TITLE STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES AND OF THEIR OXIDATION OF AMINES

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INSTITUTION and DATE NORTH LONDON POLYTECHNIC
1988

STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES AND OF THEIR OXIDATION OF AMINES.

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

by

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The Polytechnic of
North London in
collaboration with
Beecham Pharmaceuticals

July 1988

Dedicated to my family.

Declaration

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

K.W.P. White

Keith William Peter White

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Abstract

The synthesis and structure of amine adducts of Cu(qo)$_2$, where qoH = 1,2-naphthoquinone 1-oxime (1-nqoH), 1,2-naphthoquinone 2-oxime (2-nqoH), 4-chloro-1,2-benzoquinone 2-oxime (4-ClqoH), 4-methyl-1,2-benzoquinone 2-oxime (4-MeqoH) have been examined. It has been shown that 1:1 adducts of the type Cu(qo)$_2$.X (X = benzylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, quinoline, 2,2'-dipyridyl (dipy) or 1,10-phenanthroline (phen)) are obtained under mild conditions. No structural conclusions could be drawn from magnetochemical and spectral studies of these adducts.

A study on the behaviour of the Cu(2-nqo)$_2$ complex and of its adducts involving benzylamine, pyridine, quinoline, 1,2-diaminoethane, 1,4-diaminobutane, 2,2'-dipyridyl, and 1,10-phenanthroline towards the Lewis bases, acetonitrile, heptane, propan-2-ol, pyridine, tetrahydropyran, toluene, 1,1,2-trichlorotrifluoroethane, and triphenylphosphine has been carried out. The tendency of the Cu(2-nqo)$_2$ complex and of its amine adducts to exhibit internal redox behaviour in the presence of a Lewis base has been shown to be dependent on: (1) the solvent having a readily abstractable hydrogen atom, (2) the donicity of the Lewis base, (3) the temperature employed, (4) the molecular environment of the complex, (5) adduct formation between the Lewis base and the complex, and (6) the nature of the amine.

1,2-Quinone mono-oximes have been prepared by the reaction of the Cu(qo)$_2$.X (X = dipy or phen) adducts on silica and by the ligand exchange of 1,2-quinone mono-oximato metal complexes, using a strong acid cation exchanger. Alkali metal 1,2-quinone mono-oximates have been synthesised by the reaction of alkali metal cyanides with transition metal complexes derived from 1,2-quinone mono-oximes.

The system M(qo)$_n$/O$_2$ has been found to be a powerful catalyst for the oxidation of amines. It is proposed that the oxidation involves oxygen transfer to the amine mediated by the quinone oximato catalyst and the concomitant formation of an amine N-oxide intermediate. It is also proposed that the oxidation involves reduction of the M(qo)$_n$ via an internal redox process. In all cases, the rate of conversion of the amine was shown to be dependent on the nature of the ligands and of the metal in the M(qo)$_n$ complex. The nature of amine oxidation product was shown to be independent of the reaction conditions employed. Comparative studies involving metal compounds such as copper(II) acetate and bis(acetylacetonato)copper(II) showed them to be inactive as catalysts for the oxidation of amines.

Acknowledgements

I would like to express my sincere thanks to my supervisors, Dr J. Charalambous and Dr L.I.B. Haines, for their guidance and encouragement throughout the course of this work.

My thanks are due to Dr E.G. Brain of Beecham Pharmaceuticals, for his many useful comments. I would also like to thank those many colleagues in the Department, especially to Mr J. Lota, for their interest and help.

Finally, my thanks go to my parents for their continual support and encouragement.

Whilst pursuing this research programme, the author was supported by a Research Scholarship from the Science and Engineering Research Council.

Abbreviations

qoH	any 1,2-quinone mono-oxime
bqoH	any 1,2-benzoquinone mono-oxime
nqoH	any 1,2-naphthoquinone mono-oxime
4-BrqoH	4-bromo-1,2-benzoquinone 2-oxime
4-ClqoH	4-chloro-1,2-benzoquinone 2-oxime
4,6-Cl_2qoH	4,6-dichloro-1,2-benzoquinone 2-oxime
5-MeOqoH	5-methoxy-1,2-benzoquinone 2-oxime
4-MeqoH	4-methyl-1,2-benzoquinone 2-oxime
1-nqoH	1,2-naphthoquinone 1-oxime
2-nqoH	1,2-naphthoquinone 2-oxime
dnrH_2	2,4-dinitrosoresorcinol
6-CldnrH_2	6-chloro-2,4-dinitrosoresorcinol
g.l.c.	gas liquid chromatography
i.r.	infra-red
m.s.	mass spectrum
n.m.r.	nuclear magnetic resonance
t.l.c.	thin layer chromatography
py	pyridine
quin	quinoline
dipy	2,2'-dipyridyl
phen	1,10-phenanthroline
bza	benzylamine
en	1,2-diaminoethane
pn	1,3-diaminopropane
bn	1,4-diaminobutane
chelH	chelating ligand
LB	Lewis base

CN	coordination number
IRR	internal redox reaction
r.t.	room temperature

Contents

6.8 References.

Chapter 1

1 1,2-Quinone mono-oximes and their metal complexes.

1.1 The structure of 1,2-quinone mono-oximes.

1,2-Quinone mono-oximes have been known for a considerable length of time. They are considered as tautomeric with 2-nitrosophenols (Figure 1.1). The structure of 1,2-quinone mono-oximes has been assessed using various techniques, e.g. i.r. spectroscopy,[1-3] u.v. spectrophotometry,[4] and mass spectrometry.[5] However, only X-ray crystallography has fully established their solid state structure.[6-11]

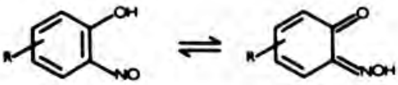
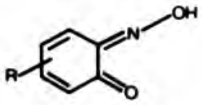


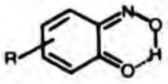
Figure 1.1

The X-ray crystallographic determinations of α-5-methoxy-1,2-benzoquinone 2-oxime,[6] β-5-n-propoxy-1,2-benzoquinone 2-oxime,[7] α-5-(2'-chloroethoxy)-1,2-benzoquinone 2-oxime,[8] 6-t-butyl-1,2-naphthoquinone 1-oxime,[9] 1,2-naphthoquinone 2-oxime-5-sulphonic acid monohydrate,[10] and potassium 1,2-naphthoquinone 1-oxime-7-sulphonate monohydrate[11] show that these compounds are all essentially quinone oximic. In all cases, the short C-O and C-N bond lengths, and the long N-O and C_1-C_2 bond lengths indicate the quinone oximic structure (Table 1.1). The C-O bond lengths are similar to those of a double bond rather than of a phenolic C-O group as for example, 1.36 Å in resorcinol.[6] The lengths of the bonds in the side chain, >C=N-O, are consistent with values obtained for other compounds containing the oxime grouping as for example in dimethyldioxime, >C=N, (1.27 Å), =N-O, (1.38 Å).[6]

In α-5-methoxy-1,2-benzoquinone 2-oxime, α-5-(2'-chloroethoxy)-1,2-benzoquinone 2-oxime, 1,2-naphthoquinone 2-oxime-5-sulphonic acid monohydrate and potassium 1,2-naphthoquinone 1-oxime-7-sulphonate monohydrate, the oxygen of the oxime group is in an <u>anti</u> configuration (1.1). In contrast, β-5-n-propoxy-1,2-benzoquinone 2-oxime and 6-t-butyl-1,2-naphthoquinone 1-oxime have the oxygen of the oxime group directed towards the quinone oxygen in a <u>syn</u> configuration (1.2).



(1.1)

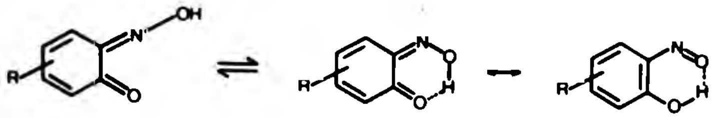


(1.2)

Table 1.1 Selected bond distances (Å) of 1,2-quinone mono-oximes.

Compound	C-O	C-N	N-O	C_1-C_2
α-5-Methoxy-1,2-benzoquinone 2-oxime[6]	1.23	1.22	1.36	1.51
β-5-n-Propoxy-1,2-benzoquinone 2-oxime[7]	1.27	1.32	1.35	1.48
α-5-(2'-Chloroethoxy)-1,2-benzoquinone 2-oxime[8]	1.25	1.31	1.37	1.50
6-t-Butyl-1,2-naphthoquinone 1-oxime[9]	1.24	1.30	1.36	1.50
1,2-Naphthoquinone 2-oxime-5-sulphonic acid monohydrate[10]	1.24	1.30	1.38	1.47
Potassium 1,2-naphthoquinone 1-oxime-7-sulphonate monohydrate[11]	1.22	1.31	1.39	1.52

In view of the above, a better representation of the quinone oximic/nitrosophenolic system is as shown in Scheme 1.1.

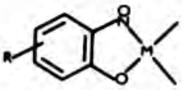


Scheme 1.1

The preparation of 1,2-quinone mono-oximes is discussed in Chapter 4.

1.2 The nature and structure of metal complexes derived from 1,2-quinone mono-oximes.

The formation of a 1,2-quinone mono-oximato metal complex involves the replacement of the acidic proton by the metal in the 1,2-quinone mono-oxime tautomeric system (Scheme 1.1). The complexes have been formulated with either a quinone oximic or a nitrosophenolic structure. They might also be described as being a resonance hybrid of these two extremes. A further complication arises from the possibility that the oximato (nitroso) group can potentially coordinate to the metal through the nitrogen and/or oxygen atom. The possible valence bond structures are given below (1.3-1.7).



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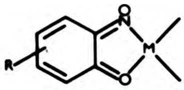

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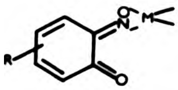

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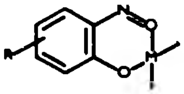

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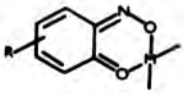

(1.7)

The structure of 1,2-quinone mono-oximato metal complexes has been assessed using various techniques which have included i.r. spectroscopy,[12-18] u.v. spectrophotometry,[14] and mass spectrometry,[13, 15, 19-20] but only X-ray crystallography has fully established their structure in the solid state.[21-28]

The crystal structures of several metal complexes derived from 1,2-quinone mono-oximes are available (Table 1.2). The results show that in most complexes, e.g. ferroverdin K[Fe(qo)$_3$] (qoH = 4-vinyl phenyl ester of 3-nitroso-4-hydroxybenzoic acid),[21] K[Ni(4-Clqo)$_3$].(CH$_3$)$_2$CO,[22] Cu(4-Meqo)$_2$.py,[23] Cu(1-nqo)$_2$.2(CH$_3$)$_2$CO,[24] Cu(2-nqo)$_2$.H$_2$O,[25] Cu(4-Clqo)$_2$.dipy,[26] and [pyH][Ir(1-nqo)(py)Cl$_3$],[27] the nitrogen atom of the NO group is bonded to the metal atom and the chelate rings are thus five membered (1.3). In all cases, the ligands are essentially quinone oximic in nature. This is indicated by the presence of two short and four long carbon-carbon bonds in the hexagonal ring of the 1,2-quinone mono-oximato ligands. Futhermore in all of the complexes,[21-27] the respective carbon-oxygen and carbon-nitrogen bonds are shorter than would be expected for a nitrosophenolic structure. The carbon-oxygen bond lengths observed are in the range of 1.24-1.30 Å, which are shorter than the equivalent bond in salicylaldoxime and salicylaldehyde complexes which varies from 1.31 Å to 1.36 Å, but longer than the carbon-oxygen bond in naphthoquinones (1.22 Å).[24] The observed carbon-nitrogen bond lengths (1.33-1.42 Å) are longer than those in several typical

Table 1.2 Selected bond distances (Å) of transition metal complexes derived from 1,2-quinone mono-oximes.

Compound		C-O	C-N	N-O	M-O	M-N
Ferroverdin[21]		1.30	1.42	1.25	1.95	1.84
$K[Ni(4\text{-}Clqo)_3].(CH_3)_2CO$[22]		1.25	1.33	1.27	2.06	2.01
$Cu(4\text{-}Meqo)_2.py$[23]		1.27	1.35	1.25	1.97	2.00
$Cu(1\text{-}nqo)_2.2(CH_3)_2CO$[24]		1.30	1.35	1.26	1.95	1.99
$Cu(2\text{-}nqo)_2.H_2O$[25]		1.28	1.35	1.26	1.97	1.98
$Cu(4\text{-}Clqo)_2.dipy$[26]	A'	1.24	1.36	1.25	2.32	2.02
	A''	1.24	1.34	1.27	2.03	2.00
	B'	1.25	1.37	1.26	2.26	2.11
	B''	1.26	1.38	1.24	2.11	1.99
$[pyH][Ir(1\text{-}nqo)(py)Cl_3]$[27]		1.30	1.35	1.27	2.03	2.10
$[UO_2(2\text{-}nqo)_2(H_2O)_2].2CHCl_3$[28]		1.23	1.30	1.34		2.44
$[UO_2(1\text{-}nqo)_2(OPh_3P)(H_2O)]$[28]		1.25 1.21	1.33 1.33	1.35 1.32		2.48 2.47

A and B denote two crystallographically nonequivalent molecules. Within each molecule the primes are used for the two nonequivalent 4-chloro-1,2-benzoquinone 2-oximato ligands.

oximates (the average value for the <u>vic</u>-dioximates is 1.30 Å),[24] but shorter than the carbon-nitrogen bond length (1.45 Å) found in the nitrosobenzene dimer.[29]

In the 1,2-quinone mono-oximato complexes of heavier metals, the type of bonding of the 1,2-quinone mono-oximato ligands can differ. For example, the 1,2-naphthoquinone 2-oximato anions in [UO_2(2-nqo)$_2$(H_2O)$_2$].2$CHCl_3$ are bonded to the metal through the oxime group only.[28] The carbonyl group is not coordinated to the metal. The latter feature is reflected in the short carbon-oxygen bond length (1.23 Å) compared to that of coordinated carbon-oxygen groups of 1,2-quinone mono-oximato ligands. Bonding of the ligands to the metal through the oxime group only is also shown by the [UO_2(1-nqo)$_2$(OPh_3P)(H_2O)] complex.[28] In the platinum and gold complexes derived from 4-isonitroso-3(R)-isoxazol-5(4H)-one, coordination is via the nitrogen atom of the NO group only (Figures 1.2-1.3).[30]

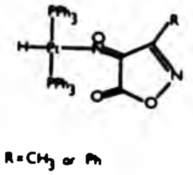

Figure 1.2

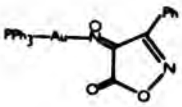

Figure 1.3

The various structural studies carried out on 1,2-quinone mono-oximato metal complexes of the type $M(qo)_3$ and $[M(qo)_3]^-$ have shown that they have, as expected, octahedral geometry.[16, 21-22] The complexes of the type $M(qo)_2$ generally exhibit association. This type of behaviour has been indicated by relative molecular mass determinations (M = Ni(II)),[19] magnetic susceptibility measurements (M = Ni(II)[19] or Fe(II)),[31] Mössbauer spectroscopy (M = Fe(II)),[31] and mass spectrometry (M = Ni(II)).[19-20]

1.3 The synthesis of metal complexes derived from 1,2-quinone mono-oximes.

The principal methods used for the preparation of 1,2-quinone mono-oximato metal complexes are:

(1) the direct reaction of the 1,2-quinone mono-oxime with a metal salt or hydroxide (Direct method);

(2) the nitrosation of a phenol, using sodium nitrite, in the presence of a transition metal salt (Nitrosation method);

(3) the reaction of a metal carbonyl with the 1,2-quinone mono-oxime (Metal carbonyl method).

The direct method.-1,2-Quinone mono-oximato metal complexes can be obtained by the direct reaction of the 1,2-quinone mono-oxime with a metal salt or hydroxide (Reaction 1.1). This procedure is suitable for the preparation of various transition metal complexes[12-14, 27] as well as of non-transition metal complexes.[32] However, the applicability of this approach is limited because only a small number of 1,2-quinone mono-oximes are available (see Chapter 4).

$$n\ \mathrm{qoH} + \mathrm{MX}_n \longrightarrow \mathrm{M(qo)}_n + n\ \mathrm{HX}$$

Reaction 1.1

The nitrosation method.-Nitrosation of a phenol in the presence of a transition metal salt has been used to prepare a large number of a wide range of transition metal 1,2-quinone mono-oximato complexes.[12-13, 15-16] A feature of the nitrosation method is that it does not always yield solely a neutral complex of type, $M(qo)_n$. In addition, this method may give various other types of complex. For example, the nitrosation of 4-chlorophenol, using potassium nitrite, in the presence of nickel(II) chloride gives $K[Ni(4\text{-}Clqo)_3].(CH_3)_2CO$, as well as the hydrated neutral bis-chelate $Ni(4\text{-}Clqo)_2(H_2O)_2$.[13] Similarly, the nitrosation of 1-naphthol, using sodium nitrite, in the presence of cobalt(II) chloride gives $Na[Co(2\text{-}nqo)_2(NO_2)_2]$ and the neutral tris-chelate $Co(2\text{-}nqo)_3$.[16]

The metal carbonyl method.-This method has been applied for the synthesis of neutral iron and cobalt 1,2-quinone mono-oximato complexes.[33-34] Pentacarbonyliron(0) has been shown to react with 1,2-naphthoquinone 2-oxime to give mainly bis(1,2-naphthoquinone 2-oximato)iron(II) and various organic products.[33] Similarly, the reaction of octacarbonyldicobalt(0) with 1,2-naphthoquinone 2-oxime gives bis(1,2-naphthoquinone 2-oximato)cobalt(II), tris(1,2-naphthoquinone 2-oximato)cobalt(III) and organic products.[34]

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Chapter 2

2 Lewis base adducts of bis(1,2-quinone mono-oximato)copper(II) complexes.

Adducts of type $Cu(qo)_2.X$ (qoH = 1,2-naphthoquinone 1-oxime (1-nqoH), 1,2-naphthoquinone 2-oxime (2-nqoH), 4-chloro-1,2-benzoquinone 2-oxime (4-ClqoH), and 4-methyl-1,2-benzoquinone 2-oxime (4-MeqoH)) have been prepared, where X = benzylamine (bza), quinoline (quin), 1,2-diaminoethane (en), 1,3-diaminopropane (pn), 1,4-diaminobutane (bn), 2,2'-dipyridyl (dipy) or 1,10-phenanthroline (phen). The adducts have been investigated by elemental analysis, thermal gravimetric analysis, magnetic susceptibility measurements, infra-red spectroscopy and ultraviolet / visible spectrophotometry.

2.1 Introduction.

In modern usage, a Lewis acid is defined as any substance capable of accepting electron density, and a Lewis base as any substance capable of donating electron density.[1] Many substances are capable of being either one or the other, and some materials are capable of being both. A Lewis acid/base interaction requires coordination of the two so that the bonding electron density is shared by both the acid and the base. With this definition it becomes difficult to find chemical reactions which do not involve Lewis acid-base interactions in at least some stage of the process.

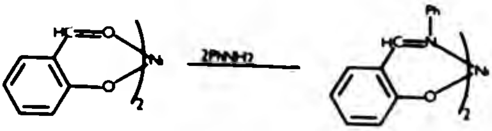
Neutral chelates of the type $M(chel)_2$ and $M(chel)_3$ can undergo a variety of reactions with Lewis bases. These reactions include: (1) adduct formation, (2) reaction with the coordinated chelated ligands, and (3) internal redox reaction.

Adduct formation is shown by complexes of type $M(chel)_2$, and often involves a change in the coordination number of the metal. In such reactions, the oxidation state of the metal remains unchanged. For example, the bis-(acetylacetonato)nickel(II) complex readily reacts with pyridine to give the adduct, bis(acetylacetonato)bis(pyridine)nickel(II) (Reaction 2.1).[2]

Reactions with the coordinated ligands can occur for complexes of the type $M(chel)_2$ (e.g. Reaction 2.2)[3] and $M(chel)_3$. In such reactions the coordination number of the metal may change, but its oxidation state remains unaffected.

$$Ni_3(acac)_6 \xrightarrow{py} 3Ni(acac)_2(py)_2$$

Reaction 2.1



Reaction 2.2

Internal redox reactions are shown by complexes of type $M(chel)_2$ and $M(chel)_3$. The metal is reduced to a lower oxidation state and the coordination number of the complex may change. For example, bis(acetylacetonato)copper(II) undergoes an internal redox reaction in the presence of triphenylphosphine to give acetylacetonatobis(triphenylphosphine)copper(I) (Reaction 2.3).[4]

$$Cu(acac)_2 \xrightarrow{Ph_3P} Cu(acac)(Ph_3P)_2 + [acac^{\cdot}]$$

Reaction 2.3

This chapter is mainly concerned with reactions of complexes of the type $M(qo)_2$ with Lewis bases which lead to adduct formation. Other types of reaction of Lewis bases with $M(qo)_n$ ($n = 2$ or 3) complexes are discussed in Chapters 3-5.

2.2 Lewis base adducts of bis-chelated metal(II) complexes.

In general, bis-chelated complexes of metals such as copper(II), cobalt(II), zinc(II), manganese(II) and ruthenium(II) can behave as Lewis acids and form adducts with Lewis bases.[2] As noted above, such a reaction usually involves an increase in the coordination number of the complex, but the oxidation state of the metal remains unchanged. The product obtained, either 1:1 or 1:2 adduct, is dependent on the metal, the electron withdrawing strength of the anionic chelating ligands, the donor strength of the Lewis base, and the mode of coordination of the Lewis base. The ease of adduct formation is dependent on the degree of association of the bis-chelate. In general, monomeric $M(chel)_2$ complexes tend to form adducts with Lewis bases more readily than associated $M(chel)_2$ complexes (Figure 2.1).

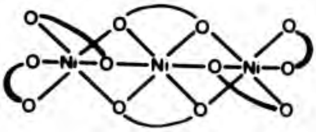


Figure 2.1

Extensive research has been carried out on the Lewis base adducts of metal bis-chelates derived from β-diketones.[2] The reactions of Lewis bases with bis-chelates of type $M(qo)_2$ involving adduct formation have received considerable attention, but it has been of an unsystematic nature (Table 2.1).[5-16]

Copper(II) bis-chelates.-In the case of bis-chelated complexes of copper(II), the more usual product of the reaction with Lewis bases is the five-coordinate square pyramidal 1:1 adduct.[2] Six-coordination can be obtained when the electron withdrawing nature of the chelating ligands increases the residual positive charge on the copper ion. For instance, the bis(hexafluoroacetylacetonato)copper(II) complex forms an isolable 1:2 adduct with pyridine at room temperature, as opposed to the bis(acetylacetonato)copper(II) complex which forms an unstable 1:1 adduct which loses pyridine on exposure to air.[17] When bidentate chelating ligands such as 2,2'-dipyridyl, 1,10-phenanthroline and 1,2-diaminoethane form adducts with metal(II) bis-chelates, it does not necessarily imply that the metal attains six-coordination despite the presence of three bidentate and potentially chelating ligands. For example, it has recently been shown by crystal stucture determination that in Cu(acac)(hfac)(1,10-phen) (hfac = hexafluoroacetylacetonate) the copper is five-coordinate, with the hexafluoroacetylacetonate anion acting as a monodentate ligand (Figure 2.2).[18]

Table 2.1 Lewis base adducts of bis(1,2-quinone mono-oximato)metal(II) complexes.

1:1 Adducts	CN	1:2 Adducts (CN = 6)
Cu(qo)$_2$.py[5]	5	Cu(1-nqo)$_2$.2(CH$_3$)$_2$CO[7]
Cu(2-nqo)$_2$.H$_2$O[6]	5	Cu(4-Clqo)$_2$.2Bu$_4$NI[10]
Cu(nqo)$_2$(nicotine)[8]	5	Ni(bqo)$_2$.2py[11]
Cu(4-Clqo)$_2$.dipy[9]	6	Ni(nqo)$_2$.2py[13]
Cu(4-Clqo)$_2$.phen[9]	6	Ni(nqo)$_2$.2NH$_3$[13]
Cu(4-Clqo)$_2$(imidazole)[9]	5	Fe(nqo)$_2$.2py[14]
Cu(4-Clqo)$_2$(pyrazole)[9]	5	Fe(5-MeOqo)$_2$.2py[14]
Cu(4-Clqo)$_2$.Bu$_4$NBr[10]	5	Co(nqo)$_2$.2py[15]
Cu(4-Clqo)$_2$.Bu$_4$NCl[10]	5	Ru(nqo)$_2$.2py[16]
Cu(4-Clqo)$_2$.MeOH[10]	5	Ru(nqo)$_2$.2Ph$_3$P[16]
Ni(5-MeOqo)$_2$.PhNH$_2$[12]	5	
Ni(4-Clqo)$_2$.PhNH$_2$[12]	5	

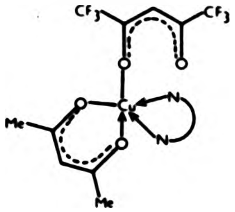


Figure 2.2

A number of Lewis base adducts of bis(1,2-quinone mono-oximato)copper(II) complexes have been isolated (Table 2.1).[5-10] The $Cu(qo)_2$ complexes are known to form crystalline 1:1 adducts with pyridine.[5] Recently, the behaviour of the bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) complex towards halides was studied.[10] With chlorides and bromides, the 1:1 adducts were formed. These adducts were isolated as the crystalline tetrabutylammonium salts, by employing propan-2-ol as the solvent. With methanol as the reaction medium, the 1:1 methanol adduct was generally obtained as the main product. With iodides, two different types of adducts were obtained, i.e. $Cu(4\text{-}Clqo).2Bu_4NI$ and $3Cu(4\text{-}Clqo)_2.2KI$.

The crystal structures of several Lewis base adducts of bis(1,2-quinone mono-oximato)copper(II) complexes have been determined. The adducts bis(4-methyl-1,2-benzoquinone 2-oximato)(pyridine)copper(II),[19] bis(4-chloro-1,2-benzoquinone 2-oximato)(methanol)copper(II),[20] and bis(1,2-naphthoquinone 2-oximato)(aquo)copper(II)[6] have been shown to have distorted square pyramidal geometries. The chelate rings are in trans-position and have a distorted square planar configuration. The donor atom of the neutral ligand is in the axial position. The bis(1,2-naphthoquinone 1-oximato)bis(acetone)copper(II) adduct is octahedral.[7] Again the trans-chelated rings form a square planar configuration. The octahedral arrangement is completed by the oxygen atoms of the two acetone molecules. Bis(4-choro-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)copper(II) has a tetragonally distorted octahedral geometry with the 4-chloro-1,2-benzoquinone 2-oximato ligands in a cis,cis arrangement.[9] The 2,2'-dipyridyl ligand is chelated to the metal. By analogy, six-coordination has also been suggested for the bis(4-chloro-1,2-benzoquinone 2-oximato)(1,10-phenanthroline)copper(II) adduct.[9] Potassium bis(μ-iodo)tris[bis-(4-chloro-1,2-benzoquinone 2-oximato)cuprate(II)] is the potassium salt of a trinuclear anionic species, $[Cu(4\text{-}Clqo)_2\text{-}I\text{-}Cu(4\text{-}Clqo)_2\text{-}I\text{-}Cu(4\text{-}Clqo)_2]^{2-}$, in which the copper(II) centres are linked by single iodide bridges.[10] The central copper atom, which lies on an inversion centre, reaches hexacoordination through tetragonally distorted octahedral geometry. The coordination of the 4-chloro-1,2-benzoquinone 2-oximato ligands around it is disordered. The outer copper atoms have a distorted square pyramidal coordination.

