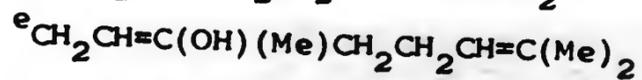
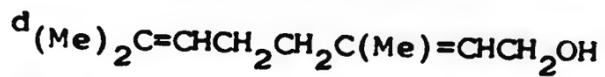


Table 3 Catalytic aerobic oxidation of olefins at 65 °C (1 week oxidation time).

Olefin	Catalyst	% Conversion
Methyl oleate	2	85
Methyl oleate	1	87
Geraniol	2	89
Geraniol	1	a
Vernol	2	35
Vernol	1	37
Linalool	2	72
Linalool	1	70

^a100 % polymerisation

APPENDIX THREE

**Synthesis and Magnetic and Spectral Studies of Metal
Complexes of *N*-Nitrosophenylhydroxylamine (Cupferron).
Reduction of the Copper(II) Complex by Triphenylphosphine
and X-Ray Crystal Structure of Cupferronatobis(triphenyl-
phosphine)copper(I)**

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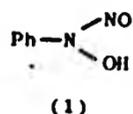
Synthesis and Magnetic and Spectral Studies of Metal Complexes of *N*-Nitrosophenylhydroxylamine (Cupferron). Reduction of the Copper(II) Complex by Triphenylphosphine and X-Ray Crystal Structure of Cupferronatobis(triphenylphosphine)copper(I)

J. Chem. Research (S),
1984, 220-221
J. Chem. Research (M),
1984, 2101-2162

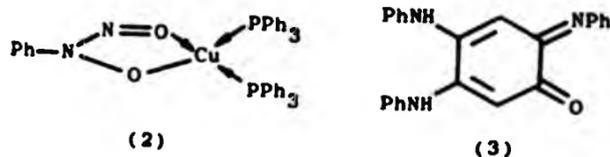
JOHN CHARALAMBOUS,* L. IAN B. HAINES,* NIGEL J. HARRIS,
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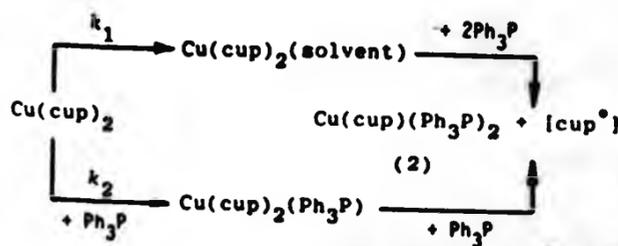
Although metal complexes of *N*-nitrosophenylhydroxylamine (cupferron) (cupH) (1) have been investigated extensively for analytical purposes¹ their composition, properties, and reactions have received very little attention. Here we report on the synthesis and properties of several complexes of (1).



The complexes $M(\text{cup})_2$ ($M = \text{Mn, Co, Fe, Ni, Cu, Zn}$) were prepared by the reaction of ammonium *N*-nitrosophenylhydroxylamine with the appropriate metal sulphate in water. All except the zinc(II) complex reacted readily with pyridine to give either the mono- ($M = \text{Co, Cu}$) or di-pyridine ($M = \text{Mn, Fe, Ni}$) adducts. Only $\text{Cu}(\text{cup})_2$ gave a reaction with triphenylphosphine. In acetone or pyridine at 20 °C the reaction gave the diamagnetic copper(I) complex (2), benzene, aniline, triphenylphosphine oxide, and (3). Reduction of copper(II) complexes by Lewis bases has been observed by several workers. However the fate of the ligand radical which is eliminated in such reactions has only been established in a few cases.^{5,6}

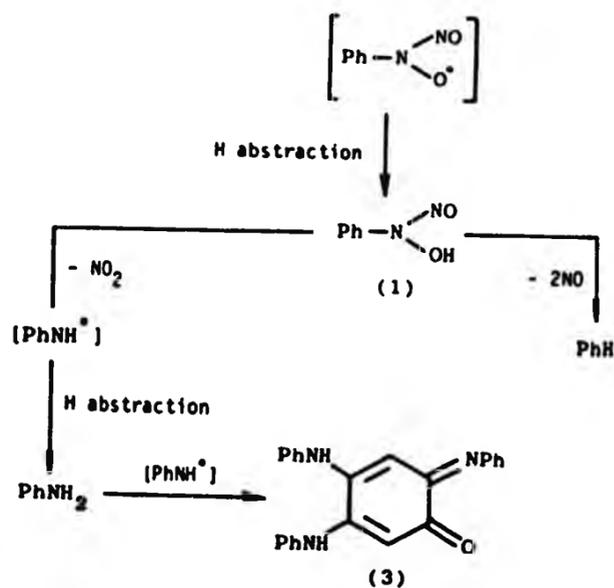


Kinetic studies of the reaction between $\text{Cu}(\text{cup})_2$ and triphenylphosphine in pyridine indicate that the reaction is proceeding by two concurrent pathways (Scheme 1) to give (2) and a ligand radical with the overall reaction



rate given by equation (1). Hydrogen abstraction by the ligand radical gives the free ligand which then decomposes to give the organic products (Scheme 2). This suggestion is supported by the behaviour of (1) towards triphenylphosphine and by its ready decomposition in pyridine to give benzene, aniline, and (3).