Nickel(II), cobalt(II) and iron(II) bis-chelates.- Nickel(II), cobalt(II) and iron(II) bis-chelates normally form six-coordinate adducts with Lewis bases.[2] Several adducts of bis(acetylacetonato)nickel(II) of the type $Ni(acac)_2(LB)_2$ have been reported with monodentate Lewis bases such as water, ethanol, ammonia, pyridine, butylamine, and benzylamine.[2] Similarly, bis(acetylacetonato)-cobalt(II) and bis(acetylacetonato)iron(II) both form 1:2 adducts with pyridine. Crystal structure determinations have shown that the $Ni(acac)_2(py)_2$ and $Co(acac)_2(py)_2$ adducts have distorted octahedral geometries.[2]

The bis(1,2-quinone mono-oximato)nickel(II) complexes form 1:2 six-coordinate adducts with pyridine.[11, 13] In contrast, the complexes bis(5-methoxy-1,2-benzoquinone 2-oximato)nickel(II) and bis(4-chloro-1,2-benzoquinone 2-oximato)nickel(II) react with aniline to give 1:1 five-coordinate adducts.[12]

Zinc(II), manganese(II) and ruthenium(II) bis-chelates.-Zinc(II) and manganese(II) bis-chelates are known to form both five- and six-coordinate adducts.[2] Bis(acetylacetonato)zinc(II) is isolated as a monohydrate.[2] By reaction with heterocyclic Lewis bases, the water molecule can be replaced giving five-coordinate adducts of the type $Zn(acac)_2(LB)$ (LB = pyridine, 2-methylpyridine or 4-methylpyridine). Established six-coordinate complexes are $Zn(acac)_2(NH_3)_2$ and $Zn(acac)_2(dipy)$. Bis(acetylacetonato)-manganese(II) resembles the zinc(II) complex in forming both five- and six-coordinate adducts. The former include 1:1 adducts with pyridine and 4-methylpyridine. The six-coordinate compounds include 1:1 adducts with 2,2'-dipyridyl and 1,10-phenanthroline.

The bis(1,2-naphthoquinone mono-oximato)manganese(II) complexes fail to form isolable adducts with pyridine and triphenylphosphine.[21] This is due to the polymeric nature of these complexes. However, the corresponding ruthenium(II) complexes readily form 1:2 six-coordinate adducts with pyridine and triphenylphosphine.[16]

The significance of adduct formation between bis(1,2-quinone mono-oximato)copper(II) complexes and Lewis bases.- Adduct formation between bis(1,2-quinone mono-oximato)copper(II) complexes and Lewis bases is of considerable significance. This type of interaction has been inferred to be involved in many synthetically important reactions of $Cu(qo)_2$ complexes such as Diels-Alder cycloadditions,[22-23] and internal redox reactions.[24-26]

In view of the above, a better understanding of the reactivity and synthetic utility of the $Cu(qo)_2$ complexes, and of other metal(II) complexes derived from 1,2-quinone mono-oximes, could be obtained if more is known about the formation and the molecular structure of their Lewis base adducts.

2.3 A study of the amine adducts of bis(1,2-quinone mono-oximato)copper(II) complexes.

2.3.1 Introduction and procedure.

Previous studies in these laboratories have shown that the heating of a bis(1,2-quinone mono-oximato)copper(II) complex with benzylamine[26] or 1,2-diaminoethane[24, 26] in toluene gives rise to an internal redox reaction with the formation of a copper(I) species and various organic products derived from the 1,2-quinone mono-oximato ligand. There was no isolation of the $Cu(qo)_2$ amine adduct. In this study, it proved possible to isolate these adducts as well as many others by carrying out the reaction of the bis(1,2-quinone mono-oximato)copper(II) complex with the amine at room temperature, and using acetonitrile as the solvent (Table 2.2).

2.3.2 Results.

The bis(1,2-quinone mono-oximato)copper(II) amine adducts were formulated on the basis of their elemental analysis and i.r. spectra which indicated the presence of coordinated amine. In the case of bis(1,2-naphthoquinone 2-oximato)(quinoline)copper(II), further support for the proposed formulation was obtained from a thermal gravimetric study of the adduct.

Thermal gravimetric analysis of the bis(1,2-quinone mono-oximato)(pyridine)copper(II) adducts has previously shown that one mole of pyridine is lost per mole of adduct between 150 and 200 °C to give the respective bis(1,2-

Table 2.2 The amine adducts of $Cu(qo)_2$.

Monodenate amines	Bidentate amines
$Cu(1\text{-}nqo)_2.bza$	$Cu(2\text{-}nqo)_2.en$
$Cu(2\text{-}nqo)_2.bza$	$Cu(2\text{-}nqo)_2.pn$
$Cu(4\text{-}Clqo)_2.bza$	$Cu(1\text{-}nqo)_2.bn$
$Cu(4\text{-}Meqo)_2.bza$	$Cu(2\text{-}nqo)_2.bn$
$Cu(2\text{-}nqo)_2.quin$	$Cu(4\text{-}Clqo)_2.bn$
	$Cu(4\text{-}Meqo)_2.bn$
	$Cu(1\text{-}nqo)_2.dipy$
	$Cu(2\text{-}nqo)_2.dipy$
	$Cu(4\text{-}Clqo)_2.dipy$
	$Cu(4\text{-}Meqo)_2.dipy$
	$Cu(1\text{-}nqo)_2.phen$
	$Cu(2\text{-}nqo)_2.phen$
	$Cu(4\text{-}Clqo)_2.phen$
	$Cu(4\text{-}Meqo)_2.phen$

quinone mono-oximato)copper(II) complexes which subsequently decompose in the region 170-275 °C.[5] As noted above, similar behaviour was shown by the bis(1,2-naphthoquinone 2-oximato)(quinoline)copper(II) adduct. Thermal gravimetric analysis of the adduct gave a quantitative loss of quinoline (1 mol/1 mol of adduct) between 120 and 160 °C with the parent Cu(2-nqo)$_2$ complex decomposing at ca. 200 °C. However, in the case of the Cu(qo)$_2$ adducts involving benzylamine, 1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane, there was no similar loss of amine. Instead, the adducts decomposed in a single stage between 140 and 180 °C. The difference in behaviour can be accounted for in terms of the primary amine group(s) present which could interact with the 1,2-quinone mono-oximato ligands.

2.3.3 Discussion.

Both the monodentate and bidentate amines afforded 1:1 adducts with the various bis(1,2-quinone mono-oximato)-copper(II) complexes examined. The behaviour of benzylamine and quinoline is in accordance with the other described adducts involving monodentate ligands.[5, 6, 10] The formation of isolable adducts with all the wide variety of amines studied gives further indication of the notable electron withdrawing power of the 1,2-quinone mono-oximato ligands. Recently, it has been found by chemical or electrochemical reduction of the Cu(4-Clqo)$_2$ complex, that the [Cu(4-Clqo)$_2$]$^-$ anionic species is obtained where the electron is mainly localised on the 4-chloro-1,2-benzoquinone 2-oximato ligands, while the copper centre remains in the +2 oxidation state.[10]

In the case of the bis(1,2-quinone mono-oximato)copper(II) adducts involving 2,2'-dipyridyl, 1,10-phenanthroline, 1,2-diaminoethane, 1,3-diaminopropane, and 1,4-diaminobutane, the amine may act as a monodentate or bidentate ligand giving rise to five- or six-coordinate species, respectively.

No structural conclusions on the bis(1,2-quinone mono-oximato)copper(II) amine adducts could be drawn from magnetochemical or spectral studies of these adducts. Nevertheless, it is possible to make some proposals regarding their structure by analogy to several X-ray crystallographic structure determinations of various Lewis base adducts of $Cu(qo)_2$ complexes.

In the bis(1,2-quinone mono-oximato)(benzylamine)-copper(II) and bis(1,2-naphthoquinone 2-oximato)(quinoline)copper(II) adducts, square pyramidal geometry around the copper can be assumed, by analogy to the bis(4-methyl-1,2-benzoquinone 2-oximato)(pyridine)copper(II),[19] bis(4-chloro-1,2-benzoquinone 2-oximato)(methanol)copper(II),[20] and bis(1,2-naphthoquinone 2-oximato)(aquo)copper(II)[6] adducts. Similarly, octahedral geometry can be intuitively predicted for the bis(1,2-quinone mono-oximato)copper(II) adducts involving 2,2'-dipyridyl, 1,10-phenanthroline, 1,2-diaminoethane, and 1,3-diaminopropane, by analogy to the bis(4-choro-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)-

copper(II) adduct.[9] Further evidence for the proposed structures is given by the behaviour of the bis(1,2-naphthoquinone 2-oximato)copper(II) amine adducts towards Lewis base solvents (see Chapter 3).

There are several possibilities for the mode of coordination of 1,4-diaminobutane in the bis(1,2-quinone mono-oximato)(1,4-diaminobutane)copper(II) adducts, and therefore their structure cannot be defined.

Magnetic susceptibilities of the amine adducts of bis(1,2-quinone mono-oximato)copper(II) complexes were measured, and the calculated magnetic moments are presented in Table 2.3.

At room temperature, magnetically dilute copper(II) complexes have magnetic moments in the range 1.72-2.20 μ_B.[27-28] These values are irrespective of stereochemistry and independent of temperature except at extremely low temperatues. In magnetically concentrated copper(II) systems low magnetic moments are observed, e.g. in the copper(II) carboxylates.[28] This is due to coupling of unpaired electrons between neighbouring copper atoms. The magnetic moments of the $Cu(qo)_2$ amine adducts examined in this study lie in the range 1.74-2.05 μ_B, suggesting that they are magnetically dilute and hence monomeric. In all cases, the magnetic moments of the adducts were higher than those of the respective parent bis(1,2-quinone mono-oximato)copper(II) complexes.[5] This is in accordance with the possibility of some degree of association in the latter.[5]

Virtually all complexes and compounds of copper(II)

Table 2.3 The magnetic moments of Cu(qo)$_2$ and of their amine adducts (μ_{eff} = μ_B at ca. 293 K).

Cu(qo)$_2$ / Amine	Cu(1-nqo)$_2$	Cu(2-nqo)$_2$	Cu(4-Clqo)$_2$	Cu(4-Meqo)$_2$
	μ_B	μ_B	μ_B	μ_B
	1.81[5]	1.65[5]	1.80[5]	1.76[5]
py	1.82[5]	1.67[5]	1.82[5]	1.83[5]
quin		1.77		
dipy	1.95	1.74	2.05	2.01
phen	1.93	1.74	2.00	2.01
bza	2.02	1.85	1.86	1.78
en		1.82		
pn		1.93		
bn	2.04	2.03	1.87	1.86

are blue or green. Exceptions are generally caused by strong ultraviolet bands---charge-transfer bands---tailing off into the blue end of the visible spectrum, thus causing the substances to appear red or brown. The blue or green colours are due to the presence of the absorption bands of the d-d transitions, in the 600-900 nm region of the spectrum. The envelopes of these bands are generally unsymmetrical, seeming to encompass several overlapping transitions.

In this study, the electronic spectra of the bis(1,2-naphthoquinone 2-oximato)copper(II) complex and of the bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = pyridine, quinoline, 2,2'-dipyridyl, 1,10-phenanthroline, benzylamine, 1,2-diaminoethane, 1,3-diaminopropane or 1,4-diaminobutane) adducts in methanol were investigated (Table 2.4). All the complexes, which are red or brown in the solid state, gave two maxima in the region 400-505 nm. The absorption spectra of the complexes all included very intense charge-transfer or ligand bands. Ligand complexity prevents unambiguous conclusions to be drawn from the electronic spectral data obtained. Thus, no structural information about the $Cu(2\text{-}nqo)_2$ amine adducts was provided. Similar observations have previously been reported for other bis(1,2-quinone mono-oximato)copper(II) complexes.[5] The intensities of the bands in the solution electronic spectra of the $Cu(2\text{-}nqo)_2$ complex and of its amine adducts, illustrates the chromophoric character of 1,2-naphthoquinone 2-oxime.

Table 2.4 The solution electronic spectra of $Cu(2\text{-}nqo)_2$ and of its amine adducts.

	λ_{max} (nm)	ϵ (m^2 mol^{-1})	λ_{max} (nm)	ϵ (m^2 mol^{-1})
$Cu(2\text{-}nqo)_2$	420	232	505	295
Amine				
py	418	778	503	1037
quin	420	620	503	792
dipy	413	838	492	786
phen	410	619	492	583
bza	412	603	505	634
en	400	917	475	933
pn	400	705	480	764
bn	413	800	497	952

The electron impact mass spectra of the bis(1,2-quinone mono-oximato)copper(II) amine adducts could not be obtained due to their decomposition on heating prior to ionisation. Similar behaviour has previously been shown by the bis(1,2-quinone mono-oximato)(pyridine)copper(II) adducts.[5]

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Chapter 3

3 A study of the internal redox behaviour of bis(1,2-naphthoquinone 2-oximato)copper(II) and of its amine adducts.

A study is reported of the behaviour of the Cu(2-nqo)$_2$ complex and of its adducts involving benzylamine, pyridine, quinoline, 1,2-diaminoethane, 1,4-diaminobutane, 2,2'-dipyridyl, and 1,10-phenanthroline towards the Lewis bases, acetonitrile, heptane, propan-2-ol, pyridine, tetrahydropyran, toluene, 1,1,2-trichlorotrifluoroethane, and triphenylphosphine. The tendency of the Cu(2-nqo)$_2$ complex and of its amine adducts to exhibit internal redox behaviour in the presence of a Lewis base has been shown to be dependent on: (1) the solvent having a readily abstractable hydrogen atom, (2) the donicity of the Lewis base, (3) the temperature employed, (4) the molecular environment of the complex, (5) adduct formation between the Lewis base and the complex, and (6) the nature of the amine.

3.1 Introduction.

Metal complexes can undergo internal redox reactions as illustrated by Reaction 3.1. Such reactions involve homolytic cleavage of the metal-ligand bond, and lead to a ligand radical species and a metal-containing product in which the oxidation state of the metal has been reduced.

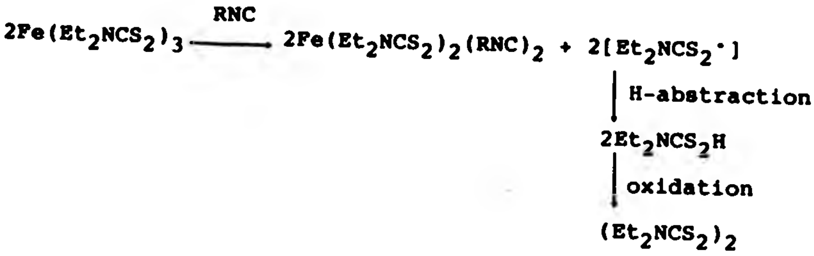
$$L_xM^n\overset{\frown\frown}{-}L \longrightarrow L_xM^{n-1} + [L^\bullet]$$

Reaction 3.1

The term internal redox reaction[1] was initially used to describe the manner in which nickel(IV) and iron(III), in their dithiocarbamate complexes, are reduced by their interaction with Lewis bases to nickel(II) (Reaction 3.2)[2] and iron(II) (Reaction 3.3),[1-2] respectively. Often terms such as redox reactions, charge transfer reactions, and electron transfer reactions have been used to describe this type of behaviour.

$$[Ni(Et_2NCS_2)_3]PF_6 \xrightarrow{RNC} [Ni(Et_2NCS_2)(RNC)_2]PF_6 + (Et_2NCS_2)_2$$

Reaction 3.2



$$\begin{tikzcd}[column sep=small] 2Fe(Et_2NCS_2)_3 \arrow[r, "RNC"] & 2Fe(Et_2NCS_2)_2(RNC)_2 + 2[Et_2NCS_2\cdot] \arrow[d, "\text{H-abstraction}"] \\ & 2Et_2NCS_2H \arrow[d, "\text{oxidation}"] \\ & (Et_2NCS_2)_2 \end{tikzcd}$$

Reaction 3.3

In most studies of internal redox reactions, the metal-containing products have been fully investigated, but, in contrast, little attention has been paid to the fate of the displaced ligand radical species. Because of this, the mechanistic understanding of internal redox reactions and the realization of their importance in catalysis, synthesis and biological processes have been of a rather superficial nature. However, the fate of the ligand radical species has recently been systematically examined in these laboratories.[3-6] On the basis of the results obtained, it appears that in most cases, the ligand radical reacts with the solvent to abstract a hydrogen to give the neutral ligand. The latter may then react further with the Lewis base, the solvent or the parent metal complex to give various other products (Reactions 3.2-3.4).[1-2, 6]

A large number of catalytic reactions involve an internal redox reaction.[7-9] For example, the copper(II)

$$\mathrm{Fe(nqo)_3 \xrightarrow{py} Fe(nqo)_2(py)_2 + nqoH}$$

Reaction 3.4

acetate-catalysed reaction between amines and carbon tetrachloride is initiated by an internal redox reaction promoted by the amine.[9] The initial processes give chloroform, amine hydrochloride, N-chloroamine and a trichloromethyl radical species (Scheme 3.1).

Initiation

$$\mathrm{Cu(O_2CCH_3)_2 + RCH_2NH_2 \longrightarrow [Cu(O_2CCH_3)] + [RCH_2\dot{N}H] + CH_3CO_2H}$$

Propagation

$$\mathrm{[Cu(O_2CCH_3)] + CCl_4 \longrightarrow [Cl\text{-}Cu(O_2CCH_3)] + [{}^{\bullet}CCl_3]}$$

$$\mathrm{RCH_2NH_2 + [{}^{\bullet}CCl_3] \longrightarrow CHCl_3 + [RCH_2\dot{N}H]}$$

$$\mathrm{[RCH_2\dot{N}H] + [Cl\text{-}Cu(O_2CCH_3)] \longrightarrow RCH_2NHCl + [Cu(O_2CCH_3)]}$$

Termination

$$\mathrm{[RCH_2\dot{N}H] + RCH_2NHCl \longrightarrow RCH_2NH_2.HCl + RCH{=}NH}$$

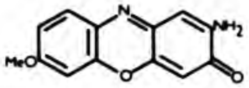
$$\mathrm{RCH{=}NH + RCH_2NH_2 \longrightarrow RCH{=}NCH_2R + NH_3}$$

$$\mathrm{RCH{=}NH \xrightarrow{oxidation} RC{\equiv}N}$$

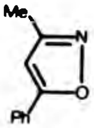
$$\mathrm{RCH{=}NH + H_2O \longrightarrow RCHO + NH_3}$$

Scheme 3.1

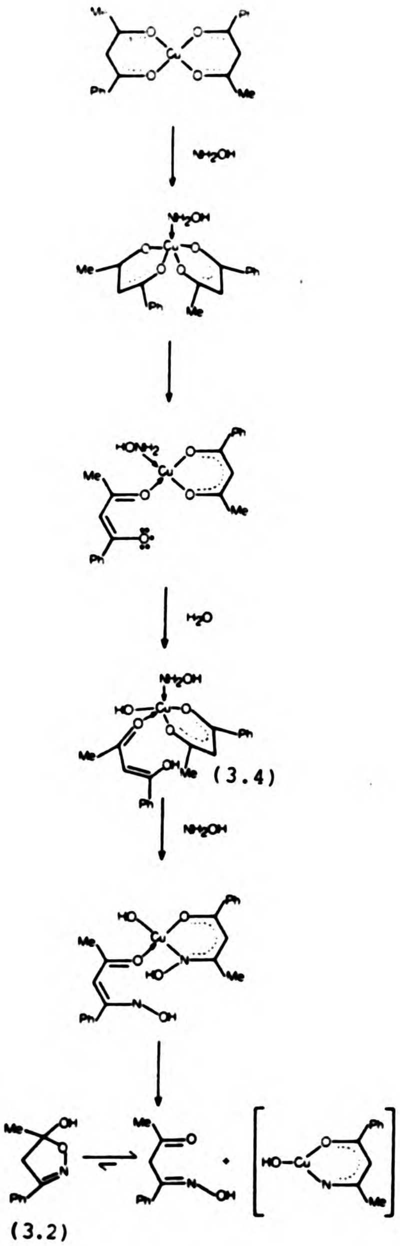
Internal redox reactions are of considerable significance in organic synthesis.[3-6, 10] Such reactions often give rise to organic products which are not readily available by other synthetic means. For example, the reaction of triphenylphosphine with bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) gives 2-amino-7-methoxy-3H-phenoxazin-3-one (3.1).[4, 10] Another interesting example is the formation of the isoxazoline (3.2) from the reaction of $Cu(bzac)_2$ (bzacH = 1-phenyl-1,3-butanedione) with hydroxylamine (Scheme 3.2).[11] Significantly, the direct reaction of 1-phenyl-1,3-butanedione with hydroxylamine affords the isomeric isoxazoline (3.3). The latter is formed via condensation involving the methyl substituted carbonyl group. This is in contrast to the condensation of hydroxylamine with the coordinated neutral β-diketone which occurs at the phenyl substituted carbonyl group. The reason for this difference in behaviour is that in species (3.4) arising from an internal redox reaction, attack at



(3.1)



(3.3)



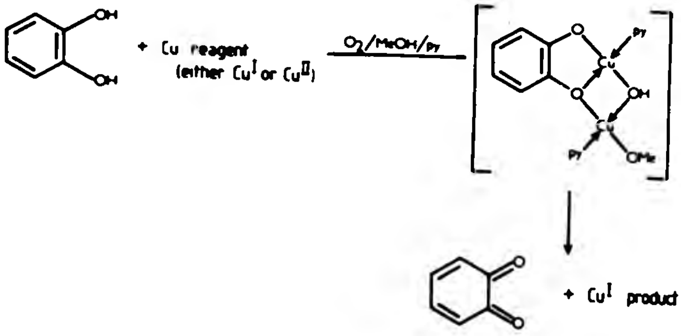
(3.4)

(3.2)

Scheme 3.2

the methyl substituted carbonyl group is highly hindered by the Cu(chel) species onto which it is bonded.

The significance of internal redox reactions in biological systems,[12-13] such as the oxygenase promoted opening of aromatic rings is exemplified by studies of model reactions using copper reagents in the presence of pyridine and methanol.[12] These reactions demonstrate that the oxidation of catechols involves formation of a copper(II) catecholate derivative which affords a quinone via an internal redox reaction (Scheme 3.3). Subsequent oxygenation of the quinone leads to ring opening.



Scheme 3.3

3.2 Factors affecting the inducement of internal redox reactions.

In general, internal redox reactions are induced by Lewis bases and/or thermal or photochemical means. Whether or not a metal complex undergoes an internal redox reaction in the presence of a Lewis base depends on **the metal, the nature of the ligands, the Lewis base, and the solvent.**

Generally, internal redox reactions occur only when the metal of the complex can undergo reduction. For example, low spin iron(III) (d^5) complexes readily undergo an internal redox reaction to give low spin iron(II) (d^6) complexes (Reaction 3.3).[1-2] Similarly, copper(II) (d^9) and nickel(IV) (d^6) complexes are readily reduced to copper(I) (d^{10}) and nickel(II) (d^8) (Reaction 3.2)[2] complexes respectively.

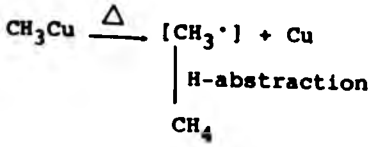
Internal redox reactions are favoured by ligands which can stabilize low oxidation states by means of their strong ligand field effects, e.g. the dithiocarbamato[1-2] and 1,2-quinone mono-oximato ligands.[3-4]

The nature of the Lewis base used also has an effect on whether a metal complex undergoes an internal redox reaction in its presence. Lewis bases which stabilise low oxidation states, e.g. triphenylphosphine, will favour the occurrence of an internal redox reaction. Thus $Cu(1\text{-nqo})_2$ reacts with triphenylphosphine to give the copper(I) complex, $Cu(1\text{-nqo})(Ph_3P)_2$,[4] whereas under similar conditions it reacts with pyridine to give the 1:1 adduct of the copper(II) complex, $Cu(1\text{-nqo})_2(py)$.[14]

The vast majority of compounds used as reaction solvents such as acetone, ethanol, propan-2-ol, and pyridine are capable of acting as Lewis bases. Therefore, these Lewis base solvents are likely to participate in an internal redox reaction and to compete in the reaction with the Lewis base reactant. Significantly, recent kinetic studies have indicated that in some reactions the Lewis base solvent is participating in the internal redox reaction. For example, the reaction between the bis(cupferronato)copper(II) complex and triphenylphosphine in pyridine,[15] and the reactions between the Fe(nqo)$_3$ complexes and triphenylphosphine in acetone.[5]

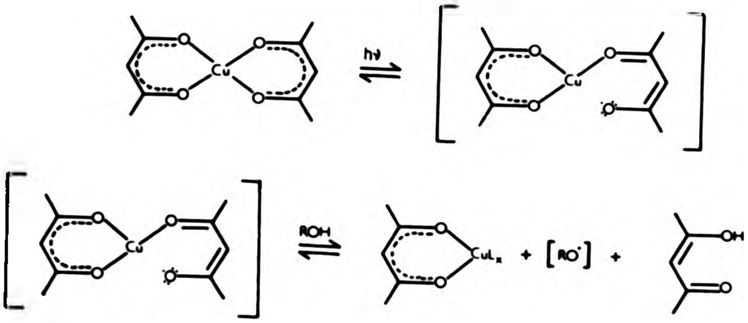
The displaced ligand radical, formed from an internal redox reaction, usually reacts with the solvent to abstract a hydrogen to give the neutral ligand. As a consequence, the solvent must have an abstractable hydrogen for the internal redox reaction to occur. Significantly, the Fe(nqo)$_3$ complexes do not react with triphenylphosphine in 1,1,2-trichlorotrifluoroethane, but, in contrast, the complexes readily exhibit internal redox behaviour with the phosphine when acetone is employed as the solvent.[5]

There have been a number of reactions reported in the literature in which an internal redox reaction is initiated by thermal or photochemical means. For example, methylcopper(I) when heated in methanol or ethanol gives methane (Reaction 3.5),[16-18] and the first row transition metal β-diketonate complexes readily undergo reduction upon irradiation to yield the free diketone (Reaction 3.6).[19-21]



$$\begin{tikzcd} CH_3Cu \arrow[r, "\Delta"] & {[CH_3^{\bullet}]} + Cu \arrow[d, "\text{H-abstraction}"] \\ & CH_4 \end{tikzcd}$$

Reaction 3.5



L = a ligand derived from the solvent

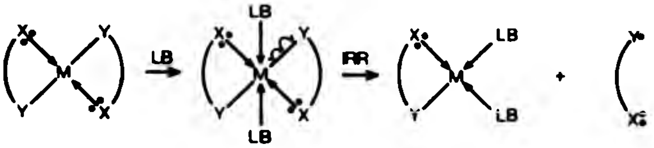
Reaction 3.6

As in the case of the Lewis base induced internal redox reactions, the thermally and photochemically promoted reactions are often carried out in solvents which are capable of acting as Lewis bases. In such cases, it is probable that the internal redox reaction is Lewis base induced rather than thermally or photochemically initiated or the reaction may occur via both mechanisms. Support for the suggestion that the reactions are promoted by a combination of processes is provided by the observation that the photoreduction of bis(acetylacetonato)copper(II) readily occurs in the Lewis base solvents propan-2-ol, ethanol and methanol, but not in either benzene or chloroform.[21]

3.3 Adduct formation in internal redox reactions.

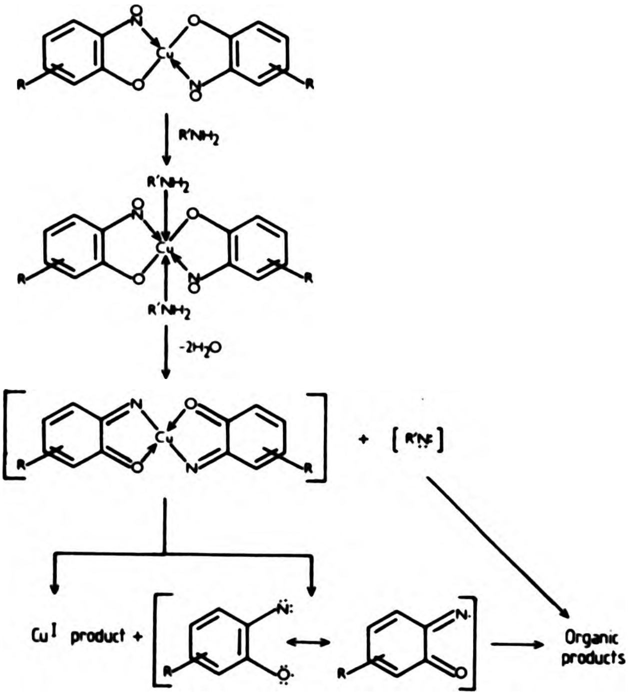
The formation of an adduct between the Lewis base solvent and/or the Lewis base, and the metal complex has been suggested or inferred for a number of systems exhibiting internal redox behaviour. These include the reactions of the $Cu(qo)_2$ complexes with primary amines (Scheme 3.4)[3] and triphenylphosphine,[4] the reactions of the $Fe(nqo)_3$ complexes with pyridine,[6] and that of the bis(cupferronato)copper(II) complex with triphenylphosphine.[15] In the latter reaction, the initial formation of adduct between either the phosphine or the Lewis base solvent, pyridine, and the bis(cupferronato)copper(II) complex has been indicated by kinetic studies.

In internal redox reactions involving metal bis-chelates of type $M(chel)_2$, the initial adduct formation involves an increase in the coordination number of the metal (Scheme 3.5). In the formation of the adduct, the metal-chelate ligand bonds in the $M(chel)_2$ remain unaffected.



Scheme 3.5

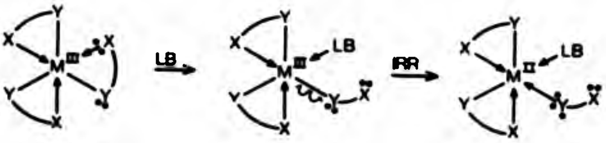
In the case of internal redox reactions involving metal tris-chelates of type $M(chel)_3$, adduct formation is



Scheme 3.4

again proposed. For this to occur, a metal-chelate ligand bond in the M(chel)$_3$ must be cleaved. Formally this cleavage has been represented either as involving breaking of the metal-chelate covalent bond to give a ligand radical which remains coordinated to the reduced metal (Scheme 3.6), or breaking of the metal-chelate coordinate bond to give a species in which the oxidation state of the metal remains unchanged (Scheme 3.7). In the latter approach, the

Scheme 3.6



Scheme 3.7

coordinated Lewis base subsequently causes the reduction of the metal and the formation of a ligand radical species. The first approach (Scheme 3.6) has been proposed for the reactions of nicotine,[5] pyridine,[6] and triphenylphosphine[5] with the Fe(nqo)$_3$ complexes, and for the reactions of thiols with the Mn(acac)$_3$ complex.[5] The second approach (Scheme 3.7) has been proposed for the reactions of 1,2-diaminoethane and other primary amines with the Mn(acac)$_3$ complex.[22]

Consideration of the previous observations suggests that the formation of an adduct between the Lewis base solvent and/or the Lewis base, and the M(chel)$_n$ (n = 2 or 3) complex is a key stage in many internal redox reactions. This has been firmly established in this study by systematically assessing the behaviour of the bis(1,2-naphthoquinone 2-oximato)copper(II) complex and of its adducts involving benzylamine, pyridine, quinoline, 1,2-diaminoethane, 1,4-diaminobutane, 2,2'-dipyridyl, and 1,10-phenanthroline towards Lewis bases such as acetonitrile, propan-2-ol, pyridine, tetrahydropyran, 1,1,2-trichlorotrifluoroethane, and triphenylphosphine. These studies and the results obtained are presented in the following sections of this Chapter.

3.4 A study of the behaviour of bis(1,2-naphthoquinone 2-oximato)copper(II) and of its amine adducts towards Lewis base solvents.

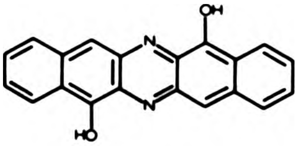
3.4.1 Introduction.

The internal redox reactions of 1,2-quinone mono-oximato metal complexes which are promoted by Lewis bases such as triphenylphosphine,[4-5, 10] aniline,[3, 23] benzylamine,[23] 1,2-diaminoethane,[3, 23] and pyridine[6] have been extensively studied in these laboratories. Generally, the reactions involving triphenylphosphine have been carried out in solvents such as pyridine and acetone which are themselves capable of acting as Lewis bases.[4-5, 10] The reactions with aniline,[3, 23] benzylamine,[23] and 1,2-diaminoethane[3, 23] were carried out in toluene which is a weak Lewis base, but a high temperature was used. The reactions involving pyridine were carried out in the absence of any other Lewis base solvent.[6] For all these systems, the initial formation of an adduct between the Lewis base solvent and/or the Lewis base, and the 1,2-quinone mono-oximato metal complex has been suggested or inferred.[3-6, 10, 23]

3.4.2 Procedure and results.

The successful synthesis of various amine adducts of $Cu(qo)_2$ in this work (see Chapter 2) allowed the assessment of the importance of adduct formation between the Lewis base solvent and/or the Lewis base, and the metal complex in internal redox reactions. The study involved the evaluation of the behaviour of the Cu(2-nqo)$_2$ complex and of the Cu(2-nqo)$_2$.X (X = bza, dipy, en, phen, py or quin) adducts towards various Lewis base solvents at room temperature and under refluxing conditions. The wide range of adducts examined allowed assessment of the effect of the molecular environment of the adduct on its tendency to exhibit internal redox behaviour in the presence of a Lewis base solvent.

Previously, it has been reported that the internal redox reactions of 1,2-diaminoethane[3, 23] and benzylamine[23] with Cu(2-nqo)$_2$ led in both cases to dibenzo[b,i]phenazine-5,12-diol (3.5) and a diamagnetic copper-containing solid of ill-defined composition.



(3.5)

The procedures followed during this investigation involved stirring the complex with the solvent at room temperature for 7 days or under refluxing conditions for 24 h. Thin layer chromatographic techniques were used to monitor the formation of dibenzo[b,i]phenazine-5,12-diol and thus assess the occurrence of an internal redox reaction.

The $Cu(2\text{-nqo})_2$ complex is coordinatively unsaturated. At room temperature, the $Cu(2\text{-nqo})_2$ complex was stable towards reduction in all of the Lewis base solvents employed (Table 3.1). Reaction was only observed with pyridine and tetrahydropyran. This led to the respective adducts of the copper(II) complex. When refluxing conditions were employed, the $Cu(2\text{-nqo})_2$ complex showed varying degrees of internal redox reactivity towards the various Lewis base solvents used (Table 3.1). The complex failed to react with 1,1,2-trichlorotrifluoroethane and heptane, but exhibited internal redox behaviour with acetonitrile, propan-2-ol, pyridine and tetrahydropyran. The qualitative order of decreasing internal redox reactivity of the Lewis base solvents studied towards the $Cu(2\text{-nqo})_2$ complex followed the order:

acetonitrile ≈ pyridine ≈ tetrahydropyran > propan-2-ol.

The $Cu(2\text{-nqo})_2.py$ adduct is monomeric in solution and is coordinatively unsaturated with five-coordinate copper.[14] A similar structure is assumed for the $Cu(2\text{-nqo})_2.X$ (X = bza or quin) adducts. At room temperature, all three adducts failed to react with 1,1,2-trichlorotrifluoroethane, propan-2-ol and acetonitrile. When refluxing conditions were used, the $Cu(2\text{-nqo})_2.X$ (X = bza or py) adducts again failed to react with 1,1,2-trichlorotrifluoroethane (Table 3.2). However, both adducts underwent an internal redox reaction in refluxing propan-2-ol and acetonitrile. For the $Cu(2\text{-nqo})_2.X$ (X = bza or py) adducts, reaction was less pronounced in propan-2-ol than in aceto-

Table 3.1 The behaviour of Cu(2-nqo)$_2$ towards Lewis base solvents at room temperature and under refluxing conditions.

Solvent	**Room temperature**	**Under refluxing conditions**
1,1,2-Trichloro-trifluoroethane	NR	NR
Heptane	NR	NR
Propan-2-ol	NR	IRR
Acetonitrile	NR	IRR
Pyridine	AF	IRR
Tetrahydro-pyran	AF	IRR

NR = No reaction of complex with neat Lewis base solvent.

IRR = Internal redox reaction of complex promoted by neat Lewis base solvent.

AF = Adduct formation of complex with neat Lewis base solvent.

Table 3.2 The behaviour of $Cu(2\text{-}nqo)_2.X$ (X = bza, py or quin) towards refluxing Lewis base solvents.

Solvent **Adduct**	1,1,2-Trichloro-trifluoroethane	Propan-2-ol	Acetonitrile
$Cu(2\text{-}nqo)_2.bza$	NR	IRR	IRR
$Cu(2\text{-}nqo)_2.py$	NR	IRR	IRR$^+$

NR = No reaction of complex with neat Lewis base solvent.

IRR = Internal redox reaction of complex promoted by neat Lewis base solvent.

$^+$ Similar behaviour exhibited by $Cu(2\text{-}nqo)_2.quin$.

nitrile. The Cu(2-nqo)$_2$.bza adduct showed greater internal redox reactivity than the Cu(2-nqo)$_2$.py adduct towards both acetonitrile and propan-2-ol. The Cu(2-nqo)$_2$.quin adduct exhibited similar behaviour to the Cu(2-nqo)$_2$.py adduct in acetonitrile.

The Cu(2-nqo)$_2$.X (X = dipy, en or phen) adducts are assumed to be coordinatively saturated with six-coordinate copper. Such a structure has been established by X-ray cystallography for the analogous Cu(4-Clqo)$_2$.dipy adduct.[24] The Cu(2-nqo)$_2$.X (X = dipy or phen) adducts showed no tendency to exhibit internal redox behaviour in 1,1,2-trichlorotrifluoroethane, propan-2-ol and acetonitrile, even when refluxed. In contrast, the Cu(2-nqo)$_2$.en adduct readily reacted in refluxing acetonitrile and toluene.

The qualitative order of decreasing internal redox reactivity of the Cu(2-nqo)$_2$ complex and of its amine adducts involving benzylamine, 1,2-diaminoethane, pyridine, and quinoline in acetonitrile followed the order:
Cu(2-nqo)$_2$ ≈ Cu(2-nqo)$_2$.bza ≈ Cu(2-nqo)$_2$.en >
Cu(2-nqo)$_2$.py ≈ Cu(2-nqo)$_2$.quin.

3.4.3 Factors affecting the occurrence of an internal redox reaction.

From the findings outlined above, the tendency of the Cu(2-nqo)$_2$ complex and of its amine adducts to exhibit internal redox behaviour in the presence of a Lewis base solvent has been shown to be dependent on: (1) the Lewis base solvent having a readily abstractable hydrogen atom, (2) the Lewis basicity of the solvent, (3) the temperature employed, (4) the molecular environment of the complex, (5) adduct formation between the Lewis base solvent and the complex, and (6) the reactivity of the amine.

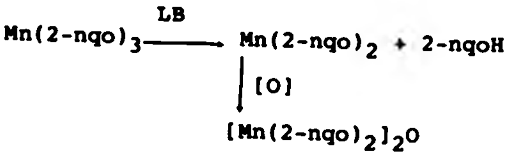
The hydrogen donating character of solvent.-The results summarised in Tables 3.1-3.2 clearly indicate that internal redox behaviour is only observed in solvents which have an abstractable hydrogen atom. This is demonstrated by the complete lack of reaction of the $Cu(2\text{-nqo})_2$ complex and of its amine adducts in 1,1,2-trichlorotrifluoroethane, and of the facile reaction of the $Cu(2\text{-nqo})_2$ complex in acetonitrile, propan-2-ol, pyridine and tetrahydropyran. The requirement of a hydrogen donating solvent has also been observed in other related systems. For example, the $Fe(nqo)_3$ complexes have been shown not to react with triphenylphosphine in 1,1,2-trichlorotrifluoroethane, even when refluxing conditions were employed.[5] In contrast, the $Fe(nqo)_3$ complexes readily exhibited internal redox behaviour in the presence of triphenylphosphine at room temperature when acetone was employed as the solvent. Also, the photoreduction of tris(trifluoroacetylacetonato)cobalt(III) has been shown to occur to a much lesser extent in hexane than in ethanol.[20]

The Lewis base character of the solvent.-Previously, it was shown that the $Cu(2\text{-nqo})_2.py$ adduct was obtained when the

$Cu(2\text{-}nqo)_2$ complex (1 mol) and pyridine (2 mol) were refluxed together in acetone.[14] In this study, the $Cu(2\text{-}nqo)_2$ complex was shown to form an adduct when the reaction with pyridine was performed in the absence of any other Lewis base solvent at room temperature, and to undergo an internal redox reaction when refluxed. The $Cu(2\text{-}nqo)_2$ complex exhibited similar behaviour in tetrahydropyran. Therefore, the type of reaction that a $Cu(qo)_2$ complex undergoes in the presence of a strong Lewis base is dependent on the amount of Lewis base present and the temperature employed. Internal redox behaviour is enhanced by using a large excess of Lewis base, and employing refluxing conditions. Similarly, the $Cr(nqo)_3$ complexes do not react in pyridine at room temperature, but exhibit internal redox behaviour when refluxed.[25]

Propan-2-ol is a strong hydrogen atom donor.[21] It would be expected that if hydrogen atom abstraction is the crucial stage in the internal redox reactions of $Cu(qo)_2$ complexes, the reductions would be accelerated by the use of propan-2-ol. It has been shown in this study that the Lewis base strength of the solvent is more important than its hydrogen atom donating properties. Thus, the $Cu(2\text{-}nqo)_2$ complex reacts to a greater extent with the poor hydrogen atom donors pyridine and tetrahydropyran than with propan-2-ol. Similarly, the internal redox reactions of the $Fe(nqo)_3$ complexes with triphenylphosphine have been shown to be slower in propan-2-ol than in acetone.[5] This was accounted for by the increased Lewis basicity of acetone over propan-2-ol and on its smaller size even though the α-hydrogen of propan-2-ol is more acidic.

Recently, the rates of reaction of $Mn(2\text{-}nqo)_3$ with various Lewis base solvents at 30 ^oC were determined spectrophotometrically (Reaction 3.7).[25] The Lewis base



$$\begin{tikzcd} Mn(2\text{-}nqo)_3 \arrow[r, "LB"] & Mn(2\text{-}nqo)_2 + 2\text{-}nqoH \arrow[d, "{[O]}"] \\ & {[Mn(2\text{-}nqo)_2]_2O} \end{tikzcd}$$

Reaction 3.7

reactivity towards the $Mn(2\text{-}nqo)_3$ complex followed the order pyridine › dimethyl sulphoxide › tetrahydrofuran › acetone › acetonitrile › benzene. The decreasing order of reactivity of the Lewis base solvents towards $Mn(2\text{-}nqo)_3$ is also the order of decreasing Lewis basicity of the solvent in the Donor number (D.N.) approach of V. Gutmann (Table 3.3).[26-27] Donor numbers give an empirical measure of the Lewis base strength of solvents. These numbers correlate the behaviour of a solute (such as its solubility, redox potential or degree of ionization) with a given solvent's coordinating ability, that is with its basicity or donicity. A relative measure of the basicity of a solvent is given by the enthalpy of its reaction with an arbitrarily chosen reference Lewis acid. For Gutmann's scale, the reference acid is $SbCl_5$. The heat of reaction of the donor (D)

Table 3.3 Donor numbers of Lewis base solvents.[26-27]

Solvent	D.N.
Acetone	17.0
Acetonitrile	14.1
Benzene	0.1
1,2-Diaminoethane	55.0
Dimethyl sulphoxide	29.8
Ethanol	20.0
Methanol	19.0
Pyridine	33.1
Tetrahydrofuran	20.0

with $SbCl_5$ in a 10^{-3} mol dm^{-3} solution of 1,2-dichloroethane is called the D.N. or donicity of the solvent (Reaction 3.8). It is assumed that entropy effects are constant and that 1:1 adducts are formed so that the D.N. is a reflection of the inherent solvent to $SbCl_5$ bond strength. $SbCl_5$ is a very strong acceptor and this allows fairly complete adduct formation, even with very weak donors. However, the most important assumption of the D.N. approach is that the order of Lewis base strengths established by the $SbCl_5$ scale remains constant for all other Lewis acids.

$$D + SbCl_5 \longrightarrow D.SbCl_5$$

Reaction 3.8

In this study, the $Cu(2\text{-}nqo)_2$ complex has been shown to readily undergo an internal redox reaction in refluxing acetonitrile, whereas the stronger Lewis base acetone[26-27] shows no tendency to react with the complex.[28] This difference in behaviour between acetonitrile and acetone towards the $Cu(2\text{-}nqo)_2$ complex can therefore be accounted for in terms of the ability of acetonitrile to stabilise copper(I).[29] The metal donates d electrons into a π^* antibonding orbital of the nitrile group in acetonitrile. A synergistic effect between back bonding and the normal weak acid-base interaction between the acidic cation and the basic acetonitrile provides a strong interaction.

The reaction of the Cu(2-nqo)$_2$ complex with acetonitrile illustrates a deficiency of the D.N. approach. Acetonitrile behaves as a rather weak donor towards SbCl$_5$, whereas it shows a high affinity relative to other donors with Lewis acids such as copper(I) and silver(I).[27] Copper(I) is more stable than copper(II) in acetonitrile.

The behaviour of Cu(2-nqo)$_2$ in acetone and acetonitrile contrasts that of Mn(2-nqo)$_3$. Reduction of Mn(2-nqo)$_3$ occurs more rapidly in acetone than in acetonitrile.[25] The internal redox reactions of the Mn(2-nqo)$_3$ complex do not involve stabilisation of the reduced metal species by the Lewis base solvent. These reactions are very much dependent on the Lewis base solvent causing the homolytic cleavage of a metal-ligand bond of the Mn(2-nqo)$_3$ complex. Hence, reduction of Mn(2-nqo)$_3$ occurs rapidly in strong Lewis base solvents.

The copper-containing solids obtained from the reactions of the Cu(2-nqo)$_2$ and Cu(2-nqo)$_2$.X (X = bza or en) complexes with acetonitrile are all diamagnetic inferring that they contain copper in the +1 oxidation state. This is indicative of the occurrence of an internal redox reaction.[3, 23]

The molecular environment of the complex.-The Cu(2-nqo)$_2$ complex and its five-coordinate adducts with benzylamine and pyridine underwent internal redox reactions in refluxing acetonitrile and propan-2-ol. In contrast, the six-coordinate Cu(2-nqo)$_2$.X (X = dipy or phen) adducts failed to react under similar conditions. The differences in behaviour demonstrate the importance of the molecular environment of the $Cu(2-nqo)_2$ complex and of its amine adducts in their tendency to exhibit internal redox behaviour. The inertness of the adducts $Cu(2-nqo)_2$.dipy and $Cu(2-nqo)_2$.phen can be accounted for in terms of the metal being coordinatively saturated. However, the $Cu(2-nqo)_2$.en adduct, which is also assumed to be six-coordinate, readily reacted in refluxing acetonitrile. This apparent exception reflects both the reactivity of 1,2-diaminoethane and the weaker bonding of the amine to the copper.

For the $Cu(2-nqo)_2$.X (X = dipy or phen) adducts, if a ligand bond was to be cleaved and the Lewis base solvent coordinate to the metal, reduction would lead to a highly unfavourable six-coordinate copper(I) species. The coordination number of copper(I) complexes is normally two or more generally four.[30]

The significance of the molecular environment in internal redox reactions has previously been shown in a study of the electrochemistry of various iron porphyrins.[31] Their superstructure was shown to exert three types of effect on their redox ability: (1) protection against external solvation by steric hindrance of the approach of solvent molecules, (2) local solvation by secondary amide groups of the porphyrin ligands, and (3) steric discrimination between axially bound ligands including coordinating solvating molecules. The choice of solvents used was made on the basis of the Donor number approach.[31] The significance of the solvent medium both as a Lewis acid and as a Lewis base was also noted. As a Lewis acid, the solvent is able to solvate negatively charged species. As a Lewis base, the solvent is involved in axial coordination of the iron(II) complexes.

Spectral studies of solutions of the $Cu(4\text{-}Clqo)_2$ complex in the ligand-field region have shown that the main visible envelope is slightly shifted towards lower wavelengths in going from chloroform to better donor solvents such as acetonitrile, propan-2-ol, ethanol and methanol.[32] This is an indication that in solution there is adduct formation between the Lewis base solvent and the $Cu(4\text{-}Clqo)_2$ complex. Spectrophotometric studies of the $Cu(4\text{-}Clqo)_2.X$ (X = imidazole, pyrazole or py) adducts have revealed that these compounds are largely dissociated in acetonitrile solution.[24] At high values of amine:Cu molar ratio (50:1), the absorption spectra indicated formation of 1:2 adducts. Therefore, Lewis base solvents in solution can coordinate to the analogous $Cu(2\text{-}nqo)_2$ and $Cu(2\text{-}nqo)_2.X$ (X = bza, py or quin) complexes, thus promoting internal redox behaviour.

Studies of the absorption spectra of $Cu(4\text{-}Clqo)_2.X$ (X = dipy or phen) have shown that the bond between the amine and the copper not to be dissociated in solution.[24] The 2,2'-dipyridyl and 1,10-phenanthroline behave as chelating ligands both in the solid state and in solution. Therefore, the presence of 2,2'-dipyridyl and 1,10-phenanthroline in the $Cu(qo)_2.X$ (X = dipy or phen) adducts gives protection against external solvation by steric hindrance of the approach of solvent molecules. Thus, the steric protection stops coordination of the solvent molecule to the $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) adducts, and prevents them from exhibiting internal redox behaviour.

The Lewis base strengths of 2,2'-dipyridyl and 1,10-phenanthroline are greater than that of acetonitrile and propan-2-ol. This is exemplified by the inability of the $Cu(qo)_2$ complexes to form isolable adducts with acetonitrile,[14] and the readiness of these complexes to form 1:1 adducts with 2,2'-dipyridyl and 1,10-phenanthroline which has been shown both in this study (see Chapter 2) and by other workers.[24]

The inertness of the $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) adducts towards exhibiting internal redox behaviour in acetonitrile and propan-2-ol is significant as both 2,2'-dipyridyl and 1,10-phenanthroline are very effective at stabilising low oxidation states.

The behaviour of $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) in acetonitrile contrasts with that of $Cu(2\text{-}nqo)_2.en$. The two nitrogen atoms in 2,2'-dipyridyl and 1,10-phenanthroline are located in heteroaromatic rings and so their environment is very different from that of the donor atoms in 1,2-diaminoethane. The stabilities of metal complexes of 2,2'-dipyridyl and 1,10-phenanthroline are usually higher than those of the corresponding complexes of 1,2-diaminoethane. 2,2'-Dipyridyl and 1,10-phenanthroline usually show greater rigidity than 1,2-diaminoethane in their bonding with metals.[33] The differences in behaviour between Cu(2-nqo)$_2$.X (X = dipy or phen) and Cu(2-nqo)$_2$.en towards acetonitrile can therefore be accounted for by the weaker bonding of 1,2-diaminoethane to the copper. The amine bonds of Cu(2-nqo).en can be more readily cleaved than those of Cu(2-nqo)$_2$.X (X = dipy or phen). This allows coordination of the Lewis base solvent to the Cu(2-nqo)$_2$.en adduct (as in the case of the Cu(2-nqo)$_2$ and Cu(2-nqo)$_2$.X (X = bza, py or quin) complexes), thus causing the internal redox reaction to occur.

The coordination of the Lewis base solvent molecule to the metal complex, i.e. adduct formation, is a crucial stage in the internal redox reactions of Cu(2-nqo)$_2$ and of its amine adducts.

Adduct formation.-As stated earlier, Cu(2-nqo)$_2$ has been shown to react with 1,2-diaminoethane in refluxing toluene to give dibenzo[b,i]phenazine-5,12-diol and a diamagnetic copper-containing solid of ill-defined composition.[3, 23] The initial formation of an adduct between the 1,2-diaminoethane and the Cu(2-nqo)$_2$ complex was suggested. In this study, the Cu(2-nqo)$_2$.en adduct was prepared and isolated (see Chapter 2). Its reaction in refluxing toluene followed the same pathway as that of the free 1,2-diaminoethane with the parent Cu(2-nqo)$_2$ complex. As toluene is a weak Lewis base, the 1,2-diaminoethane promotes the internal redox reaction. The precoordination of the amine to the Cu(2-nqo)$_2$ complex does not alter the course of the reaction. As indicated above, adduct formation is therefore a key stage in the internal redox reactions of Cu(2-nqo)$_2$ and of its amine adducts.