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{Ph}_3\text{P}] \quad (1)$$



The structure of $\text{Cu}(\text{cup})_2$ was shown earlier by X-ray crystallography to be square planar.³ The complexes $M(\text{cup})_2$ ($M = \text{Mn, Fe, Ni, Zn}$) are monomeric in chloroform solution and their X-ray powder patterns are similar but differ from that of the copper(II) complex. Variable-temperature magnetic measurements indicate no association in the solid state. These observations suggest that the complexes have tetrahedral structures. The increasing magnetic moment with temperature shown by $\text{Co}(\text{cup})_2$ and the positive value of θ suggest ferromagnetic behaviour and association in the solid state.¹⁰ Its diffuse reflectance spectrum is indicative of octahedral geometry. Significantly the X-ray powder pattern of the cobalt complex is different from that of the other $M(\text{cup})_2$ complexes. In solution the cobalt complex is monomeric.

The complexes $M(\text{cup})_2(\text{py})_2$ are monomeric in solution and have magnetic properties and/or electronic spectra indicative of octahedral geometry. The complexes $\text{Co}(\text{cup})_2(\text{py})$ and $\text{Cu}(\text{cup})_2(\text{py})$ are also monomeric in solution but the former is associated in the solid state as indicated by its magnetic behaviour.

*To receive any correspondence.

The X-ray structure of (2) was undertaken and a perspective view of the molecule is shown in the Figure. The Cu^I atom adopts a tetrahedral co-ordination geometry with the *N*-nitrosophenylhydroxylamine anion bonding through both the oxygen atoms.

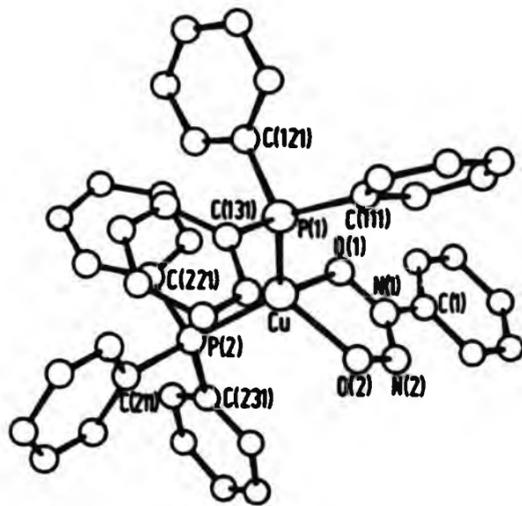


Figure The structure of (2). Important bond lengths: Cu—O(1), 2.102; Cu—O(2), 2.078; Cu—P(1), 2.240; Cu—P(2), 2.283 Å. Bond angles: P(2)—Cu—P(1), 125.6; O(1)—Cu—P(1), 113.5; O(1)—Cu—P(2), 104.2; O(2)—Cu—P(1), 115.0; O(2)—Cu—P(2), 111.5; O(2)—Cu—O(1), 75.1°

Crystal data for Cu(cup)(Ph₃P)₂(2). C₁₂H₁₅CuN₂O₂P₂, *M* = 724.5, triclinic, *a* = 10.097(4), *b* = 12.955(4), *c* = 14.740(6) Å, α = 88.384(3), β = 104.438(3), γ = 103.332(5)°, *V* = 1816.00 Å³, *Z* = 2, *D*_c = 1.25 g cm⁻³, *F*(000) 752, space group *PT*.

Single-crystal data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo-*K*_α radiation. The structure was solved and refined using 4642 unique reflections [*I* > 3σ(*I*)] to a final *R* factor of 0.042, using the SHELX76 program suite.