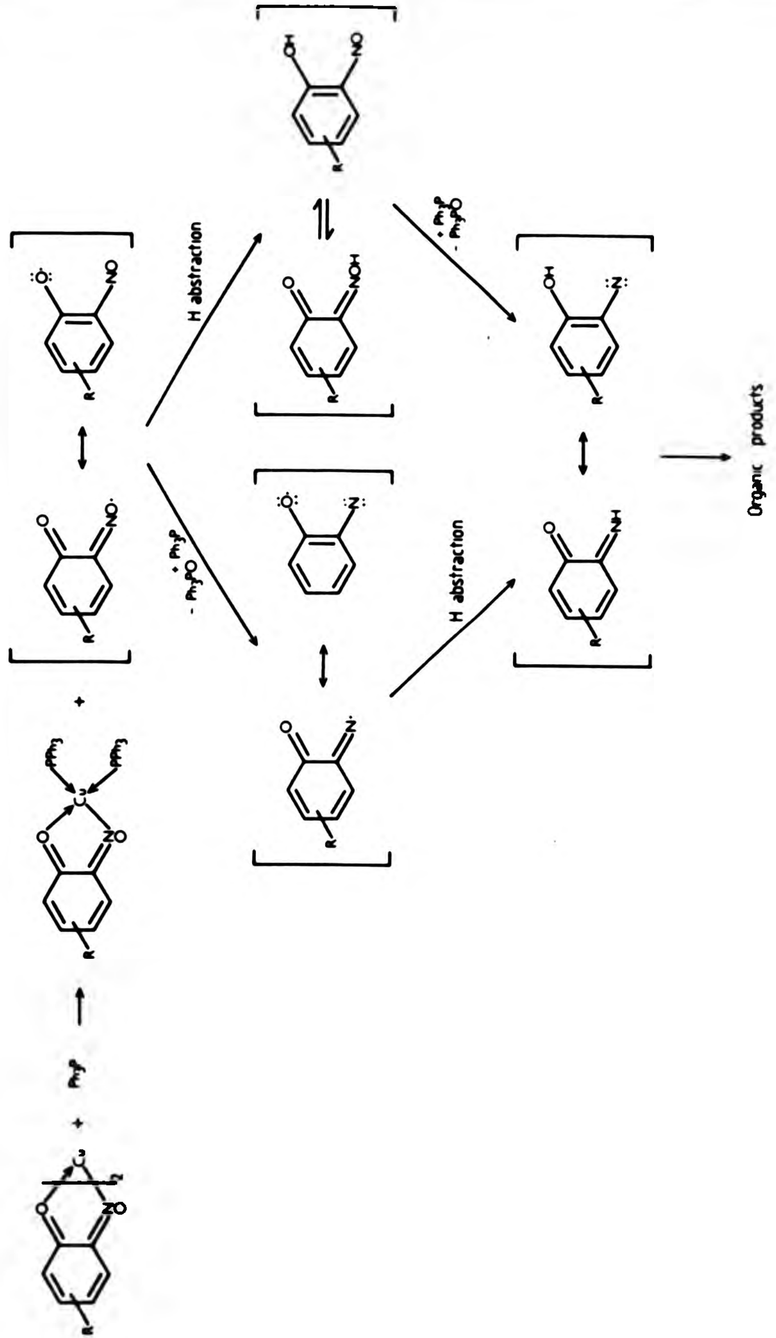
The reactivity of the amine.-The Cu(2-nqo)$_2$.X (X = bza or en) adducts were seen to react to a greater extent in acetonitrile than the Cu(2-nqo)$_2$.X (X = py or quin) adducts. This reflects the higher reactivity of the primary amine group(s) in benzylamine and 1,2-diaminoethane than of the tertiary amine group in pyridine and quinoline. It also illustrates the effect of the reactivity of the coordinated Lewis base on the internal redox behaviour of a metal complex.

3.5 The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) and of its amine adducts with triphenylphosphine in acetone.

The number and variety of tertiary phosphine complexes of transition metals that have been characterised has accelerated rapidly during the past thirty years. The electronic versatility of the tertiary phosphine ligands appears to be reflected in their ability to form stable transition metal complexes with the formal oxidation states of the metal ranging from +IV to -I.[34-35] This feature is often attributed to the metal-phosphorus bond having both σ- and π-components.

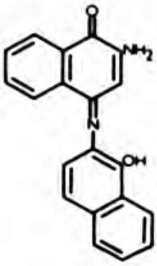
Reduction of copper(II) to copper(I) by triphenylphosphine leading to formation of relatively stable complexes has frequently been used for the synthesis of copper(I) triphenylphosphine complexes.[36-37] The isolation of stable copper(I) species can be rationalised by the assumption that back bonding occurs by a drift of the electron density from the filled copper d-orbitals into the empty phosphorus d-orbitals.

Previously, the reactions of bis(1,2-quinone mono-oximato)copper(II) complexes with triphenylphosphine were carried out in pyridine.[4, 23] These reactions lead to reduction of the metal to give a complex of type $Cu(qo)(Ph_3P)_2$, and involve deoxygenation of one of the 1,2-quinone mono-oximato ligands (Scheme 3.8). The latter is accompanied by the formation of triphenylphosphine oxide. In the case of the $Cu(2\text{-}nqo)_2$ complex, 2-amino-N(4)-(1-


+ Ph3P
H abstraction
+ Ph3P
- Ph3PO
+ Ph3P
- Ph3PO
H abstraction
Organic products

Scheme 3.8

hydroxy-2-naphthyl)-1,4-naphthoquinone mono-imine (3.6) was



(3.6)

obtained as the major organic product.[4, 23] In all these reactions, the involvement of an adduct of the $Cu(qo)_2$ complex with triphenylphosphine was suggested.[4, 23] As stated earlier, kinetic studies of the analogous reaction of bis(cupferronato)copper(II) with triphenylphosphine in pyridine indicated the formation of an adduct between either the phosphine or the Lewis base solvent, and the bis(cupferronato)copper(II) complex.[15]

In this study, the behaviour of the $Cu(2\text{-nqo})_2$ and $Cu(2\text{-nqo})_2.X$ (X = bn or dipy) complexes towards triphenylphosphine was examined in order to assess how the molecular environment of the metal complex affected its reactivity towards the phosphine. Acetone was employed as the solvent as it is a weaker Lewis base than pyridine,[26-27] and was expected to be less of a competitor to the triphenylphosphine.

The complex and triphenylphosphine in acetone were stirred at room temperature for 24 h. Under these conditions, the $Cu(2\text{-}nqo)_2$ and $Cu(2\text{-}nqo)_2.X$ (X = dipy or bn) complexes all readily reacted with triphenylphosphine to give in each case, triphenylphosphine oxide, $Cu(2\text{-}nqo)(Ph_3P)_2$, and a complex mixture of organic products.

The presence of 2,2'-dipyridyl in the coordinatively saturated $Cu(2\text{-}nqo)_2$.dipy adduct did not prevent it from undergoing an internal redox reaction in the presence of triphenylphosphine. This is in contrast to the adduct's inertness in refluxing Lewis base solvents (see Section 3.4.2). Triphenylphosphine readily displaced the 2,2'-dipyridyl in the $Cu(2\text{-}nqo)_2$.dipy adduct. Significantly, 2,2'-dipyridyl was shown not to displace the phosphine from the $Cu(1\text{-}nqo)(Ph_3P)_2$ complex.[23] As in the case of $Cu(2\text{-}nqo)_2$.dipy, the coordinated amine in $Cu(2\text{-}nqo)_2$.bn was readily displaced by triphenylphosphine. Similarly, kinetic studies of the internal redox reaction of bis(5-hydroxy-1,2-benzoquinone 2-oximato)(pyridine)copper(II) with triphenylphosphine in methanol indicated the displacement of the pyridine and the formation of an intermediate phosphine copper(II) adduct.[10]

The reactions of the $Cu(2\text{-}nqo)_2.X$ (X = dipy or bn) adducts with triphenylphosphine in acetone were more complicated than that of the $Cu(2\text{-}nqo)_2$ complex. For $Cu(2\text{-}nqo)_2$, the major organic product obtained was 1,2-naphthoquinone 2-oxime. This contrasts the analogous reaction in pyridine, where the major organic product obtained was 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine.[4, 23] In the case of the Cu(2-nqo)$_2$.X (X = dipy or bn) adducts, the main organic products obtained were 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine, dibenzo[b,i]phenazine-5,12-diol, and 1,2-naphthoquinone 2-oxime.

3.6 The behaviour of bis(1,2-naphthoquinone 2-oximato)-copper(II) and of the amine adducts of bis(1.2-quinone 2-oximato)copper(II) complexes on silica.

The importance of adduct formation between the Lewis base and the metal complex in internal redox reactions is further illustrated by the behaviour of the $\mathrm{Cu(qo)_2.X}$ (X = dipy or phen) adducts with Lewis base solvents on silica. The adducts reacted on silica to give the respective 1,2-quinone mono-oxime and an immobile metal-containing product (Reaction 3.9). In contrast, the $\mathrm{Cu(2\text{-}nqo)_2}$ complex and its adducts involving benzylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, pyridine, and quinoline showed no tendency to react on silica. The novel behaviour of the $\mathrm{Cu(qo)_2.X}$ (X = dipy or phen) adducts on silica and its synthetic potential is further discussed in Chapter 4.

$$\mathrm{Cu(qo)_2.X} \xrightarrow[\text{LB}]{\text{Silica}} \text{'Cu(qo).X'} + \mathrm{qoH}$$

(where X = dipy or phen)

Reaction 3.9

3.7 Conclusion.

In general, the tendency of the $Cu(2\text{-nqo})_2$ complex and of its adducts involving benzylamine, quinoline, 1,2-diaminoethane, 1,4-diaminobutane, 2,2'-dipyridyl, and 1,10-phenanthroline to exhibit internal redox behaviour in the presence of a Lewis base has been shown to be dependent on: (1) the solvent having a readily abstractable hydrogen atom, (2) the donicity of the Lewis base, (3) the temperature employed, (4) the molecular environment of the complex, (5) adduct formation between the Lewis base and the complex, and (6) the nature of the amine.

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Chapter 4

4 The preparation of 1,2-quinone mono-oximes and of alkali metal 1,2-quinone mono-oximates from 1,2-quinone mono-oximato metal complexes.

1,2-Quinone mono-oximes have been prepared (1) by the reaction of the $Cu(qo)_2.X$ (X = dipy or phen) adducts on silica and (2) by the ligand exchange of 1,2-quinone mono-oximato metal complexes, using a strong acid cation exchanger.

Alkali metal 1,2-quinone mono-oximates have been synthesised by the reaction of alkali metal cyanides with transition metal complexes derived from 1,2-quinone mono-oximes.

4.1 Introduction.

Previously, several methods have been proposed in the literature for the synthesis of 1,2-quinone mono-oximes.

(1) Nitrosation of a phenol, using acetic acid or sulphuric acid and sodium nitrite.

(2) Nitrosation of a phenol in the presence of a metal salt (usually of copper(II)), using acetic acid and sodium nitrite. The free 1,2-benzoquinone mono-oxime is subsequently isolated by acidification of the bis(1,2-benzoquinone mono-oximato)metal(II) complex.

(3) Nitrosation of a phenol, using sodium ethoxide and amyl nitrite.

(4) The Baudisch reaction. This involves the reaction of benzene or phenol (or substituted compounds) with hydroxylamine hydrochloride and hydrogen peroxide in the presence of a copper(II) salt to give a bis(1,2-benzoquinone mono-oximato)copper(II) complex. The free 1,2-benzoquinone mono-oxime is obtained by acidification of the complex.

(5) The reaction of hydroxylamine hydrochloride with a quinone.

(6) Rearrangement of nitro compounds.

Nitrosation by sodium nitrite.-The reaction of acetic acid or sulphuric acid with sodium nitrite to produce nitrous acid has been widely used for the nitrosation of phenols. The nature of the end product is very much dependent on the phenol employed. Nitrosation of phenols unsubstituted in the 4 position produces mainly 1,4-benzoquinone 4-oximes.[1-2] In a few cases, nitrosation gives only the 1,2-benzoquinone 2-oxime,[3] whereas for the 3-alkoxyphenols mixtures of the 2- and 4-oximes are obtained.[4]

When phenols are nitrosated using nitrous acid side reactions can occur. In certain cases, the main product is not a 1,2-benzoquinone mono-oxime at all. Nitrous acid can produce nitro derivatives of phenols,[5] though it is not known if their formation is due to the reaction media or to the instability of the corresponding 1,2-benzoquinone mono-oxime towards oxidation.

Nitrosation of naphthols and dihydroxynaphthalenes, using acetic acid or sulphuric acid and sodium nitrite has widely been studied.[6] The nitrosated naphthols and dihydroxynaphthalenes tend not to undergo further side reactions.

Overall, this method of nitrosation is not very efficient due to the variety of products that can be produced.

Nitrosation and complex formation.-In this method, the phenol is nitrosated in the presence of a metal salt to give a bis(1,2-benzoquinone mono-oximato)metal(II) complex, which upon acidification gives the free 1,2-benzoquinone mono-oxime. This method has been reported for the preparation of 4-chloro-, 4-bromo- and 4-methyl-1,2-benzoquinone 2-oxime (Scheme 4.1).[7] However, only limited analytical data were given for the copper(II) complexes, and no details of analysis were presented for the free 1,2-benzoquinone mono-oximes.

$$\begin{array}{l}
\text{Phenol} + CuSO_4.5H_2O \\
\Big\downarrow \; NaNO_2/MeCO_2H/MeCO_2Na \\
Cu(qo)_2 \\
\Bigg\downarrow \; \begin{array}{l} \text{1. } H_2SO_4 \\ \text{2. Light petroleum extraction} \\ \text{3. NaOH} \end{array} \\
2Na(qo) \\
\Big\downarrow \; H_2SO_4 \\
2qoH
\end{array}$$

Phenol = 4-chlorophenol, 4-bromophenol or 4-methylphenol

Scheme 4.1

Nitrosation by amyl nitrite.-Amyl nitrite nitrosation has been used to prepare a limited number of 5-hydroxy-1,2-benzoquinone 2-oximes.[8] Generally, the reaction of nitrous acid with resorcinols leads to dinitrosation. Controlled nitrosation, using the amyl nitrite method, can be used to obtain 5-hydroxy-1,2-benzoquinone 2-oximes (e.g. Scheme 4.2).

Resorcinol
$\downarrow$ RONO/EtONa/EtOH/0 °C
Sodium salt of the 5-hydroxy-1,2-benzoquinone 2-oxime
$\downarrow$ Acidification
5-Hydroxy-1,2-benzoquinone 2-oxime

Scheme 4.2

The Baudisch reaction.-It has been reported that in the presence of copper(II), an aqueous solution of hydroxylamine hydrochloride and hydrogen peroxide reacts with benzene or phenol (or various substituted compounds) to give a bis(1,2-benzoquinone mono-oximato)copper(II) complex from which the 1,2-benzoquinone mono-oxime could be obtained by acidification of the complex.[7, 9-12] However in all the reports describing this reaction,[7, 9-12] only limited experimental details were given, and no analytical data were presented.

Quinones and oxime formation.-The heating of hydroxylamine hydrochloride with the corresponding quinone of the desired compound has been used to a limited extent to obtain 1,2-quinone mono-oximes.[13-14] A limitation to the applicability of this method is that the appropriate quinone must be available as a starting material.

Rearrangement of nitro compounds.-The mono-oxime of 1,10-phenanthroline-5,6-quinone has recently been prepared by heating 5-nitro-1,10-phenanthroline with aqueous sodium hydroxide to give the sodium salt of the quinone mono-oxime, which on acidification gives the free quinone mono-oxime.[15]

Conclusion.-There is no general method for the preparation of 1,2-quinone mono-oximes, and hence there are only a limited number of these compounds available. In contrast, transition metal complexes derived from 1,2-quinone mono-oximes can be readily obtained by the nitrosation, with acetic acid and sodium nitrite, of the appropriate phenol in the presence of a transition metal salt. This synthetic approach cannot be employed for the preparation of non-transition metal complexes derived from 1,2-quinone mono-oximes. The synthesis of these complexes has only be accomplished by the direct reaction of the appropriate 1,2-quinone mono-oxime or its alkali metal complex with a metal salt or hydroxide.

In view of the above, one of the aims of this work was to discover and develop new techniques for the preparation of 1,2-quinone mono-oximes and of alkali metal 1,2-quinone mono-oximates. The methods established during this study involve:

(1) the internal redox reaction of the $Cu(qo)_2.X$ (X = dipy or phen) adducts on silica;

(2) the ligand exchange of metal complexes of 1,2-quinone

mono-oximes, using a strong acid cation exchanger;

(3) the ligand exchange of transition metal complexes of 1,2-quinone mono-oximes by their reaction with the cyanide ion.

4.2 The preparation of 1,2-quinone mono-oximes by the reaction of bis(1,2-quinone mono-oximato)(2,2'-dipyridyl)copper(II) or of bis(1,2-quinone mono-oximato)(1,10-phenanthroline)copper(II) on silica.

When the purity of the bis(1,2-quinone mono-oximato)-copper(II) amine adducts prepared in this study (see Chapter 2) was assessed using thin layer chromatographic techniques, the $Cu(qo)_2.X$ (X = dipy or phen) adducts in methanol were found to exhibit novel behaviour on silica. The adducts reacted to give an immobile copper-containing product and the free 1,2-quinone mono-oxime (Reaction 4.1). Similarly, the $Fe(nqo)_3$ complexes have been shown to react on silica, in the presence of a Lewis base solvent, to give respectively $Fe(nqo)_2$ and nqoH (Reaction 4.2).[16] In contrast, the $M(nqo)_3$ (M = Co,[17] Rh[18] or Ir[18]) complexes do not react on silica.

$$\mathrm{Cu(qo)_2.X} \xrightarrow[\mathrm{LB}]{\mathrm{Silica}} \mathrm{'Cu(qo).X'} + \mathrm{qoH}$$

(X = dipy or phen)

Reaction 4.1

$$\mathrm{Fe(nqo)_3} \xrightarrow[\mathrm{LB}]{\mathrm{Silica}} \mathrm{Fe(nqo)_2} + \mathrm{nqoH}$$

Reaction 4.2

In this work, thin layer chromatographic techniques were used to qualitatively study the behaviour of the complexes $Cu(qo)_2$ (qoH = 1-nqoH, 2-nqoH or 4-ClqoH), $Cu(2\text{-}nqo)_2.X$ (X = bza, bn, en, pn, py or quin), $Cu(2\text{-}nqo)(Ph_3P)_2$, K(2-nqo), $Ni(2\text{-}nqo)_2$, $Cu(nqo)_2.X$ (X = dipy or phen), and $Cu(4\text{-}Clqo)_2$.dipy on silica and cellulose. The complexes were dissolved in methanol. For silica plates, the developing solvents used were methanol and toluene-ethanol-ethyl acetate (9:2:1). For cellulose plates, the developing solvents used were toluene and diethyl ether.

The complexes $Cu(qo)_2$ (qoH = 1-nqoH, 2-nqoH or 4-ClqoH), $Cu(2\text{-}nqo)_2.X$ (X = bza, bn, en, pn, py or quin), $Cu(2\text{-}nqo)(Ph_3P)_2$, K(2-nqo), and $Ni(2\text{-}nqo)_2$ all gave a single component corresponding to the respective complex on both silica and cellulose plates. However, the $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) adducts underwent internal redox reactions on silica to give 1,2-naphthoquinone 2-oxime and an immobile red component. Similarly, the $Cu(1\text{-}nqo)_2.X$ (X = dipy or phen) adducts reacted on silica to give 1,2-naphthoquinone 1-oxime and an immobile brown component, whilst the $Cu(4\text{-}Clqo)_2$.dipy adduct gave a mobile yellow component and an immobile mauve component. In contrast, the $Cu(nqo)_2.X$ (X = dipy or phen) and $Cu(4\text{-}Clqo)_2$.dipy adducts on cellulose plates did not react. In each case, a single component corresponding to the respective adduct was obtained.

The reactions of the adducts $Cu(qo)_2$.dipy (qoH = 2-nqoH or 4-ClqoH) and $Cu(2\text{-}nqo)_2$.phen on silica were carried out on a macro scale to isolate the respective 1,2-quinone mono-oximes. The adduct in methanol was stirred with silica for 0.5 h. The solvent was removed. In the case of the $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) adducts, extraction of the impregnated silica with toluene gave 1,2-naphthoquinone 2-oxime. Further extraction with methanol gave more 1,2-naphthoquinone 2-oxime and some of the respective unreacted $Cu(2\text{-}nqo)_2.X$ (X = dipy or phen) adduct. For both adducts, an immobile red component remained on the silica. In the case of $Cu(4\text{-}Clqo)_2.dipy$, column chromatography of the impregnated silica gave 4-chloro-1,2-benzoquinone 2-oxime which was isolated as its potassium complex, potassium 4-chloro-1,2-benzoquinone 2-oximate hemihydrate, and some unreacted $Cu(4\text{-}Clqo)_2.dipy$.

The tendency of the $Cu(qo)_2.X$ (X = dipy or phen) adducts to react on silica is due to the presence of 2,2'-dipyridyl and 1,10-phenanthroline which stabilise a copper(I) species. This is emphasised by the unreactivity of the complexes $Cu(qo)_2$, $Cu(2\text{-}nqo)_2.X$ (X = bza, bn, en, pn, py or quin), $Cu(2\text{-}nqo)(Ph_3P)_2$, K(2-nqo), and $Ni(2\text{-}nqo)_2$ on silica.

The acidic nature of the silica (Figure 4.1) must also be a factor in the promotion of the internal redox reactions of the $Cu(qo)_2.X$ (X = dipy or phen) adducts on this solid support, as reaction does not occur on neutral cellulose. It is assumed that the silica acts as an active site for the adducts to react.

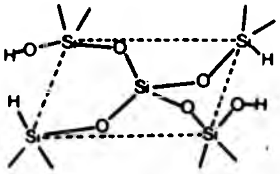

Figure 4.1

The novel behaviour of the $Cu(2\text{-nqo})_2$.dipy adduct on silica was shown to occur in a wide range of solvents, i.e. acetonitrile, benzene, benzyl chloride, butyronitrile, 1,2-dichloroethane, 1,2-dimethoxyethane, methanol, propan-2-ol, pyridine, and toluene. Reaction was even observed in the very weak Lewis base 1,2-dichloroethane.

4.3 The preparation of 1,2-quinone mono-oximes by ligand exchange of metal complexes derived from 1,2-quinone mono-oximes, using a strong acid cation exchanger. 'Dowex' 50W-X8(H).

The term ion exchange is used to describe the exchange of ions of like charge between a solution and a highly insoluble solid body (an ion exchanger) in contact with it.[19] Ion exchangers are usually polymeric in nature. The polymer carries an electric charge which is neutralised by the charges on the counter ions. These active ions are cations in a cation exchanger and anions in anion exchanger. Thus, a cation exchanger consists of a polymeric anion and active cations, while an anion exchanger consists of a polymeric cation with active anions.

Investigations in aqueous systems have established many of the fundamental principles of ion exchange as well as providing many useful applications. The scope of the ion exchange process has, however, been extended during the last thirty years by the use of both organic and mixed aqueous-organic solvent systems.[20-21]

Cation exchangers have found much use in the study of metal complexes. The simplest kind of ligand exchange is that in which the fixed ion is the proton (H^+). Ion exchangers have, for example, been used for the determination of the metal-ligand combination ratio and for the calculation of the dissociation constants of Fe(III), Co(II), and Zn(II) complexes with catechol, hydroquinone, and salicylic acid.[22]

In this work, the complexes Cu(1-nqo)$_2$, Cu(2-nqo)$_2$, Cu(2-nqo)$_2$.dipy, Ni(2-nqo)$_2$, and K(2-nqo) were exchanged using 'Dowex' 50W-X8(H) ion exchange resin, a strong acid cation exchanger. A solution of the complex in methanol was added to a suspension of 'Dowex' 50W-X8(H) ion exchange resin in methanol-water (4:1). Elution with methanol-water (4:1) gave in each case a high yield of the respective 1,2-naphthoquinone mono-oxime. Using the same technique for the ion exchange of the Cu(4-Clqo)$_2$ complex, a yellow multi-component eluate was produced which showed no tendency to complex with transition metal ions or potassium ions. It appears that the liberated 4-chloro-1,2-benzoquinone 2-oxime decomposed under the acidic conditions employed. In contrast, other workers in these laboratories using this technique were able to isolate N-acetyl-5-amino-1,2-benzoquinone 2-oxime from the bis(N-acetyl-5-amino-1,2-benzoquinone 2-oximato)copper(II) complex.^{23} Significantly, this 1,2-quinone mono-oxime cannot be prepared from N-acetyl-3-aminophenol by nitrosation, using either acetic acid and sodium nitrite or sodium ethoxide and amyl nitrite.

4.4 The preparation of alkali metal 1,2-quinone mono-oximates by the reaction of transition metal complexes derived from 1,2-quinone mono-oximes with alkali metal cyanides.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) has recently been shown to react with potassium cyanide to give potassium 4-chloro-1,2-benzoquinone 2-oximate hemihydrate[24-25] and copper(I) cyanide.[24] The reaction was carried out in order to verify whether the 4-chloro-1,2-benzoquinone 2-oximato ligands are able to stabilise copper(II) against reduction by the cyanide ion. The synthetic potential of the reaction of the cyanide ion with 1,2-quinone mono-oximato metal complexes was not realised. In this study, a wide range of transition metal complexes derived from 1,2-quinone mono-oximes were reacted with alkali metal cyanides. The procedure was shown to be a widely applicable method for the preparation of alkali metal 1,2-quinone mono-oximates.

The complex Cu(1-nqo)$_2$, M(2-nqo)$_2$ (M = Cu or Ni), Cu(2-nqo)$_2$.dipy or Cu(2-nqo)(Ph$_3$P)$_2$ in methanol was refluxed for 1 h with potassium cyanide or sodium cyanide. In all cases, reaction readily occurred to give a high yield of the respective potassium or sodium 1,2-naphthoquinone mono-oximate. From the reactions of the complexes Cu(2-nqo)$_2$.dipy and Cu(2-nqo)(Ph$_3$P)$_2$, respectively, 2,2'-dipyridyl and triphenylphosphine were also obtained.

As all the complexes Cu(2-nqo)$_2$, Cu(2-nqo)(Ph$_3$P)$_2$, and Ni(2-nqo)$_2$ reacted with the cyanide ion, it is clear that the reaction is simple exchange and does not involve an internal redox process as was suggested by the workers who initially investigated such systems.[24]

The ability of the cyanide ion to displace 1,2-quinone mono-oximato ligands from their transition metal complexes reflects its strong ligand field.[26] Significantly, the acetate and hydroxide ions cannot displace the 1,2-naphthoquinone 2-oximato ligands from bis(1,2-naphthoquinone 2-oximato)copper(II). This is in accord with the weak ligand fields of the acetate and hydroxide ions.

4.5 Conclusion.

The three novel methods established in this study for the synthesis of 1,2-quinone mono-oximes and/or of alkali metal 1,2-quinone mono-oximates are potentially useful for the preparation of a wide range of such compounds. These can subsequently be employed as starting reagents in the synthesis of a wide variety of metal complexes and organic materials.

The reaction of the $Cu(qo)_2.X$ (X = dipy or phen) adducts on silica involves an internal redox reaction, and as a consequence, only one of the 1,2-quinone mono-oximato ligands is utilised in the formation of the free 1,2-quinone mono-oxime whereas the other ligand remains, either intact or modified, with the metal. The optimum conversion of the 1,2-quinone mono-oximato ligands of the $Cu(qo)_2.X$ (X = dipy or phen) adducts is therefore limited to 50%. The ion exchange of bis(1,2-quinone mono-oximato)metal(II) complexes and the reaction of the cyanide ion with such complexes are essentially ligand exchange processes. Thus, the conversion of both chelated ligands to the free 1,2-quinone mono-oxime or its alkali metal complex is possible and achievable. However, the ion exchange technique is limited in its applicability because the acidic environment employed does not allow isolation of unstable 1,2-quinone mono-oximes such as 4-chloro-1,2-benzoquinone 2-oxime. In contrast, the reaction of alkali metal cyanides with transition metal complexes derived from 1,2-quinone mono-oximes is a widely applicable method for the preparation of alkali metal 1,2-quinone mono-oximates.

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Chapter 5

5 The aerobic oxidation of amines catalysed by 1,2-quinone mono-oximato metal complexes.

The system $M(qo)_n/O_2$ has been found to be a powerful catalyst for the oxidation of amines. It is proposed that the oxidation involves oxygen transfer mediated by the quinone oximato catalyst and the concomitant formation of an amine N-oxide intermediate. It is also proposed that the oxidation entails reduction of the $M(qo)_n$ complex via an internal redox process. The nature of the amine oxidation product has been shown to be independent of the reaction conditions employed.

5.1 Introduction.

Molecular oxygen is a potentially strong oxidising agent. Nevertheless, reactions of molecular oxygen with most substrates proceed slowly at room temperature, both in the gas phase and in homogeneous solution. This relative inertness, which may appear remarkable in view of the biradical character of the ground state of the dioxygen molecule, is evidently the essential condition for maintaining organic life in an oxygen atmosphere.

Selective oxidations of organic substrates catalysed by transition metal complexes capable of activating oxygen have been of interest, since it was observed more than a hundred years ago that phenylacetylene underwent smooth aerial oxidation to 1,4-diphenylbutadiyne when copper(I) chloride in ammonia was used as a catalyst (Reaction 5.1).[1]

$$2C_6H_5C{\equiv}CH + 1/2O_2 \xrightarrow[NH_3]{CuCl} C_6H_5C{\equiv}CC{\equiv}C_6H_5 + H_2O$$

Reaction 5.1

The direct participation of dioxygen in the oxidation of organic molecules as mediated by transition metal complexes is referred to as oxygen activation. The term autoxidation is generally applied to slow oxidations which can be effected by free oxygen (e.g. by air) at moderate temperatures. Autoxidations are promoted by small quantities of metal catalysts.

Complexes of transition metals, containing dioxygen as a ligand, are able to oxidise certain substrates under unusually mild conditions.[2] X-Ray crystallographic studies of synthetic transition metal/dioxygen complexes have indicated that a certain activation of the oxygen molecule takes place upon coordination to the metal, as shown by elongation of the O-O bond.[3] Therefore, the coordinated dioxygen in transition metal/dioxygen complexes is more reactive than the free molecule.

The activation of molecular oxygen by its coordination to metal complexes is important in both biochemical and catalytic processes. The metals which are particularly active in this respect possess two properties: they can form π-bonds, and they can give up an electron to the oxygen. Such metals include Fe(II), Mn(II), Cu(I), and other related transition metal ions.

5.2 The transition metal complex catalysed reactions of amines.

Amines are not normally reactive towards molecular oxygen at room temperature. As a consequence, there is much interest in the transition metal complex catalysed reactions of amines. Such processes are of biological and synthetic importance.[4]

Primary amines having an activated α-hydrogen atom are converted to symmetrical tertiary amines on heating with $RuCl_3.3H_2O$ and triphenylphosphine in tetrahydrofuran.[5] Aliphatic diamines are cyclised to heterocyclic amines using the $RuCl_2(Ph_3P)_3$ complex.[5] Primary amines are converted to secondary amines by employing the $RuCl_2(Ph_3P)_3$ complex.[6] The $PtCl_2(Ph_3P)_2$ combined with $SnCl_2.2H_2O$ catalytic system (henceforth referred to as the platinum-tin complex) activates primary amines and catalyses their transformation to secondary amines.[7] Treatment of primary amines having activated α-hydrogens with palladium black affords secondary amines and/or imines.[8-9] Analogous reactions with secondary amines give tertiary amines.

Secondary amines are catalytically oxidised to nitrones by hydrogen peroxide in the presence of Na_2WO_4.[10] Other catalysts such as $VO(acac)_2$, $Ti(OBu)_4$ and $MoO_2(acac)_2$ gave high yields of the nitrones, but their rate of conversion are lower. The ruthenium(II) catalysed oxidation of secondary amines with t-butyl hydroperoxide affords the corresponding imines in high yield.[4]

Primary aromatic amines are readily oxidised to azobenzenes by copper(I) chloride and dioxygen in the presence of pyridine.[11-13] The catalytic oxidation of primary amines by dioxygen in the presence of ruthenium(III) trichloride has been reported.[14] For example, benzylamine and n-butylamine afforded the corresponding nitriles.

Recent studies in these laboratories have shown that primary arylalkylamines and 1,n-diaminoalkanes ($n = 4$ or 5) are oxidised by $Cu(qo)_2$ in the presence of pyridine.[15] Benzylamine and 2-phenylethylamine were found to give the secondary arylalkylamines, dibenzylamine and di-2-phenylethylamine, respectively. 1,4-Diaminobutane and 1,5-diaminopentane cyclised to give the secondary amines, pyrrolidine and piperidine, respectively. The conversions were low with the yields of the amine oxidation products in the order of 15-25%.

It was thought that this novel behaviour may have interesting synthetic potential, especially if the metal complex is acting as a catalyst. Consequently, an extensive investigation of the reactions of 1,2-quinone mono-oximato metal complexes and various other metal compounds with a variety of amines was undertaken. This included a detailed examination of the reaction of benzylamine with a wide range of 1,2-quinone mono-oximato metal complexes, employing various reaction conditions. The study was also extended to the reaction of $Cu(qo)_2$ with amino alcohols.

5.3 Studies of the aerobic oxidation of amines catalysed by 1,2-quinone mono-oximato metal complexes.

5.3.1 Introduction and procedure.

In this study, the potential aerobic oxidation of benzylamine, 2-methoxybenzylamine, 4-methoxybenzylamine, dibenzylamine, propylamine, butylamine, 1,4-diaminobutane, 1,5-diaminopentane, 4-amino-1-butanol and 5-amino-1-pentanol by their reaction with 1,2-quinone mono-oximato metal complexes and other metal compounds was examined at room temperature and/or at 70 ^oC. The types of 1,2-quinone mono-oximato metal complexes studied included $VO(1\text{-}nqo)_2$, $VO_2(1\text{-}nqo)$, $Mn(nqo)_n$ (n = 2 or 3), $Fe(nqo)_n$ (n = 2 or 3), $Co(nqo)_3$, $Ni(qo)_2$, $Cu(qo)_2$, $Cu(qo)(Ph_3P)_2$, $Ru(nqo)_2$ and $[UO_2(nqo)_2(H_2O)_2]$. Other metal compounds examined included the iminophosphorane complex $Ni(4\text{-}ClqoPh_3P)_2$, copper(II) acetate, bis(acetylacetonato)copper(II), copper(II) chloride, copper(II) oxalate, copper(II) sulphate pentahydrate, copper(I) bromide and copper(I) chloride.

In general, the metal complex (0.10 g) was dissolved in the amine (5.0 cm^3) and the mixture stirred in air. The progress of the reaction was monitored by g.l.c., thin layer chromatographic techniques, and i.r. spectroscopy. In some cases, the products were further characterised using n.m.r. spectroscopy and mass spectrometry.

5.3.2 The oxidation of benzylamine.

Initially, the reaction of benzylamine with the various metal complexes studied was examined at room temperature, and some systems were also investigated at 70 °C. The effect of time, the solvent, aeration, the amount of catalyst, the nature of the ligands and of the metal in the 1,2-quinone mono-oximato metal complex, and the employment of a solid support was also investigated.

Benzylamine was oxidised to N-benzylidenebenzylamine by 1,2-quinone mono-oximato metal complexes. In general, it has been established that the oxidation of the amine is catalytic in nature, and involves the activation of oxygen from air. The involvement of oxygen is demonstrated by the lack of oxidation when the reaction of benzylamine with the $Cu(4\text{-}Clqo)_2$ complex is carried out under nitrogen. The oxidation also involves reduction of the 1,2-quinone mono-oximato metal complex via an internal redox process, and the active catalyst is most probably the reduced metal species. This is supported by the effectiveness of the copper(I) complex, $Cu(4\text{-}Clqo)(Ph_3P)_2$, as an oxidative catalyst, and is in accord with the well established tendency of copper(I) to activate molecular oxygen.[2]

The oxidation of benzylamine by 1,2-quinone mono-oximato complexes was shown, as discussed below, to be dependent on the temperature, the solvent, the amount of catalyst, the nature of the ligands and of the metal in the 1,2-quinone mono-oximato complex.

The effect of the metal complex.-Most of the 1,2-quinone mono-oximato complexes studied showed catalytic activity for the oxidation of benzylamine, with the $Cu(bqo)_2$ complexes being particularly effective (Table 5.1). In contrast, $Ni(4\text{-}ClqoPh_3P)_2$, copper(II) acetate, bis(acetylacetonato)copper(II), copper(II) chloride, copper(II) oxalate, copper(II) sulphate pentahydrate, copper(I) bromide, and copper(I) chloride showed little or no tendency to oxidise benzylamine to N-benzylidenebenzylamine.

The effect of time.-The nature of the benzylamine oxidation product was not affected by time, irrespective of the 1,2-quinone mono-oximato metal complex employed.

The effect of temperature.-The catalytic activity of the $Cu(qo)_2$ complexes for the oxidation of benzylamine was increased when the reaction was carried out at 70 °C (Figures 5.1-5.2). At this temperature, there was complete conversion of the amine within 96 h when the $Cu(4\text{-}Clqo)_2$ complex was used as the catalyst. The nature of the benzylamine oxidation product was independent of the reaction temperature used.

The effect of solvent.-The oxidation of benzylamine by the $Cu(4\text{-}Clqo)_2$ complex was carried out in the presence of acetonitrile, chlorobenzene, propan-2-ol, pyridine and toluene (Figure 5.3). With the exception of pyridine, the extent of conversion of benzylamine was less than that obtained when the reaction was performed in the absence of a solvent. In the case of pyridine, the yield of N-benzylidenebenzylamine was increased.

Table 5.1 The catalytic aerobic oxidation of benzylamine to N-benzylidenebenzylamine by metal complexes at room temperature.

Complex	168 h Yield (%)	672 h Yield (%)
$VO(1\text{-nqo})_2$	8	NI
$VO_2(1\text{-nqo})$	6	NI
$Mn(2\text{-nqo})_2$	17	NI
$Mn(2\text{-nqo})_3$	25	NI
$Fe(2\text{-nqo})_2$	0	NI
$Fe(2\text{-nqo})_3$	5	NI
$Co(1\text{-nqo})_3$	4	NI
$Co(2\text{-nqo})_3$	20	NI
$Ni(2\text{-nqo})_2$	3	NI
$Ni(4\text{-Clqo})_2$	12	NI
$Ni(4\text{-ClqoPh}_3P)_2$	0	NI
$Cu(4\text{-Clqo})(Ph_3P)_2$	49	NI
$Cu(1\text{-nqo})_2$	4	5
$Cu(2\text{-nqo})_2$	4	6
$Cu(4\text{-Clqo})_2$	42	95
$Cu(4\text{-Brqo})_2$	40	92
$Cu(dnr).H_2O$	11	NI
$Cu(6\text{-Cldnr}).H_2O$	16	NI
CuCl	4	NI
$CuCl_2$	1	NI
$[UO_2(2\text{-nqo})_2(H_2O)_2]$	12	NI

NI = Reaction was not investigated.

Figure 5.1

The catalytic oxidation of benzylamine to N-benzylidenebenzylamine by bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Effect of time and temperature.

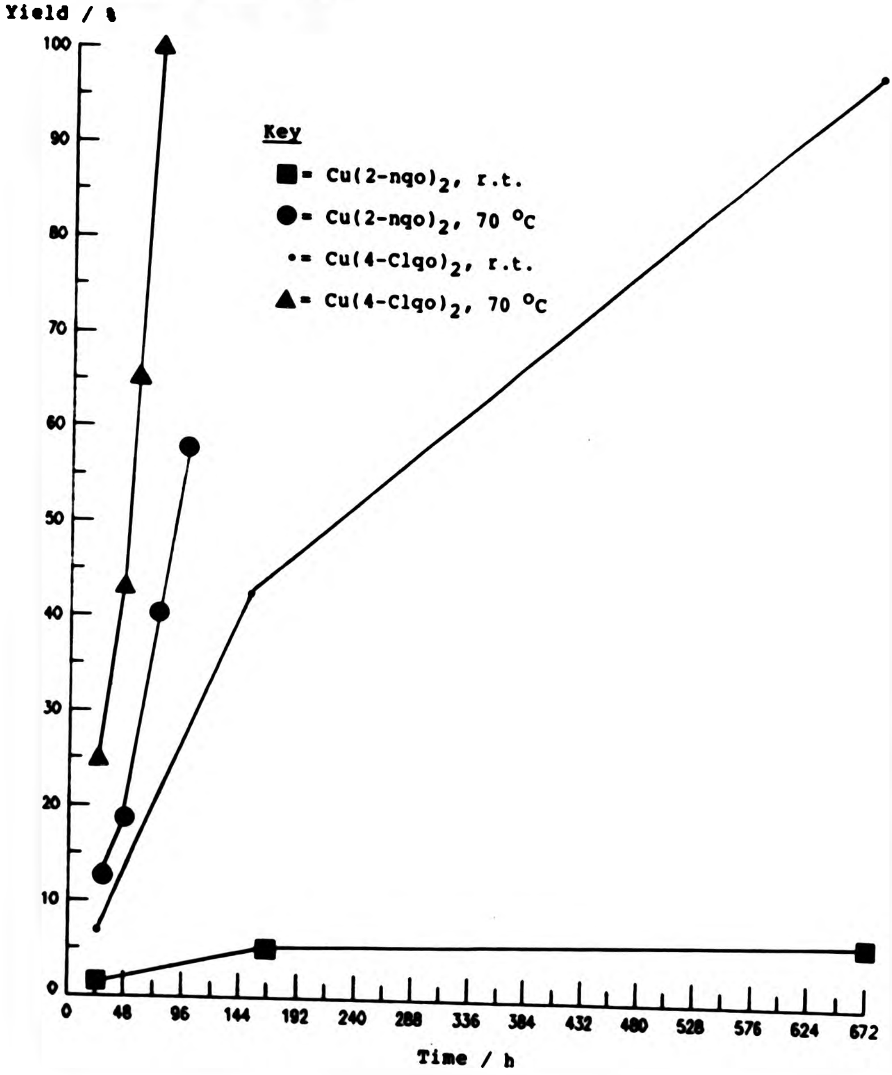


Figure 5.2

The catalytic oxidation of benzylamine to N-benzylidenebenzylamine by bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) at 70 °C.

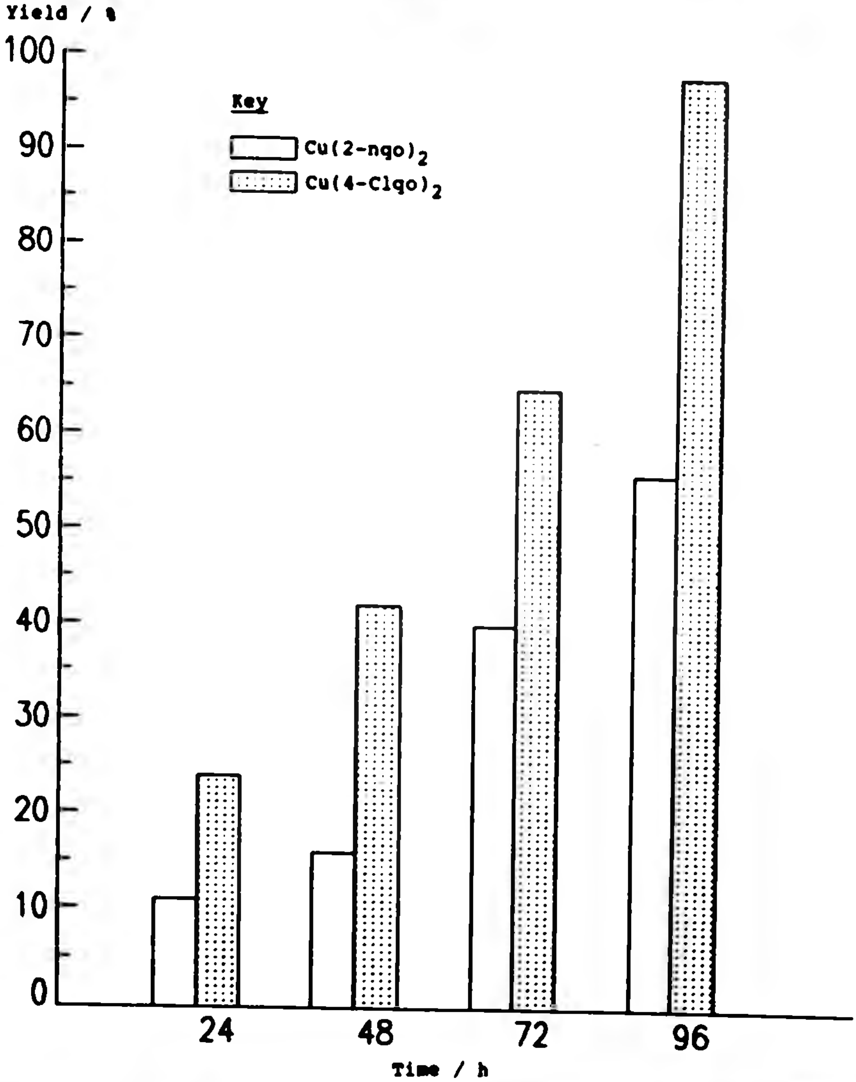
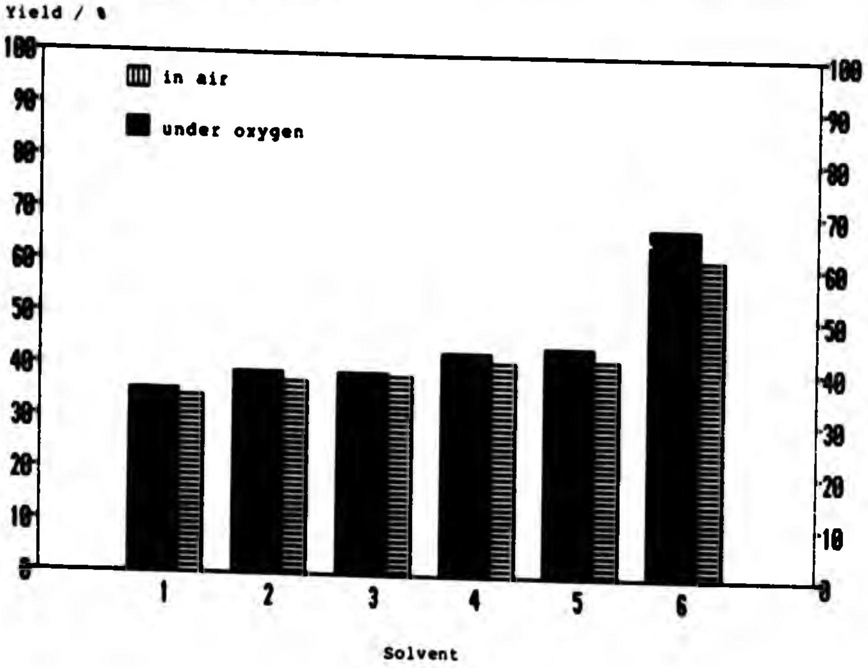


Figure 5.3

The catalytic oxidation of benzylamine to N-benzylidene-benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)-copper(II) at room temperature (168 h) in air or under oxygen. Effect of the solvent.



Key

1 = toluene

2 = propan-2-ol

3 = acetonitrile

4 = chlorobenzene

5 = no solvent

6 = pyridine

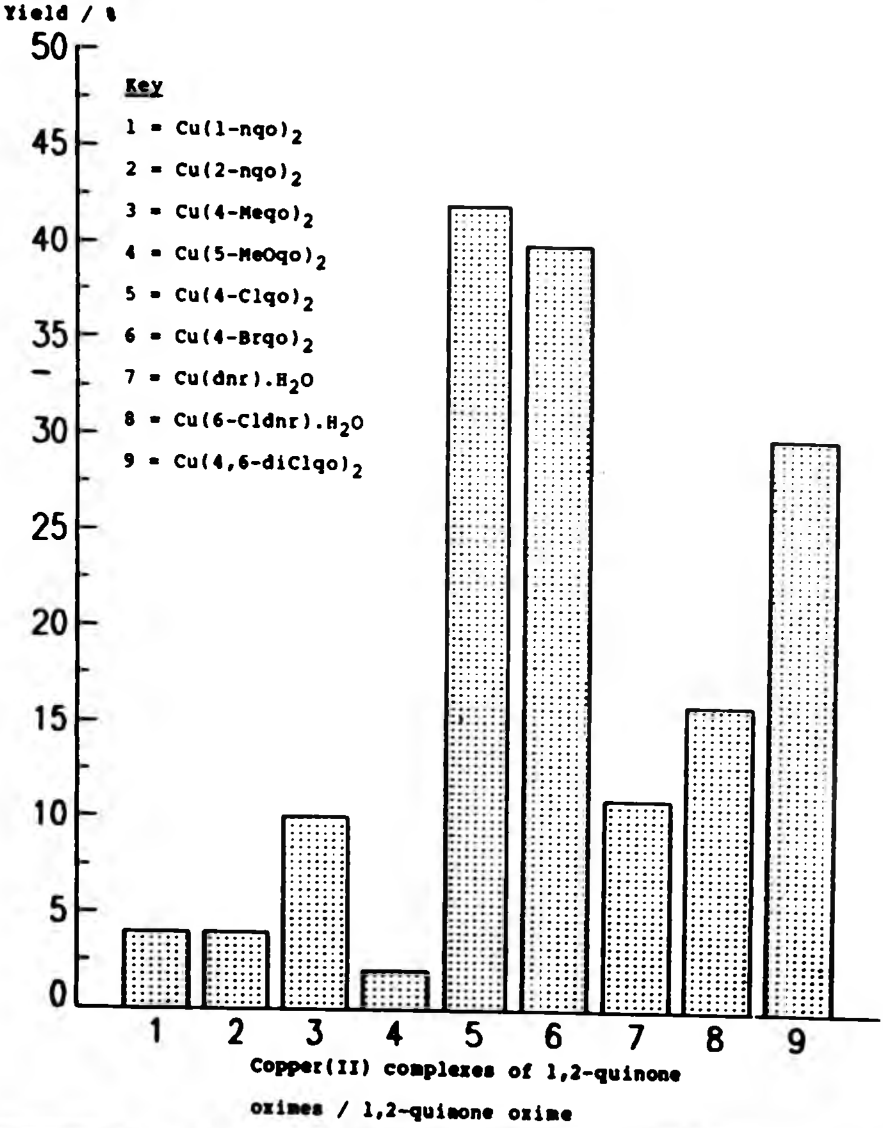
The effect of aeration.-Bubbling oxygen through benzylamine or through the reaction mixtures performed in a solvent caused only a small increase in the extent of oxidation of the amine by the $Cu(4\text{-}Clqo)_2$ complex compared with that obtained by the corresponding reactions carried out in air (Figure 5.3).

The effect of the amount of $M(qo)_n$ complex.-The oxidation of benzylamine to N-benzylidenebenzylamine was shown to be dependent on the amount of catalyst employed. For the $Cu(4\text{-}Clqo)_2$ complex, it was found that complete conversion of benzylamine could be achieved at room temperature by using 1 mmol of complex to 46 mmol of amine. The nature of the amine oxidation product was independent of the amount of catalyst employed.

The effect of the qo of the $M(qo)_n$ complex.-A wide range of 1,2-quinone mono-oximato copper(II) complexes were surveyed to find the most active ligands for the oxidation of benzylamine (Figure 5.4). In general, the $Cu(bqo)_2$ complexes were shown to be very much more active catalysts than the $Cu(nqo)_2$ complexes. The most efficient complexes were found to be those with the 1,2-quinone mono-oximato ligands containing halogeno substituents. In all cases, complexes derived from 1,2-naphthoquinone 2-oxime showed greater catalytic activity in the oxidation of benzylamine than the corresponding complexes derived from 1,2-naphthoquinone 1-oxime. This is especially apparent in the oxidations invol-

Figure 5.4

The catalytic oxidation of benzylamine to N-benzylidenebenzylamine by copper(II) complexes of 1,2-quinone oximes at room temperature (168 h). Effect of the 1,2-quinone oxime ligand.



ving the Mn(II), Mn(III), and Co(III) complexes.

The effect of the M in the M(qo)$_n$ complex.-A wide range of 1,2-naphthoquinone mono-oximato metal complexes were surveyed to investigate the effect of the metal of the complex on the oxidation of benzylamine (Figure 5.5). The extent of oxidation was shown to be depend upon the nature of the metal of the complex. The Mn(II), Mn(III), and (UO_2^{2+}) complexes derived from 1,2-naphthoquinone mono-oximes can be seen to be efficient catalysts for the oxidation of benzylamine. In contrast, the corresponding Fe(II) and Ru(II) complexes show no tendency at all to oxidise the amine.

The effect of the addition of charcoal or silica.-The addition of charcoal or silica enhanced the catalytic effectiveness of the Cu(4-Clqo)$_2$ complex.