Techniques used: X-Ray crystallography, magnetic susceptibility measurements, u.v.-visible spectroscopy

References: 13

Table 1: Properties of bis(cupferronato)metal(II) (room temperature magnetic moments, reflectance spectra, relative molecular masses)

Table 2: Variable temperature magnetic data for Co(cup)₂ and Co(cup)₂(py)

Table 3: Preparative and analytical data for bis(cupferronato)-metal(II) complexes

Table 4: Rate constants for the reaction between Cu(cup)₂ and Ph₃P

Tables 5 and 6: Fractional atomic co-ordinates for Cu(cup)-(Ph₃P)₂

Table 7: Thermal parameters

Table 8: Bond lengths

Table 9: Bond angles

Table 10: Intermolecular distances

Table 11: Intramolecular distances

Table 12: Observed and calculated structure factors

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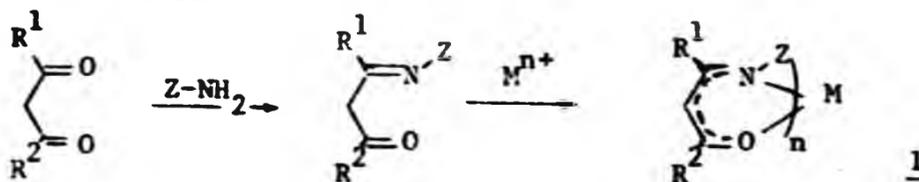
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Presented at the XXIII ICCO Conference, July 1984.

SYNTHESIS OF NEW SCHIFF BASES AND SCHIFF BASE COMPLEXES VIA METAL CONTROLLED STEREOSPECIFIC CONDENSATIONS OF COPPER(II) β -DIKETONATO COMPLEXES WITH $Z-NH_2$ ($Z = OH, NHAr, -(CH_2)_n-NH_2$)

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Schiff base complexes of type 1 are usually prepared directly from the Schiff base.

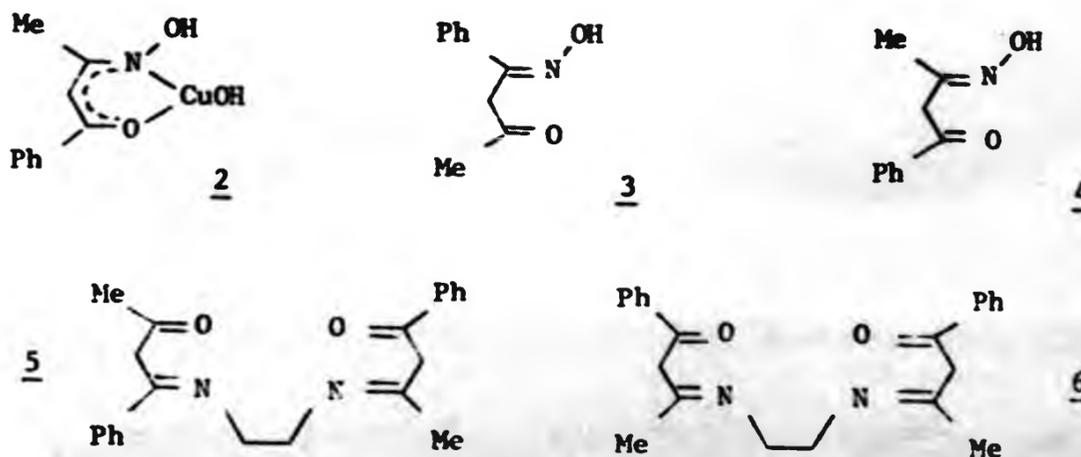


In complexes obtained from Schiff bases derived from unsymmetrical β -diketones the position of condensation is determined by the nature of groups R^1 and R^2 in the diketone and is the same in both ligands.

Condensation of $Z-NH_2$ ($Z = \text{e.g. OH, aryl, NHAr}$) with metal β -diketonates provides an alternative route to Schiff base complexes. We report that in such reactions in addition to the effect of groups R^1 and R^2 some metals have a pronounced effect on the position of condensation.

Our studies of the reaction of copper(II) β -diketonates demonstrate the role of the metal and its control on the stereospecificity of the condensation. Thus, for example, $Cu(bzac)_2$ ($bzACH = 1\text{-phenyl-1,3-butanedione}$) on treatment with NH_2OH affords two condensation products 2 and 3 in equimolar amounts in which condensation occurs at different carbonyl groups of the diketone moiety. This contrasts the behaviour of $bzACH$ towards NH_2OH which involves condensation of the carbonyl group adjacent to methyl to give 4. Similarly 5 has been obtained from $Cu(bzac)_2$ and 1,2-diaminoethane whereas the 1:2 reaction between $bzACH$ and the diamine gives the symmetrically condensed product 6.

The novel behaviour of the copper complexes is rationalised in terms of their ability to undergo Lewis base induced internal redox reactions. Detailed mechanistic proposals will be presented and discussed.



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