5.3.3 The oxidation of 2-methoxybenzylamine and 4-methoxybenzylamine.

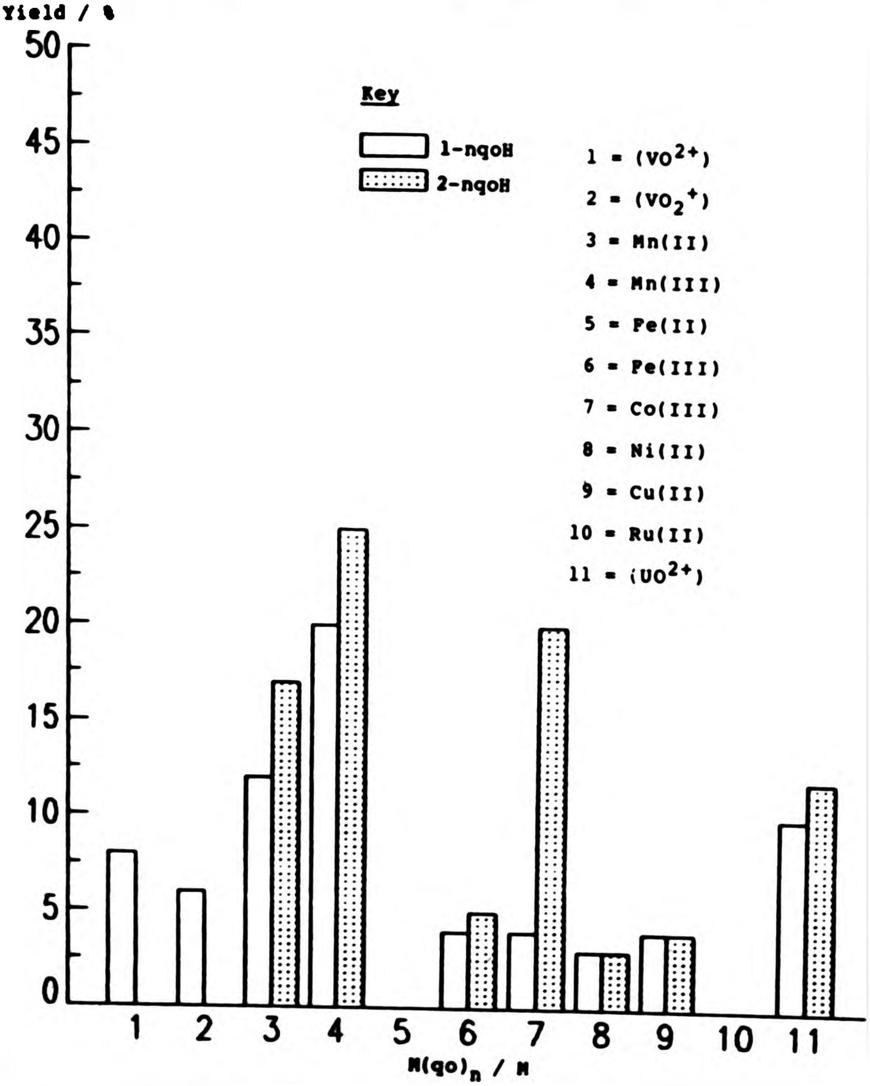
2-Methoxybenzylamine and 4-methoxybenzylamine were readily oxidised to N-2-methoxybenzylidene-2-methoxybenzylamine and 4-methoxybenzylidene-4-methoxybenzylamine, respectively, by the Cu(4-Clqo)$_2$ complex at 70 °C.

5.3.4 The oxidation of dibenzylamine.

Dibenzylamine was oxidised to N-benzylidenebenylamine by Cu(qo)$_2$. The rate of oxidation of dibenzylamine to N-benzylidenebenzylamine by Cu(qo)$_2$ was slower than that for

Figure 5.5

The catalytic oxidation of benzylamine to N-benzylidene-benzylamine by metal complexes of 1,2-naphthoquinone mono-oximes at room temperature (168 h). Effect of the metal.



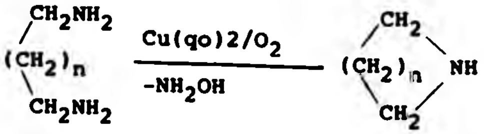
the oxidation of benzylamine to the imine. The oxidation of dibenzylamine was shown to be dependent on the temperature employed and the amount of catalyst used.

5.3.5 The attempted oxidation of propylamine and butylamine.

Propylamine and butylamine were shown to be inert to oxidation by $Cu(qo)_2$. G.l.c. and i.r. analysis did not detect any amine oxidation product. However, t.l.c. analysis of the reaction mixtures showed that the $Cu(qo)_2$ complexes had undergone internal redox reactions which gave rise to a multi-component mixture of products derived from the complex.

5.3.6 The oxidation of 1,4-diaminobutane and 1,5-diaminopentane.

1,4-Diaminobutane and 1,5-diaminopentane were oxidised by $Cu(qo)_2$ to the cyclic secondary amines, pyrrolidine and piperidine, respectively (Reaction 5.2). Enhancement of the rate of oxidation of 1,4-diaminobutane by $Cu(qo)_2$ was observed when both the reaction temperature and the amount of catalyst employed were increased.



(where n = 2 or 3)

Reaction 5.2

5.3.7 The oxidation of 4-amino-1-butanol and 5-amino-1-pentanol.

The amino alcohols, 4-amino-1-butanol and 5-amino-1-pentanol, were reacted with the $Cu(4\text{-}Clqo)_2$ complex. In both cases, there was a small amount of oxidation to the cyclic ethers, tetrahydrofuran and tetrahydropyran, respectively.

5.3.8 Discussion.

Generally, the above results have demonstrated that the catalytic aerobic oxidation of amines is specific to 1,2-quinone mono-oximato metal complexes. The results have also shown that the oxidations are dependent on the temperature, the amount of catalyst, the nature of the ligands and of the metal in the 1,2-quinone mono-oximato complex. The nature of the amine oxidation product was independent of the reaction conditions employed. This contrasts the behaviour of other catalysts employed for the oxidation of amines (Table 5.2).[5-7] The specifity of the oxidations by 1,2-quinone mono-oximato complexes is illustrated by the cleanness of the reactions.

The importance of the qo in the $M(qo)_n$ complex.-The quinone and the oximato groups in 1,2-quinone mono-oximato complexes are both potential oxidants. The $Ni(4\text{-}ClqoPh_3P)_2$ complex, which does not contain an oximato group, showed no tendency to oxidise benzylamine. This indicates that the active catalytic site in 1,2-quinone mono-oximato complexes must be the oximato group.

Benzoquinones are well known oxidants in synthetic organic chemistry,[16] and in the presence of metals, they have been utilised for the catalytic oxidation of various substrates.[17-19] Catalytic systems based on the transition metal nitro-nitrosyl redox couple are also well known.[20-22] In these cases, oxygen is transferred from the nitro ligand to the substrate. This step is followed by the oxidation of the nitrosyl group to the nitro group by molecular oxygen. Both steps are mediated by the metal.

The catalytic activity of the 1,2-quinone mono-oximato metal complex was shown to depend upon the nature of the ligands. The most efficient 1,2-quinone mono-oximato copper(II) complexes for the oxidation of amines were those with ligands containing halogeno substituents. In general, the $Cu(bqo)_2$ complexes are very much more active catalysts than the $Cu(nqo)_2$ complexes. It is known that the catalytic responses of metal complexes may be increased or diminished

Table 5.2 The transition metal complex catalysed reactions of amines.

Catalytic system	Temp./^{o}C	Substrate	Product(s)
$RuCl_3.3H_2O/Ph_3P^5$	185	$PhCH_2NH_2$	$(PhCH_2)_3N^a$ (97%)
			$(PhCH_2)_2NH$ (20%) & $(PhCH_2)_3N^b$ (75%)
			$(PhCH_2)_2NH$ (65%), $(PhCH_2)_3N$ (10%) & $PhCH=NCH_2Ph^c$ (25%)
			$PhCH=NCH_2Ph^d$ (25%)
			$(PhCH_2)_2NH$ (75%) & $(PhCH_2)_3N^e$ (12%)
$RuCl_2(Ph_3P)_3{}^6$	$185^{f, g, i}$ $140\text{-}175^h$	$PhCH_2NH_2$	$(PhCH_2)_2NH^f$
			$PhCH=NCH_2Ph^{g, h}$
			$PhCH_2NH_2$ (11%), $(PhCH_2)_2NH$ (75%) & $(PhCH_2)_3N^i$ (12%)

Table 5.2 (continued)

Catalytic system	Temp./°C	Substrate	Product(s)
$PtCl_2(Ph_3P)_2$ combined with $SnCl_2.2H_2O$[7]	180	$PhCH_2NH_2$	$(PhCH_2)_2NH$ (81%)
		$H_2N(CH_2)_4NH_2$	$(CH_2)_4NH$ (8%)

[a] Reaction performed in tetrahydrofuran.

[b] Reaction performed in dioxan.

[c] Reaction performed in benzene.

[d] Reaction performed in pyridine.

[e] Reaction performed in the absence of a solvent.

[f] 2 mol % of catalyst employed, and reaction allowed to proceed for 5 h.

[g] 2 mol % of catalyst employed, and reaction allowed to proceed for 1 to 3 h.

[i] 5 mol % of catalyst employed, and reaction allowed to proceed for 5 h.

by small changes in the ligand structure.[23]

The complexes derived from 1,2-naphthoquinone 2-oxime show greater catalytic activity than those of the corresponding 1,2-naphthoquinone 1-oximato complexes, and this reflects the relative ease with which these complexes undergo internal redox reactions.[24] The greater reactivity of the 1,2-naphthoquinone 2-oximato complexes has previously been recognised in the reactions of the Cr(III), Mn(III), and Fe(III) complexes derived from 1,2-naphthoquinone mono-oximes with Lewis bases such as pyridine and triphenylphosphine.[24] This was particularly apparent in the reactions involving triphenylphosphine. Thus, $Cr(2\text{-nqo})_3$ reacts completely in fifty minutes, but, in contrast, $Cr(1\text{-nqo})_3$ fails to react with the phosphine. This behaviour was accounted for by the oximato group in the 1,2-naphthoquinone 2-oximato ligands being sterically more accessible than the oximato group in the 1,2-naphthoquinone 1-oximato ligands.

The importance of the M in the $M(qo)_n$ complex.-Of the 1,2-quinone mono-oximato metal complexes examined, only those involving (VO^{2+}), (VO_2^{+}), Mn(II), Mn(III), Fe(III), Co(III), Ni(II), Cu(I), Cu(II), and (UO_2^{2+}) showed catalytic activity for the oxidation of amines. In contrast, the Fe(II) and Ru(II) complexes were catalytically inactive. This suggests that only complexes in which the metal can be reduced or in which the metal is in an appropriate reduced state, e.g. copper(I), are active as catalysts. The reduction of the metal in the oxidation of the amine involves an internal redox process via the initial formation of an adduct. Similarly, the catalytic oxidation of primary aromatic amines to azobenzenes by copper(I) chloride and dioxygen in pyridine has been reported to involve an internal redox process (Scheme 5.1).[13]

$$4\mathrm{Cu(I)} + O_2 + 2H_2O \longrightarrow 4\mathrm{Cu(II)} + 4OH^-$$

$$4\mathrm{Cu(II)} + PhNH_2 \longrightarrow 4\mathrm{Cu(I)} + PhN{=}NPh + 4H^+$$

$$PhNH_2 + O_2 \xrightarrow{\mathrm{Cu(I)}} PhN{=}NPh + 2H_2O$$

Scheme 5.1

Since both the Cu(qo)$_2$ complexes and Cu(acac)$_2$ are capable of undergoing Lewis base promoted internal redox reactions, but only the former are catalytically active, the formation of the oxidation products cannot be accounted for in terms of this process alone. It also further emphasises that the active catalytic site in 1,2-quinone mono-oximato complexes is the oximato group.

The importance of oxygen.-As stated earlier, the oxidation of amines by 1,2-quinone mono-oximato complexes entails the activation of molecular oxygen. The oxidations do not involve the use of alternative oxygen sources as is the case in the Na_2WO_4 catalysed oxidation of secondary amines to nitrones with hydrogen peroxide,[10] and the ruthenium(II) catalysed oxidation of secondary amines to imines with t-butyl hydroperoxide.[4]

The efect of the nature of the amine.-The oxidation of 1,4-diaminobutane and 1,5-diaminopentane by $Cu(qo)_2$ is slower than that of benzylamine. This is due to the presence of an activated α-hydrogen in benzylamine. Similar behaviour has been previously exhibited by the platinum-tin catalytic system (Table 5.2).[7]

The effect of temperature and time.-Increases in the reaction temperature and time, although naturally led to increased yields, do not alter the nature of the amine oxidation product. This contrasts with the behaviour of other catalytic systems which give products dependent on the temperature and the time employed (Table 5.2).[6]

It is noteworthy that the temperatures used for the oxidation of amines by 1,2-quinone mono-oximato complexes are much lower than those for amine conversions by other catalytic systems (180-235 °C).[5-7]

The effect of solvent.-The nature of the solvent is an important factor in the activity of catalysts. Lewis base solvents can often participate in the reaction mechanism by coordinating to and being displaced from the active site of reaction during the catalytic cycle. By suitably adjusting the Lewis basicity of the reaction medium, it is possible to enhance or inhibit substrate migration to the active catalytic site.

In this study, it was shown that the addition of pyridine increased the oxidation of benzylamine by the $Cu(4\text{-}Clqo)_2$ complex. This is presumably due to the pyridine assisting inducement of an internal redox reaction in the $Cu(4\text{-}Clqo)_2$ complex and/or by promoting oxygen transfer to the amine. Similarly, the induction periods for the catalytic oxidation of alkenes by the $Mn(nqo)_n$ (n = 2 or 3) complexes have recently been shown to be reduced by the addition of pyridine.[24] This behaviour was accounted for by the pyridine: (1) promoting oxygen transfer to the alkene, (2) assisting breakdown of the polymeric chains in the $Mn(nqo)_2$ complexes, and (3) inducing internal redox reactions in the $Mn(nqo)_3$ complexes.

The oxidation of primary amines to azobenzenes by copper(I) chloride and dioxygen readily occurs in pyridine, collidine and 2-picoline.[11-12] The oxidations fail, however, if quinoline, alcohols, dioxan or 1,2-dichloroethane are employed as the reaction media.[12] The oxidation of benzylamine by the $RuCl_3.3H_2O/Ph_3P$ catalytic system has also been shown to be solvent dependent (Table 5.2).[5] The catalysed transformation of primary amines by the platinum-tin complex proceeds readily in benzene, whereas donor solvents such as dioxan, tetrahydrofuran or acetonitrile suppress the reaction.[7] The behaviour of the $RuCl_3.3H_2O/Ph_3P$ catalytic system and the platinum-tin complex contrasts that of the Cu(4-Clqo)$_2$ complex. For the latter, the nature of the amine oxidation product was independent of the solvent employed.

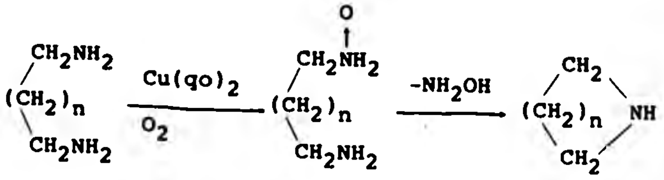
The effect of the amount of M(qo)$_n$ complex.-The nature of the amine oxidation product was found to be independent of the amount of 1,2-quinone mono-oximato complex employed. This contrasts the RuCl$_2$(Ph$_3$P)$_3$ catalytic system (Table 5.2).[6] It was shown that in order to avoid the formation of tertiary amimes, the concentration of the RuCl$_2$(Ph$_3$P)$_3$ catalyst must be kept below a particular level.

The effect of the addition of charcoal or silica.-The addition of charcoal or silica increases the catalytic effectiveness of the 1,2-quinone mono-oximato complex for the oxidation of amines.

Carbon has widely been used as a catalyst support.[25] A particular advantage of carbon is in the fact that its pore structure and internal surface can be widely varied. Carbon can also behave as an active catalyst and is used for some reactions.[26] However, this activity does not generally hinder its use as a catalyst support. Silica has also been employed as a catalyst support.[27]

5.3.9 A mechanistic appraisal.

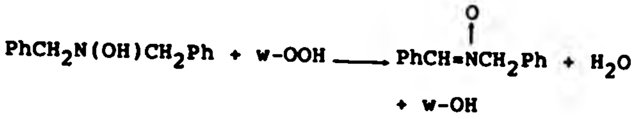
It is possible to account for the behaviour of the systems leading to cyclic secondary amines by assuming formation of an amine N-oxide intermediate, by oxygen transfer to the amine mediated by the quinone oximato catalyst (Scheme 5.2). The amine N-oxide then undergoes intramolecular nucleophilic attack on an α-methylene group. This results in the elimination of hydroxylamine, and the concomitant formation of the cyclic secondary amine. Similarly, the Na_2WO_4 catalysed oxidation of dibenzylamine with hydrogen peroxide to give the nitrone, N-benzylidenebenzylamine N-oxide, was rationalised in terms of an oxygen transfer process (Scheme 5.3).[10] The mechanism involves N-



(where n = 2 or 3)

Scheme 5.2

$$PhCH_2NHCH_2Ph + w\text{-}OOH \longrightarrow PhCH_2N(OH)CH_2Ph + w\text{-}OH$$

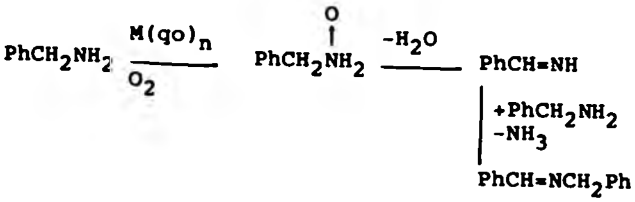


$$PhCH_2N(OH)CH_2Ph + w\text{-}OOH \longrightarrow PhCH{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}CH_2Ph + H_2O + w\text{-}OH$$

Scheme 5.3

oxidation of the dibenzylamine with tungstate peracid (w-OOH, where w = WO_3^-, WO_4^- or WO_6^-) to give the hydroxylamine, which then undergoes further oxidation to give the nitrone with the elimination of water. Oxygen transfer from the metal-hydroperoxide was assumed.

The oxidation of benzylamine to N-benzylidenebenzylamine can be accounted for by the initial formation of benzylamine N-oxide via oxygen transfer to the amine mediated by the quinone oximato catalyst (Scheme 5.4). The



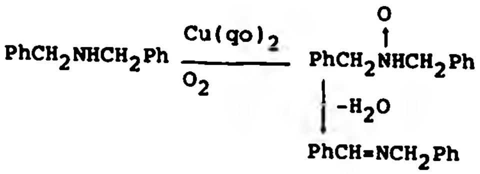
Scheme 5.4

amine N-oxide then loses water to give benzaldimine. The latter reacts with benzylamine via nucleophilic condensation to give N-benzylidenebenzylamine with the elimination of ammonia. Some evidence for this rationalisation is given by the evolution and detection of ammonia.

Benzaldimine has previously been inferred as an intermediate in the oxidation of benzylamine by the palladium black,[8-9] platinum-tin,[7] and $RuCl_3.3H_2O/Ph_3P$[5] catalytic systems.

The formation of N-2-methoxybenzylidene-2-methoxybenzylamine and N-4-methoxybenzylamine-4-methoxybenzylamine can also be rationalised for in terms of amine N-oxide intermediates.

The oxidation of dibenzylamine to N-benzylidenebenzylamine can be accounted for by the initial formation of N-benzylidenebenzylamine N-oxide which then loses water to give the imine (Scheme 5.5). The rate of oxidation of dibenzylamine to N-benzylidenebenzylamine by $Cu(qo)_2$ was much slower than that for the oxidation of benzylamine to the imine. This indicates that the oxidation of benzylamine to N-benzylidenebenzylamine does not involve the formation of dibenzylamine as an intermediate.



$$PhCH_2NHCH_2Ph \xrightarrow[O_2]{Cu(qo)_2} PhCH_2\overset{O}{\overset{\uparrow}{N}}HCH_2Ph \xrightarrow{-H_2O} PhCH{=}NCH_2Ph$$

Scheme 5.5

5.3.10 Conclusion.

Overall, the 1,2-quinone mono-oximato metal complexes have been shown to have novel catalytic properties for the aerobic oxidation of amines. The oxidation of primary arylakylamines to imines is of synthetic importance as there is a dearth of good methods, particularly in non-polar solvents, for amine to imine conversions.[28] The catalytic oxidative transformation of dibenzylamine to N-benzylidenebenzylamine is of interest, as there are only a limited number of reactions of this type reported in the literature.[4] Also of importance is the low cost and the ease of preparation of the 1,2-quinone mono-oximato complexes compared to other catalysts that have been employed for the oxidation of amines. The catalytic oxidation of amines by 1,2-quinone mono-oximato complexes does not involve the use of alternative oxygen sources such as hydroperoxides. The nature of the amine oxidation product is independent of the reaction conditions employed. The oxidation occurs using mild conditions, i.e. low temperature and atmospheric pressure.

The use of metal complexes derived from 1,2-quinone mono-oximes as catalysts for the oxidation of amines has several advantages, and could be of considerable value in a wider context.

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Chapter 6

6 Experimental.

6.1 General techniques.

The reagents and solvents employed were generally of GPR grade. Toluene was purified by distillation. T.l.c. was carried out using pre-coated silica gel and cellulose plates of 0.25 mm thickness, and dimensions of about 6 x 2 cm. Silica gel adsorbent (70-230 mesh) and 'Dowex' 50W-X8(H) ion exchange resin were supplied by BDH Chemicals Ltd.

6.2 Analytical methods.

Copper was determined quantitatively by the method of atomic absorption spectrometry, using a SP9 atomic absorption spectrometer. A known mass (ca. 0.1 g) of the material under investigation was warmed with concentrated sulphuric acid (ca. 1 cm^3), concentrated nitric acid (ca. 2 cm^3) and hydrogen peroxide (ca. 1 cm^3). After allowing the mixture to digest, the inorganic residue was diluted to a known volume with water. Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 microanalyser at the microanalytical unit of the Polytechnic of North London.

6.3 Spectroscopic techniques.

Infra-red spectra were recorded on a Perkin-Elmer 781 spectrophotometer in the region 4000-600 cm^{-1}. The samples were prepared either as a liquid film and mounted on potassium bromide plates or with pressed potassium bromide discs of the sample at a concentration of 1-2%. Ultraviolet /

visible spectra in the region 900-200 nm were obtained using a Perkin-Elmer Lambda 5 instrument. Nuclear magnetic resonance spectra were obtained using a Perkin-Elmer R12B 60 MHz spectrometer (^1H). The mass spectra were obtained on a Hitachi AEI MS9 instrument operating at 70 eV using a direct insertion probe operating at 100-200 °C.

6.4 Thermogravimetric analysis.

Thermogravimetric analysis was carried out under nitrogen using a Stanton thermobalance. A heating rate of ca. 3 °C min^{-1} was used.

6.5 Magnetic susceptibility measurements.

Room temperature magnetic moments were determined using a Johnson Matthey magnetic susceptibility balance calibrated using a solution of $MnCl_2$. All the magnetic measurements were carried out in duplicate to check on packing error. Magnetic moments were corrected for the diamagnetic effect of the metal and of the ligands.[1]

6.6 Gas liquid chromatography.

Gas liquid chromatograms were obtained using Pye Unicam instruments. A glass column 2.0 m long and 4.0 mm internal diameter packed with Carbowax 20M on Chromosorb W/HP (mesh 100/20) was used. 1 μl of sample was injected for each chromatogram. Nitrogen was used as the carrier gas with a flame ionisation detector at a temperature of 300 °C.

Conditions used were as follows:

Amine	Injection temp./°C	Column temp./°C
Benzylamine	250	210
2-Methoxybenzylamine	260	245
4-Methoxybenzylamine	260	245
Dibenzylamine	260	240
Propylamine	250	80
Butylamine	250	80
1,4-Diaminobutane	250	120
1,5-Diaminopentane	250	200
4-Amino-1-butanol	260	240
5-Amino-1-pentanol	260	150

6.7 Reactions.

The interaction of bis(1,2-quinone mono-oximato)copper(II) with benzylamine or quinoline.

Bis(1,2-quinone mono-oximato)copper(II) (10.0 mmol) and the amine (22.0 mmol) in acetonitrile (50 cm^3) were stirred at room temperature. After 24 h, bis(1,2-quinone mono-oximato)(amine)copper(II) was filtered off, washed with acetonitrile and diethyl ether, and dried at 40 °C/ 20 mm Hg (see Table 6.1 for analysis, yields, and other data).

The interaction of bis(1,2-quinone mono-oximato)copper(II) with 2,2'-dipyridyl, 1,10-phenanthroline, 1,2-diaminoethane, 1,3-diaminopropane or 1,4-diaminobutane.

Bis(1,2-quinone mono-oximato)copper(II) (10.0 mmol) and the amine (11.0 mmol) in acetonitrile (50 cm^3) were stirred at room temperature. After 24 h, bis(1,2-quinone mono-oximato)(amine)copper(II) was filtered off, washed with acetonitrile and diethyl ether, and dried at 40 °C/ 20 mm Hg (see Table 6.1 for analysis, yields, and other data). The primary amine adducts were initially washed with water.

Table 6.1 Bis(1,2-quinone mono-oximato)(amine)copper(II) adducts.

$Cu(qo)_2$.amine	Colour	Yield (%)	Found (%)				Requires (%)			
			C	H	N	Cu	C	H	N	Cu
$Cu(1\text{-}nqo)_2$.bza	brown	89	63.5	4.2	8.6	11.7	63.0	4.1	8.2	12.3
$Cu(2\text{-}nqo)_2$.bza	brown	86	63.5	4.2	8.1	11.4	63.0	4.1	8.2	12.3
$Cu(4\text{-}Clqo)_2$.bza	mauve	83	47.8	3.3	8.9	12.6	47.3	3.1	8.7	13.1
$Cu(4\text{-}Meqo)_2$.bza	mauve	95	57.5	4.5	9.6	13.8	57.0	4.8	9.5	14.3
$Cu(2\text{-}nqo)_2$.quin⁺	red	65	64.6	3.6	7.6	12.0	64.9	3.5	7.8	11.8
$Cu(1\text{-}nqo)_2$.dipy	brown	62	62.6	3.5	10.0	11.4	63.9	3.6	9.9	11.2
$Cu(2\text{-}nqo)_2$.dipy	brown	59	62.7	3.9	10.2	12.0	63.9	3.6	9.9	11.2
$Cu(4\text{-}Clqo)_2$.dipy*	mauve	49	49.2	2.2	10.0	11.3	49.7	2.6	10.5	11.9
$Cu(4\text{-}Meqo)_2$.dipy	mauve	64	58.0	4.3	10.9	12.7	58.7	4.1	11.4	12.8

⁺ Thermal gravimetric analysis.

Weight of sample (mg)	Temp./°C	Weight loss Found (mg)	Calc.[c] (mg)
296	160[a] 200[b]	74	71

[a] Temperature at which loss of quinoline occurred.
[b] Temperature at which the $Cu(2\text{-}nqo)_2$ complex decomposed.
[c] Calculated for one mol of quinoline.

* Previously reported.[2]

Table 6.1 (continued)

$Cu(qo)_2$.amine	Colour	Yield (%)	Found (%)				Requires (%)			
			C	H	N	Cu	C	H	N	Cu
$Cu(1\text{-}nqo)_2$.phen	brown	55	64.3	3.1	9.7	10.8	65.4	3.4	9.5	10.7
$Cu(2\text{-}nqo)_2$.phen	brown	48	64.1	2.9	10.0	11.0	65.4	3.4	9.5	10.7
$Cu(4\text{-}Clqo)_2$.phen*	red	40	51.8	2.3	10.2	12.0	51.9	2.5	10.1	11.4
$Cu(4\text{-}Meqo)_2$.phen	mauve	43	59.7	3.6	10.5	11.8	60.6	3.9	10.9	12.2
$Cu(2\text{-}nqo)_2$.en	brown	55	56.1	4.4	11.2	13.2	56.5	4.3	12.0	13.5
$Cu(2\text{-}nqo)_2$.pn	brown	58	56.7	5.0	11.7	13.0	57.4	4.6	11.6	13.1
$Cu(1\text{-}nqo)_2$.bn	brown	93	57.9	4.9	11.7	12.5	58.2	4.8	11.3	12.7
$Cu(2\text{-}nqo)_2$.bn	brown	89	57.4	5.1	10.9	12.3	58.2	4.8	11.3	12.7
$Cu(4\text{-}Clqo)_2$.bn	mauve	69	40.9	3.7	12.3	13.0	41.5	3.9	12.1	13.6
$Cu(4\text{-}Meqo)_2$.bn	mauve	80	50.2	5.3	12.9	14.4	51.1	5.7	13.2	14.9

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = benzylamine, pyridine, 2,2'-dipyridyl or 1,10-phenanthroline) with 1,1,2-trichlorotrifluoroethane.

Bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = benzylamine, pyridine, 2,2'-dipyridyl or 1,10-phenanthroline) (1.00 g) in 1,1,2-trichlorotrifluoroethane (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with 1,1,2-trichlorotrifluoroethane (3 x 50 cm^3) and dried at 40 $^{\circ}$C/ 20 mm Hg (see Table 6.2 for data). The filtrate was evaporated to give a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = benzylamine, pyridine, quinoline, 1,2-diaminoethane, 2,2'-dipyridyl or 1,10-phenanthroline) with acetonitrile.

Bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = quinoline, pyridine, benzylamine, 1,2-diaminoethane, 2,2'-dipyridyl or 1,10-phenanthroline) (1.00 g) in acetonitrile (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with acetonitrile (3 x 100 cm^3) and dried at 40 $^{\circ}$C/ 20 mm Hg (see Table 6.2 for data). The filtrate was evaporated to give a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = benzylamine, pyridine, 2,2'-dipyridyl or 1,10-phenanthroline) with propan-2-ol.

Bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (where X = benzylamine, pyridine, 2,2'-dipyridyl or 1,10-phenanthroline) (1.00 g) in propan-2-ol (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with propan-2-ol (3 x 100 cm^3) and dried at 40 ^{o}C/ 20 mm Hg (see Table 6.2 for data). The filtrate was evaporated to give a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) with heptane.

Bis(1,2-naphthoquinone 2-oximato)copper(II) (1.00 g) in heptane (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with heptane (3 x 50 cm^3) and dried at 40 ^{o}C/ 20 mm Hg (see Table 6.2 for data). The filtrate was evaporated to give a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) with pyridine.

Bis(1,2-naphthoquinone 2-oximato)copper(II) (1.00 g) in pyridine (50 cm^3) was heated under reflux for 24 h. The solvent was removed at 50 ^{o}C/ 30 mm Hg to give a black tarry residue (1.10 g). Toluene (100 cm^3) was added and the mixture was heated under reflux for 1 h. The hot mixture was then filtered. This process was carried out a further three times. The residue obtained was washed with acetone (3 x 100 cm^3) and dried at 40 ^{o}C/ 20 mm Hg to give a solid (see Table 6.2 for data). The combined toluene extracts on evaporation of the solvent gave a residue (see Table 6.3 for data). The combined acetone washings on evaporation of the solvent gave a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) with tetrahydropyran.

Bis(1,2-naphthoquinone 2-oximato)copper(II) (1.00 g) in tetrahydropyran (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with tetrahydropyran (3 x 100 cm^3) and dried at 40 ^{o}C/ 20 mm Hg (see Table 6.2 for data). Evaporation of the filtrate gave a residue (see Table 6.3 for data).

The interaction of bis(1,2-naphthoquinone 2-oximato)(1,2-diaminoethane)copper(II) with toluene.

Bis(1,2-naphthoquinone 2-oximato)(1,2-diaminoethane)copper(II) (1.00 g) in toluene (50 cm^3) was heated under reflux for 24 h. The hot reaction mixture was filtered and the solid obtained was washed with hot toluene (5 x 100 cm^3) and dried at 40 ^{o}C/ 20 mm Hg (see Table 6.2 for data).

The filtrate was evaporated to give a residue, which was recrystallised from toluene as fine needles of dibenzo[b,i]phenazine-5,12-diol (see Table 6.3 for data).

Table 6.2

Complex	Solvent	Solid, weight (g) / colour	Nature of solid, characterisation
$Cu(2\text{-}nqo)_2$	$Cl_2FCCClF_2$	0.90 brown	Identified as $Cu(2\text{-}nqo)_2$ by t.l.c.[a] and i.r.
$Cu(2\text{-}nqo)_2$.bza	$Cl_2FCCClF_2$	0.89 brown	Identified as $Cu(2\text{-}nqo)_2$.bza by t.l.c.[a] and i.r.
$Cu(2\text{-}nqo)_2$.py	$Cl_2FCCClF_2$	0.88 brown	Identified as $Cu(2\text{-}nqo)_2$.py by t.l.c.[a] and i.r.
$Cu(2\text{-}nqo)_2$.dipy	$Cl_2FCCClF_2$	0.95 brown	Identified as $Cu(2\text{-}nqo)_2$.dipy by t.l.c.[b] and i.r.
$Cu(2\text{-}nqo)_2$.phen	$Cl_2FCCClF_2$	0.95 brown	Identified as $Cu(2\text{-}nqo)_2$.phen by t.l.c.[b] and i.r.
$Cu(2\text{-}nqo)_2$	MeCN	0.67 black	Insoluble in MeCN and MeOH. Ill-defined i.r. Diamagnetic.

Table 6.2 (continued)

Complex	Solvent	Solid, weight (g) / colour	Nature of solid, characterisation
Cu(2-nqo)$_2$.bza	MeCN	0.55 black	Insoluble in MeCN and MeOH. Ill-defined i.r. Diamagnetic.
Cu(2-nqo)$_2$.py	MeCN	0.39 brown	T.l.c.[a] showed solid to consist of Cu(2-nqo)$_2$.py and an intractable black solid.
Cu(2-nqo)$_2$.quin	MeCN	0.44 brown	T.l.c.[a] showed solid to consist of Cu(2-nqo)$_2$.quin and an intractable brown solid.
Cu(2-nqo)$_2$.en	MeCN	0.54 black	Insoluble in MeCN and MeOH. Ill-defined i.r. Diamagnetic.
Cu(2-nqo)$_2$.dipy	MeCN	0.63 brown	Identified as Cu(2-nqo)$_2$.dipy by t.l.c.[b] and i.r.
Cu(2-nqo)$_2$.phen	MeCN	0.58 brown	Identified as Cu(2-nqo)$_2$.phen by t.l.c.[b] and i.r.

Table 6.2 (continued)

Complex	Solvent	Solid, weight (g) / colour	Nature of solid, characterisation
$Cu(2\text{-}nqo)_2$	Propan-2-ol	0.48 brown	T.l.c.[a] showed solid to consist of $Cu(2\text{-}nqo)_2$ and an intractable black solid.
$Cu(2\text{-}nqo)_2.bza$	Propan-2-ol	0.48 brown	T.l.c.[a] showed solid to consist of $Cu(2\text{-}nqo)_2.bza$ and an intractable black solid.
$Cu(2\text{-}nqo)_2.py$	Propan-2-ol	0.45 brown	T.l.c.[a] showed solid to consist of $Cu(2\text{-}nqo)_2.py$ and an intractable brown solid.
$Cu(2\text{-}nqo)_2.dipy$	Propan-2-ol	0.60 brown	Identified as $Cu(2\text{-}nqo)_2.dipy$ by t.l.c.[b] and i.r.
$Cu(2\text{-}nqo)_2.phen$	Propan-2-ol	0.74 brown	Identified as $Cu(2\text{-}nqo)_2.phen$ by t.l.c.[b] and i.r.
$Cu(2\text{-}nqo)_2$	Heptane	0.95 brown	Identified as $Cu(2\text{-}nqo)_2$ by t.l.c.[a] and i.r.

Table 6.2 (continued)

Complex	Solvent	Solid, weight (g) / colour	Nature of solid, characterisation
$Cu(2\text{-nqo})_2$	Pyridine	0.40 black	Insoluble in MeCN and MeOH. Ill-defined i.r.
$Cu(2\text{-nqo})_2$	Tetra-hydropyran	0.29 black	Insoluble in MeCN and MeOH. Ill-defined i.r.
$Cu(2\text{-nqo})_2.en$	Toluene	0.68 black	Insoluble in MeCN and MeOH. Ill-defined i.r.

Table 6.3

Complex	Solvent	Filtrate residue, weight (g) / colour	Nature of residue, characterisation
Cu(2-nqo)$_2$	Cl$_2$FCCClF$_2$	0.08 brown	Identified as Cu(2-nqo)$_2$ by t.l.c.[a] and i.r.
Cu(2-nqo)$_2$.bza	Cl$_2$FCCClF$_2$	0.08 brown	Identified as Cu(2-nqo)$_2$.bza by t.l.c.[a] and i.r.
Cu(2-nqo)$_2$.py	Cl$_2$FCCClF$_2$	0.07 brown	Identified as Cu(2-nqo)$_2$.py by t.l.c.[a] and i.r.
Cu(2-nqo)$_2$.dipy	Cl$_2$FCCClF$_2$	0.03 brown	Identified as Cu(2-nqo)$_2$.dipy by t.l.c.[b] and i.r.
Cu(2-nqo)$_2$.phen	Cl$_2$FCCClF$_2$	0.03 brown	Identified as Cu(2-nqo)$_2$.phen by t.l.c.[b] and i.r.
Cu(2-nqo)$_2$	MeCN	0.32 mauve	T.l.c.[a] showed 9 components, which include phenazine.[c]
Cu(2-nqo)$_2$.bza	MeCN	0.29 mauve	T.l.c.[a] showed 10 components, which include phenazine.[c]

Table 6.3 (continued)

Complex	Solvent	Filtrate residue, weight (g) / colour	Nature of residue, characterisation
$Cu(2\text{-}nqo)_2.py$	MeCN	0.33 brown	T.l.c.[a] showed 8 components, which include phenazine[c] and $Cu(2\text{-}nqo)_2.py$.
$Cu(2\text{-}nqo)_2.quin$	MeCN	0.50 brown	T.l.c.[a] showed 7 components, which include phenazine[c] and $Cu(2\text{-}nqo)_2.quin$.
$Cu(2\text{-}nqo)_2.en$	MeCN	0.32 mauve	T.l.c.[a] showed 7 components, which inlcude phenazine.[c]
$Cu(2\text{-}nqo)_2.dipy$	MeCN	0.29 brown	Identified as $Cu(2\text{-}nqo)_2.dipy$ by t.l.c.[b]
$Cu(2\text{-}nqo)_2.phen$	MeCN	0.36 brown	Identified as $Cu(2\text{-}nqo)_2.phen$ by t.l.c.[b]
$Cu(2\text{-}nqo)_2$	Propan-2-ol	0.43 brown	T.l.c.[a] showed 5 components, which include phenazine[c] and $Cu(2\text{-}nqo)_2$.

Table 6.3 (continued)

Complex	Solvent	Filtrate residue, weight (g) / colour	Nature of residue, characterisation
$Cu(2\text{-}nqo)_2.bza$	Propan-2-ol	0.30 brown	T.l.c.[a] showed 6 components, which include phenazine[c] and $Cu(2\text{-}nqo)_2.bza$
$Cu(2\text{-}nqo)_2.py$	Propan-2-ol	0.38 brown	T.l.c.[a] showed 4 components, which include phenazine[c] and $Cu(2\text{-}nqo)_2.py$.
$Cu(2\text{-}nqo)_2.dipy$	Propan-2-ol	0.30 brown	Identified as $Cu(2\text{-}nqo)_2.dipy$ by t.l.c.[b]
$Cu(2\text{-}nqo)_2.phen$	Propan-2-ol	0.19 brown	Identified as $Cu(2\text{-}nqo)_2.phen$ by t.l.c.[b]
$Cu(2\text{-}nqo)_2$	Heptane	0.03 brown	Identified as $Cu(2\text{-}nqo)_2$ by t.l.c.[a]

Table 6.3 (continued)

Complex	Solvent	Filtrate residue. weight (g) / colour	Nature of residue. characterisation
$Cu(2\text{-}nqo)_2$	Pyridine	Toluene - 0.52 red brown	T.l.c.[a] showed at least 9 components which include phenazine.[c]
		Acetone - 0.08 red brown	T.l.c.[a] showed at least 9 components which include phenazine.[c]
$Cu(2\text{-}nqo)_2$	Tetra-hydropyran	0.73 red brown	T.l.c.[a] showed at least 7 components which include phenazine.[c]
$Cu(2\text{-}nqo)_2.en$	Toluene	0.24 mauve	Identified as phenazine[c] by t.l.c. and i.r.

Notes

[a] silica t.l.c. plates

[b] cellulose t.l.c. plates

[c] dibenzo[b,i]phenazine-5,12-diol

Table 6.4

Data for the interaction of $Cu(2\text{-}nqo)_2$ and of its amine adducts with refluxing Lewis base solvents.

Complex	Solvent	Products
$Cu(2\text{-}nqo)_2$	$Cl_2FCCClF_2$	N.R. (98% recovery)
$Cu(2\text{-}nqo)_2$.bza	$Cl_2FCCClF_2$	N.R. (97% recovery)
$Cu(2\text{-}nqo)_2$.py	$Cl_2FCCClF_2$	N.R. (95% recovery)
$Cu(2\text{-}nqo)_2$.dipy	$Cl_2FCCClF_2$	N.R. (98% recovery)
$Cu(2\text{-}nqo)_2$.phen	$Cl_2FCCClF_2$	N.R. (98% recovery)
$Cu(2\text{-}nqo)_2$	MeCN	black solid[a] + organics[b]
$Cu(2\text{-}nqo)_2$.bza	MeCN	black solid[a] + organics[b]
$Cu(2\text{-}nqo)_2$.py	MeCN	O.S. + black intractable solid + organics[b]
$Cu(2\text{-}nqo)_2$.quin	MeCN	O.S. + brown intractable solid + organics[b]
$Cu(2\text{-}nqo)_2$.en	MeCN	black solid[a] + organics[b]
$Cu(2\text{-}nqo)_2$.dipy	MeCN	N.R. (92% recovery)
$Cu(2\text{-}nqo)_2$.phen	MeCN	N.R. (94% recovery)
$Cu(2\text{-}nqo)_2$	Propan-2-ol	O.S. + intractable black solid + organics[b]

Table 6.4 (continued)

Complex	Solvent	Products
$Cu(2\text{-nqo})_2.bza$	Propan-2-ol	O.S. + intractable black solid + organics[b]
$Cu(2\text{-nqo})_2.py$	Propan-2-ol	O.S. + intractable brown solid + organics[b]
$Cu(2\text{-nqo})_2.dipy$	Propan-2-ol	N.R. (90% recovery)
$Cu(2\text{-nqo})_2.phen$	Propan-2-ol	N.R. (93% recovery)
$Cu(2\text{-nqo})_2$	Heptane	N.R. (98% recovery)
$Cu(2\text{-nqo})_2$	Pyridine	black solid + organics[b]
$Cu(2\text{-nqo})_2$	Tetrahydropyran	black solid + organics[b]
$Cu(2\text{-nqo})_2.en$	Toluene	black solid + dibenzo[b,i]phenazine-5,12-diol (73% yield)

Notes

N.R. = no reaction

O.S. = original substance

[a] diamagnetic

[b] mainly dibenzo[b,i]phenazine-5,12-diol

The interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,4-diaminobutane) with triphenylphosphine in acetone.

Triphenylphosphine (7.5 mmol) was added to a solution of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,4-diaminobutane) (2.5 mmol) in acetone (50 cm^3) and stirred for 24 h. The mixture was then filtered. The residue obtained was washed with acetone (3 x 10 cm^3) and diethyl ether (3 x 10 cm^3) to give 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)copper(I) (identified by t.l.c. and i.r.) which was dried at 40 ^{o}C/ 20 mm Hg (see Table 6.5 for yields). The filtrate was evaporated to give in each case, a black tarry residue (see Table 6.5 for weights) which was analysed by t.l.c. (see Table 6.6).

Table 6.5

Data for the interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,4-diaminobutane) with triphenylphosphine in acetone.

Complex	$Cu(2\text{-}nqo)(Ph_3P)_2$ Yield (%)	Weight of filtrate residue (g)
$Cu(2\text{-}nqo)_2$	55	1.89
$Cu(2\text{-}nqo)_2$.dipy	65	1.76
$Cu(2\text{-}nqo)_2$.bn	54	2.12

Table 6.6

The characterisation by t.l.c. of the products of the interaction of bis(1,2-naphthoquinone 2-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,4-diaminobutane) with triphenylphosphine in acetone.

A. For bis(1,2-naphthoquinone 2-oximato)copper(II).

1. Using $CHCl_3$ (at least 8 components).

Material	R_f / colour
Ph_3P	0.83[a]
Ph_3PO	0.08[a]
$Cu(2\text{-nqo})(Ph_3P)_2$	0.30 / brown

2. Using toluene-ethanol-ethyl acetate, 9:2:1 (at least 8 components).

Material	R_f / colour
Ph_3P	0.90[a]
Ph_3PO	0.55[a]
$Cu(2\text{-nqo})(Ph_3P)_2$	0.79 / brown
1,2-naphthoquinone 2-oxime	0.60 / yellow

Table 6.6 (continued)

B. For bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)-copper(II).

1. Using $CHCl_3$ (at least 9 components).

Material	R_f	/ colour
Ph_3P	0.83^a	
Ph_3PO	0.08^a	
2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone mono-imine	0.27	/ purple
dibenzo[b,i]phenazine-5,12-diol	0.53	/ purple
$Cu(2\text{-}nqo)(Ph_3P)_2$	0.30	/ brown

2. Using toluene-ethanol-ethyl acetate, 9:2:1 (at least 9 components).

Material	R_f	/ colour
Ph_3P	0.90^a	
Ph_3PO	0.55^a	
2-amino-N(4)-(1-hydroxy-2-naphthyl)-naphthoquinone mono-imine	0.84	/ purple
dibenzo[b,i]phenazine-5,12-diol	0.78	/ purple
$Cu(2\text{-}nqo)(Ph_3P)_2$	0.79	/ brown
1,2-naphthoquinone 2-oxime	0.60	/ yellow

Table 6.6 (continued)

C. For bis(1,2-naphthoquinone 2-oximato)(1,4-diaminobutane)copper(II).

1. Using $CHCl_3$ (at least 10 components).

Material	R_f / colour
Ph_3P	0.83[a]
Ph_3PO	0.08[a]
2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone mono-imine	0.27 / purple
dibenzo[b,i]phenazine-5,12-diol	0.53 / purple
$Cu(2\text{-nqo})(Ph_3P)_2$	0.30 / brown

2. Using tolune-ethanol-ethyl acetate, 9:2:1 (at least 10 components).

Material	R_f / colour
Ph_3P	0.90[a]
Ph_3PO	0.55[a]
2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone mono-imine	0.84 / purple
dibenzo[b,i]phenazine-5,12-diol	0.78 / purple
$Cu(2\text{-nqo})(Ph_3P)_2$	0.79 / brown
1,2-naphthoquinone 2-oxime	0.60 / yellow

[a] spot made visible after exposure of t.l.c. plate to iodine vapour.

The reaction of bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,10-phenanthroline) on silica gel.

Bis(1,2-naphthoquinone 2-oximato)copper(II).X (X = 2,2'-dipyridyl or 1,10-phenanthroline) (1.00 g) was dissolved in methanol (100 cm^3) and silica gel (25 g) was stirred in. The mixture was stirred for 0.5 h and the solvent was removed under a stream of nitrogen. Toluene (250 cm^3) was added, the mixture was stirred for 1 h, and then filtered. This was repeated a further five times. The residue was stirred with methanol (250 cm^3) for 1 h and then filtered. This was repeated a further three times. Each extract was evaporated down to a minimum volume by distillation under reduced pressure. Residues were obtained by drying the concentrated samples under a stream of nitrogen. The residues were further dried at 40 ^oC/ 20 mm Hg.

For bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)-copper(II), the yellow toluene extracts were all identical (t.l.c.) and were identified as 1,2-naphthoquinone 2-oxime (0.22 g, 71%) by comparative t.l.c. and i.r. The brown methanol extracts were a mixture of more 1,2-naphthoquinone 2-oxime and bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)copper(II) (0.17 g) as indicated by t.l.c. A immobile red component remained on the silica.

For bis(1,2-naphthoquinone 2-oximato)(1,10-phenanthroline)copper(II), the yellow toluene extracts were all identical (t.l.c.) and were identified as 1,2-naphthoquinone 2-oxime (0.23 g, 79%) by comparative t.l.c. and i.r. The brown methanol extracts were a mixture of more 1,2-naphthoquinone 2-oxime and bis(1,2-naphthoquinone 2-oximato)(1,10-phenanthroline)copper(II) (0.21 g) as indicated by t.l.c. A immobile red component remained on the silica.

The reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)-(2,2'-dipyridyl)copper(II) on silica gel.

Bis(4-chloro-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)copper(II) (1.00 g) was dissolved in methanol (100 cm^3) and silica gel (25 g) was stirred in. The mixture was stirred for 0.5 h and the solvent was removed under a stream of nitrogen. The impregnated silica gel was placed on a 15.0 x 4.5 cm chromatography column (silica gel) and eluted as shown in Table 6.7. Each eluate was extracted with aqueous potassium hydroxide solution (37.5 mmol dm^{-3}, 100 cm^3). In each case, the solvent was removed to give residues A and B. A was recrystallised from toluene-methanol (5:1) to give potassium 4-chloro-1,2-benzoquinone 2-oximate hemihydrate (see Table 6.7 for data). B was dissolved in water (100 cm^3) and then filtered. The residue obtained was washed with water to give bis(4-chloro-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)copper(II) (see Table 6.7 for data). The solvent was removed from the combined water washings. The residue obtained was recrystallised from toluene-methanol (5:1) to give more potassium 4-chloro-1,2-benzoquinone 2-oximate hemihydrate (see Table 6.7 for data).

Table 6.7

Data for the reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)(2,2'-dipyridyl)copper(II) on silica gel.

Eluting solvent		Weight (g) / colour	Nature of material	Method of identification
A Light petroleum (b.p. 80-100 °C)-toluene (1:1)		0.15 / brown	$K(4\text{-}Clqo).1/2H_2O$	Identical t.l.c. and i.r. to an authentic sample.[3]
B Toluene-methanol (1:1)	1.	0.08 / mauve	$Cu(4\text{-}Clqo)_2.dipy$	t.l.c., i.r.
	2.	0.14 / brown	$K(4\text{-}Clqo).1/2H_2O$	Identical t.l.c. and i.r. to an authentic sample.[3]

Complex	Yield (%)
$K(4\text{-}Clqo).1/2H_2O$	74
$Cu(4\text{-}Clqo)_2.dipy$	8

The ion exchange of metal complexes derived from 1,2-quinone mono-oximes, using 'Dowex' 50W-X8(H) ion exchange resin.

Bis(1,2-naphthoquinone 1-oximato)copper(II), bis(1,2-naphthoquinone 2-oximato)copper(II), bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)copper(II), bis(1,2-naphthoquinone 2-oximato)nickel(II) or potassium 1,2-naphthoquinone 2-oximate (0.50 g) was dissolved in methanol (250 cm^3). The mixture was added to a 20.0 x 4.5 cm ion exchange column ('Dowex' 50W-X8(H) ion exchange resin) and eluted with methanol-water (4:1). The solvent was then removed under reduced pressure to give 1,2-naphthoquinone mono-oxime (see Table 6.8 for yields).

The ion exchange of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), using 'Dowex' 50W-X8(H) ion exchange resin.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.50 g) was dissolved in methanol (250 cm^3). The mixture was added to a 20.0 x 4.5 cm ion exchange column ('Dowex' 50W-X8(H) ion exchange resin) and eluted with methanol-water (4:1) to give a yellow eluate. T.l.c. analysis of the eluate showed it to be multi-component. Potassium hydroxide (0.20 g, 3.6 mmol) was added to the eluate and the mixture stirred for 0.5 h. The solvent was then removed under reduced pressure to give a brown residue which was recrystallised from toluene-methanol (5:1) to give a yellow brown solid (0.32 g). T.l.c. analysis of the solid showed it to consist of at least 4 components, and indicated the absence of potassium 4-chloro-1,2-benzoquinone 2-oximate hemihydrate.

Table 6.8

Data for the ion exchange of metal complexes derived from 1,2-quinone mono-oximes, using 'Dowex' 50W-X8(H) ion exchange resin.

Complex	nqoH	Yield (%)	Method of identification
$Cu(1\text{-}nqo)_2$	1-nqoH	97	t.l.c., i.r.
$Cu(2\text{-}nqo)_2$	2-nqoH	95	t.l.c., i.r.
$Cu(2\text{-}nqo)_2$.dipy	2-nqoH	84	t.l.c., i.r.
$Ni(2\text{-}nqo)_2$	2-nqoH	65	t.l.c., i.r.
K(2-nqo)	2-nqoH	85	t.l.c., i.r.

The reaction of transition metal complexes derived from 1,2-quinone mono-oximes with potassium cyanide.

A suspension of bis(1,2-naphthoquinone 1-oximato)copper(II), bis(1,2-naphthoquinone 2-oximato)copper(II), bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)copper(II), 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)copper(I) or bis(1,2-naphthoquinone 2-oximato)nickel(II) (1.0 mmol) in methanol (30 cm^3) was refluxed for 1 h with potassium cyanide (10.0 mmol). The reaction mixture was filtered and toluene (100 cm^3) added. The mixture gave, on standing, potassium 1,2-naphthoquinone mono-oximate which was filtered off, washed with toluene (3 x 10 cm^3) and dried at 40 ^oC/ 20 mm Hg (see Table 6.9 for yields and other data).

In the case of bis(1,2-naphthoquinone 2-oximato)(2,2'-dipyridyl)copper(II), the combined toluene washings were treated with charcoal and heated under reflux for 0.5 h and then filtered. The solvent was removed to give 2,2'-dipyridyl (44%) (identified by t.l.c. and i.r.).

In the case of 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)copper(I), the combined toluene washings were treated with charcoal and heated under reflux for 0.5 h and then filtered. The solvent was removed to give triphenylphosphine (63%) (identified by t.l.c. and i.r.).

The reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)-copper(II) with potassium cyanide.

A suspension of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.38 g, 1.0 mmol) in methanol (30 cm^3) was refluxed for 1 h with potassium cyanide (0.65 g, 10.0 mmol). The reaction mixture was filtered and toluene (100 cm^3) added. The mixture gave, on standing, 4-chloro-1,2-benzoquinone 2-oximate hemihydrate (0.24 g, 59%) (identified by t.l.c. and i.r.) which was filtered off, washed with toluene (3 x 10 cm^3) and dried at 40 °C/ 20 mm Hg.

The reaction of bis(1,2-naphthoquinone mono-oximato)copper(II) complexes with sodium cyanide.

A suspension of bis(1,2-naphthoquinone 1-oximato)copper(II) or bis(1,2-naphthoquinone 2-oximato)copper(II) (1.0 mmol) in methanol (30 cm^3) was refluxed for 1 h with sodium cyanide (10.0 mmol). The reaction mixture was filtered and toluene (100 cm^3) added. The mixture gave, on standing, sodium 1,2-naphthoquinone mono-oximate which was filtered off, washed with toluene (3 x 10 cm^3) and dried at 40 °C/ 20 mm Hg (see Table 6.10 for yields and other data).

The reaction of bis(1,2-naphthoquinone 2-oximato)copper(II) with potassium hydroxide or acetate.

A suspension of bis(1,2-naphthoquinone 2-oximato)-copper(II) (1.0 mmol) in methanol (30 cm^3) was refluxed for 1 h with potassium hydroxide (0.56 g, 10.0 mmol) or potassium acetate (0.98 g, 10.0 mmol). T.l.c. analysis of the mixtures showed in both cases no reaction.

Table 6.9

Data for the reaction of transition metal complexes derived from 1,2-quinone mono-oximes with potassium cyanide.

Complex	K(qo)	Yield (%)	Method of identification
$Cu(1\text{-}nqo)_2$	K(1-nqo)	71	t.l.c., i.r.
$Cu(2\text{-}nqo)_2$	K(2-nqo)	76	t.l.c., i.r.
$Cu(2\text{-}nqo)_2.dipy$	K(2-nqo)	81	t.l.c., i.r.
$Cu(2\text{-}nqo)(Ph_3P)_2$	K(2-nqo)	57	t.l.c., i.r.
$Ni(2\text{-}nqo)_2$	K(2-nqo)	74	t.l.c., i.r.

Table 6.10

Data for the reaction of bis(1,2-naphthoquinone mono-oximato)copper(II) complexes with sodium cyanide.

Complex	Na(nqo)	Yield (%)	Method of identification
$Cu(1\text{-}nqo)_2$	Na(1-nqo)	50	t.l.c., i.r.
$Cu(2\text{-}nqo)_2$	Na(2-nqo)	52	t.l.c., i.r.

The catalytic oxidation of amines by 1,2-quinone mono-oximato metal complexes and various other metal complexes.

The metal complex (0.10 g) was suspended in the amine (5.0 cm^3) and stirred (see Table 6.11). The reaction was monitored by g.l.c., t.l.c., and i.r spectroscopy. The oxidation product of the amine was identified by various techniques which included g.l.c., i.r. spectroscopy, mass spectrometry, and n.m.r. spectroscopy (see Table 6.12). The yield of the product was determined by g.l.c. (see Table 6.11).

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) in acetonitrile, chlorobenzene, propan-2-ol, pyridine or toluene under oxygen or in air.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) and benzylamine (5.0 cm^3) in acetonitrile (100 cm^3), chlorobenzene (100 cm^3), propan-2-ol (100 cm^3), pyridine (100 cm^3) or toluene (100 cm^3) were stirred at room temperature for 168 h under oxygen or in air. Acetonitrile, toluene or propan-2-ol was removed by distillation under reduced pressure. In the cases of chlorobenzene and pyridine, the solvent was removed at 50 ^{o}C/ 0.3 mm Hg. The residue remaining was analysed by g.l.c. (see Table 6.13 for yields).

Benzylamine (5.0 cm^3) in acetonitrile (100 cm^3), chlorobenzene (100 cm^3), propan-2-ol (100 cm^3), pyridine (100 cm^3) or toluene (100 cm^3) was stirred at room temperature for 168 h. Acetonitrile, propan-2-ol or toluene was removed by distillation under reduced pressure. In the cases of chlorobenzene and pyridine, the solvent was removed at 50 °C/ 0.3 mm Hg. The residue remaining was analysed by g.l.c. In all cases, benzylamine was recovered.

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) under oxygen.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) was suspended in benzylamine (5.0 cm^3) and stirred under oxygen for 168 h. The reaction mixture was analysed by g.l.c. (see Table 6.13 for yield).

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Isolation of N-benzylidenebenzylamine.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.80 g) was suspended in benzylamine (10.0 cm^3) and stirred at room temperature. After 168 h, the mixture was added to light petroleum (b.p. 30-40 °C, 1000 cm^3) with rapid stirring. The mixture was treated with charcoal and filtered. The solvent was removed from the filtrate by distillation under reduced pressure to give N-benzylidenebenzylamine (7.6 g, 85%) (identified by g.l.c., i.r., m.s. and n.m.r.).

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount

of complex used.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g, 0.20 g, 0.40 g or 0.80 g) was suspended in benzylamine (5.0 cm^3) and stirred for 168 h at room temperature. The reaction mixture was analysed by g.l.c. (see Table 6.14 for yields).

The catalytic oxidation of benzylamine by bis(1,2-quinone mono-oximato)copper(II) complexes at 70 °C.

Bis(1,2-quinone mono-oximato)copper(II) (0.10 g) was suspended in benzylamine (5.0 cm^3) and stirred for 96 h at 70 °C. The reaction mixture was analysed by g.l.c. (see Table 6.15 for yields).

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) in the presence of charcoal or silica.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) and charcoal (1.00 g) or silica (1.00 g) were suspended in benzylamine (5.00 cm^3) and stirred for 168 h at room temperature. The reaction mixture was filtered and the filtrate was analysed by g.l.c. (see Table 6.16 for yields).

Charcoal (1.00 g) or silica (1.00 g) was suspended in benzylamine (5.00 cm^3) and stirred for 168 h at room temperature. The reaction mixture was filtered and the filtrate was analysed by g.l.c. (see Table 6.16 for yields).

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Identification of gases evolved during reaction.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (1.60 g) was suspended in benzylamine (10.0 cm^3) and stirred. A current of oxygen was passed through the reaction mixture and into concentrated hydrochloric acid (10 cm^3) in methanol (10 cm^3) via a vertical condenser. After 168 h, the solvent was removed by distillation under reduced pressure to give ammonium chloride (1.40 g, 57%) (identified by i.r.).

The interaction of benzylamine with bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) under nitrogen.

Deoxygenated benzylamine (5.00 cm^3) was added to bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) and stirred under nitrogen for 168 h. G.l.c. analysis of the reaction mixture indicated the presence of N-benzylidenebenzylamine (0.20 cm^3, 5%).

The catalytic oxidation of 2-methoxybenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Isolation of N-2-methoxybenzylidene-2-methoxybenzylamine.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) was suspended in 2-methoxybenzylamine (5.0 cm^3) and stirred at 70 °C. After 72 h, the mixture was added to diethyl ether (500 cm^3) with rapid stirring. The mixture was treated with charcoal and filtered. The solvent was removed from the filtrate by distillation under reduced pressure to give N-2-methoxybenzylidene-2-methoxybenzylamine (2.54 g, 52%) (identified by g.l.c., i.r. and m.s.).

The catalytic oxidation of 4-methoxybenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Isolation of N-4-methoxybenzylidene-4-methoxybenzylamine.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) was suspended in 4-methoxybenzylamine (5.0 cm^3) and stirred at 70 °C. After 48 h, the mixture was added to diethyl ether (500 cm^3) with rapid stirring. The mixture was treated with charcoal and filtered. The solvent was removed from the filtrate by distillation under reduced pressure to give N-4-methoxybenzylidene-4-methoxybenzylamine (3.00 g, 62%) (identified by g.l.c., i.r. and m.s.).

The catalytic oxidation of dibenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount of complex used.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g, 0.20 g, 0.40 g or 0.80 g) was suspended in dibenzylamine (5.0 cm^3) and stirred for 168 h at room temperature. The reaction mixture was analysed by g.l.c. (see Table 6.17 for yields).

The catalytic oxidation of dibenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) at 70 °C.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II)

(0.10 g) was suspended in dibenzylamine (5.0 cm^3) and stirred for 168 h at 70 °C. G.l.c. analysis of the reaction mixture gave N-benzylidenebenzylamine (1.77 cm^3, 36%).

The catalytic oxidation of 1,4-diaminobutane by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount of complex used.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g, 0.20 g, 0.40 g or 0.80 g) was suspended in 1,4-diaminobutane (5.0 cm^3) and stirred for 168 h at room temperature. The reaction mixture was analysed by g.l.c. (see Table 6.18 for yields).

The catalytic oxidation of 1,4-diaminobutane by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) at room temperature or at 70 °C.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) was suspended in 1,4-diaminobutane (5.0 cm^3) and stirred at room temperature or at 70 °C for 24 h. The reaction mixture was analysed by g.l.c. (see Table 6.19 for yields).

The catalytic oxidation of 1,4-diaminobutane by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Identification of gases evolved during reaction.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.40 g) was suspended in 1,4-diaminobutane (5.0 cm^3) and stirred at 70 °C. A current of oxygen was passed through the reaction mixture and into concentrated hydrochloric acid (10 cm^3) in methanol (10 cm^3) via a vertical condenser. After 168 h, the solvent was removed by distillation under reduced pressure to give ammonium chloride (0.39 g, 14%) (identified by i.r.).

The catalytic oxidation of 5-amino-1-pentanol by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) at 70 °C.

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.10 g) was suspended in 5-amino-1-pentanol (5.0 cm^3) and stirred at 70 °C for 168 h. G.l.c. analysis of the reaction mixture showed a small amount of tetrahydropyran.

5-Amino-1-pentanol (5.0 cm^3) was heated at 70 °C for 168 h. G.l.c. analysis showed tetrahydropyran not to be present.

Table 6.11

The catalytic oxidation of amines by 1,2-quinone mono-oximato metal complexes and various other metal complexes.

6.11.1 The oxidation of benzylamine.

Copper complex	Yield of N-benzylidenebenzylamine (cm^3)		(%)	
	168 h	672 h	168 h	672 h
$\mathrm{Cu(1\text{-}nqo)_2}$	0.16	0.22	4	5
$\mathrm{Cu(2\text{-}nqo)_2}$	0.17	0.27	4	6
$\mathrm{Cu(4\text{-}Meqo)_2}$	0.40	0.88	10	20
$\mathrm{Cu(5\text{-}MeOqo)_2}$	0.08	0.27	2	6
$\mathrm{Cu(4\text{-}Clqo)_2}$	1.80	4.10	42	95
$\mathrm{Cu(4\text{-}Brqo)_2}$	1.73	4.00	40	92
$\mathrm{Cu(dnr).H_2O}$	0.46		11	
$\mathrm{Cu(6\text{-}Cldnr).H_2O}$	0.68		16	
$\mathrm{Cu(4,6\text{-}Cl_2qo)_2}$	1.30		30	
$\mathrm{Cu(4\text{-}Clqo)(Ph_3P)_2}$	2.14		49	
Copper(II) acetate	0.00		0	
$\mathrm{Cu(acac)_2}$	0.00		0	
Copper(II) sulphate pentahydrate	0.00		0	
Copper(II) oxalate	0.00		0	

Table 6.11 (continued)

6.11.1 The oxidation of benzylamine (continued).

Copper complex	Yield of N-benzylidenebenzylamine (cm^3)	(%)
	168 h	
Copper(II) chloride	0.05	1
Copper(I) chloride	0.19	4
Copper(I) bromide	0.23	5
Blank	0.00	0

Table 6.11 (continued)

6.11.1 The oxidation of benzylamine (continued).

Metal complex	Yield of N-benzylidenebenzylamine (cm^3) 168 h	(%)
$VO(1\text{-nqo})_2$	0.36	8
$VO_2(1\text{-nqo})$	0.27	6
$Mn(1\text{-nqo})_2$	0.53	12
$Mn(2\text{-nqo})_2$	0.75	17
$Mn(1\text{-nqo})_3$	0.86	20
$Mn(2\text{-nqo})_3$	1.10	25
$Fe(1\text{-nqo})_2$	0.00	0
$Fe(2\text{-nqo})_2$	0.00	0
$Fe(1\text{-nqo})_3$	0.19	4
$Fe(2\text{-nqo})_3$	0.22	5
$Co(1\text{-nqo})_3$	0.16	4
$Co(2\text{-nqo})_3$	0.87	20
$Ni(1\text{-nqo})_2$	0.12	3
$Ni(2\text{-nqo})_2$	0.13	3
$Ni(4\text{-Meqo})_2$	0.50	12
$Ni(4\text{-Clqo})_2$	0.52	12
$Ni(4\text{-Brqo})_2$	0.48	11
$Ni(4\text{-ClqoPh}_3P)_2$	0.00	0
$Ru(1\text{-nqo})_2$	0.00	0
$Ru(2\text{-nqo})_2$	0.00	0
$Ru(2\text{-nqo})_2(Ph_3P)_2$	0.15	4
$[UO_2(1\text{-nqo})_2(H_2O)_2]$	0.42	10
$[UO_2(2\text{-nqo})_2(H_2O)_2]$	0.50	12

Table 6.11 (continued)

6.11.2 The oxidation of dibenzylamine.

Complex	Yield of N-benzylidenebenzylamine (cm^3) 168 h	(%)
$Cu(2\text{-}nqo)_2$	0.14	3
$Cu(4\text{-}Clqo)_2$	0.24	5

6.11.3 The attempted oxidation of propylamine.

No oxidation product after reacting for 168 h with $Cu(2\text{-}nqo)_2$ or $Cu(4\text{-}Clqo)_2$.

6.11.4 The attempted oxidation of butylamine.

No oxidation product after reacting for 168 h with $Cu(2\text{-}nqo)_2$ or $Cu(4\text{-}Clqo)_2$.

6.11.5 The oxidation of 1,4-diaminobutane.

Complex	Yield of pyrrolidine (cm^3) 168 h	(%)
$Cu(2\text{-}nqo)_2$	0.23	5
$Cu(4\text{-}Clqo)_2$	0.43	10

Table 6.11 (continued)

6.11.6 The oxidation of 1,5-diaminopentane.

Complex	Yield of piperidine	
	(cm^3)	(%)
	168 h	
$Cu(2\text{-}nqo)_2$	0.26	6
$Cu(4\text{-}Clqo)_2$	0.48	11

6.11.7 The oxidation of 4-amino-1-butanol.

A small amount of oxidation of 4-amino-1-butanol by $Cu(4\text{-}Clqo)_2$ after 168 h, to tetrahydrofuran.

Table 6.12

The products obtained from the catalytic oxidation of amines by 1,2-quinone mono-oximato metal complexes.

Amine	Oxidation product	Identification	Analysis
benzylamine	N-benzylidene-benzylamine	g.l.c., i.r., m.s. & n.m.r.	g.l.c.
dibenzylamine	N-benzylidene-benzylamine	g.l.c & i.r.	g.l.c.
1,4-diamino-butane	pyrrolidine	g.l.c.	g.l.c.
1,5-diamino-pentane	piperidine	g.l.c.	g.l.c.
4-amino-1-butanol	tetrahydrofuran	g.l.c.	

Table 6.13

The catalytic oxidation of benzylamine to N-benzylidenebenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) in acetonitrile, chlorobenzene, propan-2-ol, pyridine or toluene under oxygen or in air.

Solvent	Under oxygen Yield (cm^3)	(%)	In air Yield (cm^3)	(%)
toluene	1.53	35	1.46	34
propan-2-ol	1.67	39	1.61	37
acetonitrile	1.68	39	1.63	38
chlorobenzene	1.83	43	1.78	41
pyridine	2.90	67	2.66	61
no solvent	1.92	44	1.80	42

Table 6.14

The catalytic oxidation of benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount of complex used.

Amount of $Cu(4\text{-}Clqo)_2$ used (g)	Yield of N-benzylidenebenzylamine (cm^3)	(%)
0.10	1.80	42
0.20	2.06	48
0.40	4.30	99
0.80	4.33	100

Table 6.15

The catalytic oxidation of benzylamine to N-benzylidene-benzyalmine by bis(1,2-quinone mono-oximato)copper(II) complexes at 70 °C.

Complex	Yield of N-benzylidenebenzylamine (%)			
	24 h	48 h	72 h	96 h
$Cu(2\text{-}nqo)_2$	11	19	40	56
$Cu(4\text{-}Clqo)_2$	24	42	65	98

Table 6.16

The catalytic oxidation of benzylamine to N-benzylidene-benzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) in the presence of charcoal or silica.

	Charcoal		Silica	
	Yield		Yield	
	(cm^3)	(%)	(cm^3)	(%)
$Cu(4\text{-}Clqo)_2$	2.19	51	1.94	45
blank	0.22	5	0.00	0

Table 6.17

The catalytic oxidation of dibenzylamine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount of complex used.

Amount of $Cu(4\text{-}Clqo)_2$ used (g)	Yield of N-benzylidenebenzylamine (cm^3)	(%)
0.10	0.24	5
0.20	0.34	7
0.40	0.53	11
0.80	0.78	16

Table 6.18

The catalytic oxidation of 1,4-diaminobutane by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II). Variation of the amount of complex used.

Amount of $Cu(4\text{-}Clqo)_2$ used (g)	Yield of pyrrolidine (cm^3)	(%)
0.10	0.42	10
0.20	0.56	13
0.40	1.01	24
0.80	1.65	39

Table 6.19

The catalytic oxidation of 1,4-diaminobutane to pyrrolidine by bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) at room temperature or at 70 °C.

Complex	Room temperature Yield (cm^3)	 (%)	At 70 °C Yield (cm^3)	 (%)
$Cu(4\text{-}Clqo)_2$	0.06	1	1.01	24

6.8 References.

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Polyhedron Vol. 6, No. 5, pp. 1033–1035, 1987
Printed in Great Britain

0277-5387/87 $3.00 + .00

COMPLEXES OF COPPER(II) WITH MONONITROSO- AND DINITROSORESORCINOLS

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(*Received* 20 *June* 1986 ; *accepted* 16 *September* 1986)

Abstract Polymeric complexes of the type Cu(X-dnr)·H_2O (X-dnrH_2 = 2,4 - dinitrosoresorcinol and 4 - ethyl -, 4 - chloro- or 5 - methyldinitrosoresorcinol) have been prepared by nitrosation of resorcinol, 4-ethylresorcinol, 4-chlororesorcinol and 5-methylresorcinol with sodium nitrite acetic acid in the presence of copper(II) chloride. Nitrosation of 2 - methylresorcinol gives Cu(2 - Memnr)$_2$·4H_2O (2 - MemnrH = 2 - methyl - 4 - nitrosorcinol). Reaction of the complexes Cu(X-dnr)·H_2O (X = H, 6-Et or 6-Cl) with hot pyridine gives the respective Cu(X-dnr)·py complexes. Magnetic-susceptibility studies indicate antiferromagnetic interaction through the X-dnr^{2-} ligand in the complexes Cu(X-dnr)·L (L = H_2O or py) and association of Cu(2-Memnr)$_2$ units in the complex Cu(2-Memnr)$_2$·4H_2O.

Metal complexes of 1,2 - quinonemono - oximes (2 - nitrosophenols) have synthetic, analytical and other uses.[1–3] We have previously reported that polymeric complexes of the type Ni(X-dnr)·2H_2O where X-dnrH_2 (1) is 2,4 - dinitrosoresorcinol, 6 - ethyl - 2,4 - dinitrosoresorcinol or 5 - methyl - 2,4 - dinitrosoresorcinol are obtained by nitrosation of resorcinol, 4 - ethylresorcinol and 5 - methylresorcinol, respectively, in the presence of nickel chloride.[4] In contrast nitrosation of 2 - methylresorcinol in the presence of nickel chloride gives a bischelated complex derived from the mononitrosated resorcinol **2**.[4] In this paper we describe the preparation, characterization and magnetic properties of analogous copper(II) complexes.

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2

EXPERIMENTAL

Elemental analyses were carried out by the microanalytical laboratory of the Polytechnic of North London. Copper was determined by atomic absorption with a Pye Unicam SP9 spectrophotometer, after decomposing the complexes with concentrated sulphuric acid and hydrogen peroxide. IR spectra, magnetic susceptibilities and thermal gravimetric data were obtained as described earlier.[5] Magnetic moments were corrected for the diamagnetic effect of the ligands.[6]

Preparation of the complexes Cu(X-dnr)·H_2O (X = H, 6-Et, 6-Cl *or* 5-Me) *and* Cu(2-Memnr)$_2$·4H_2O *by nitrosation of resorcinols*

The resorcinol (0.05 mol) in ethanol (100 cm^3) was added to a solution of copper(II) chloride dihydrate (8.5 g, 0.05 mol), acetic acid (20 cm^3) and sodium acetate (20 g) in water (120 cm^3). Sodium

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Table 1 Analytical and room-temperature magnetic data for Cu(II) complexes of nitrosoresorcinols

Phenol	Product formula	No	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Found (%) Cu	Required (%) C	Required (%) H	Required (%) N	Required (%) Cu	μ_{eff} (BM) (*ca* 295 K)
Resorcinol	Cu(dnr) · H_2O	**1**	87	29.1	1.8	10.2	25.9	29.1	1.6	11.3	25.7	1.00
4-Ethylresorcinol	Cu(6-Etdnr) · H_2O	**2**	61	34.1	2.8	9.8	22.8	34.8	2.3	10.1	23.0	1.40
4-Chlororesorcinol	Cu(6-Cldnr) · H_2O	**3**	79	25.2	1.5	8.8	22.8	25.5	1.1	9.9	22.5	1.25
5-Methylresorcinol	Cu(5-Mednr) · H_2O	**4**	62	31.4	2.1	10.7	23.9	32.1	2.3	10.7	24.3	1.33
2-Methylresorcinol	Cu(2-Memnr)$_2$ · $4H_2O$	**5**	50	37.5	4.0	6.4	14.6	38.2	4.6	6.3	14.7	1.48
	Cu(dnr) · py	**6**	62	42.9	2.7	13.2	21.2	42.8	2.3	13.6	20.6	1.34
	Cu(6-Etdnr) · py	**7**	65	45.1	3.0	10.6	18.7	46.3	3.3	12.5	18.9	1.55
	Cu(6-Cldnr) · py	**8**	56	38.4	1.9	12.4	18.8	38.5	1.8	12.3	18.5	1.37

nitrite (10 g) in water (60 cm^3) was added with stirring. The resulting mixture was stirred at 20 C for 1 week and then the *product* was filtered off, washed thoroughly by stirring with water (3 × 100 cm^3) and ethanol (3 × 100 cm^3) for several hours and dried at 50 C 0.1 mm (see Table 1 for analysis and other data).

Interaction of the complexes Cu(X - dnr) · H_2O (X = H, 6-Et *or* 6-Cl) *with pyridine*

The hydrated complex (*ca* 3 g) was heated under reflux in pyridine (100 cm^3) for 1 h. The reaction mixture was filtered hot, the filtrate was evaporated to dryness at 60 C 0.1 mm and the resultant residue of the *pyridine adduct* was washed with ethanol and ether, and dried at 50 C 0.1 mm.

RESULTS AND DISCUSSION

Bottei and McEachern[7] have reported that the interaction of copper sulphate pentahydrate with 2,4 - dinitrosoresorcinol in aqueous ethanol gave a polymeric product which they formulated as Cu(dnr). In contrast, Hunter and Webb[8] formulated the product of a similar reaction in methanol as $[Cu(dnrH)_2(H_2O)_2] \cdot 2H_2O$. We have obtained a polymeric complex of formula Cu(dnr) · H_2O by nitrosation of resorcinol in the presence of copper chloride. The analogous complexes Cu(5 - Mednr) · H_2O, Cu(6 - Etdnr) · H_2O and Cu(6 - Cldnr) · H_2O have been obtained similarly by nitrosation of 5 - methylresorcinol, 4 - ethylresorcinol and 4 - chlororesorcinol, respectively. Nitrosation of 2-methylresorcinol in the presence of copper(II) chloride, leads to mononitrosation and formation of the complex Cu(2 - Memnr)$_2$ · $4H_2O$. The formulation of the complexes was established by elemental analysis and IR spectroscopy. The position of nitrosation has been established as described previously[4]

The complexes Cu(X - dnr) · H_2O (X = H, 6-Et, 6-Cl or 5-Me) were insoluble in ethanol, acetone, chloroform and diethyl ether, but dissolved in refluxing pyridine to give 1 : 1 adducts as shown by the isolation and characterization of the pyridine

Table 2 Thermal gravimetric analysis

Compound[a]	Weight of sample (mg)	T[b] (C)	Weight loss (mg) Found	Weight loss (mg) Calc[d]	Decomposition temperature (C) of M(X-dnr)[c]
1	107	100	8	8	170
2	103	142	8	7	175
3	103	115	7	7	185
4	114	132	9	8	162

[a] Nos from Table 1

[b] Temperature of loss of water

[c] Maxima on the rate of weight loss against temperature curve

[d] Calculated for 1 mol equiv. of water.

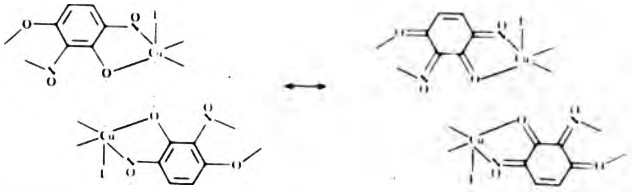

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Table 3. Variable-temperature magnetic data for Cu(6-Cldnr)·py

T (K)	293	273	253	233	213
$10^6 \times \chi$	810	845	906	960	1016
μ_{eff}	1.38	1.36	1.36	1.34	1.32
$-\theta$ (K)	75				

adducts when X = H, 6-Et or 6-Cl. Thermal gravimetric analysis (Table 2) on all the hydrates showed that water was lost quantitatively between 100 and 150 C to give Cu(X-dnr) which decomposed between 160 and 190 C.

Magnetic susceptibilities for the complexes Cu(X-dnr)·H_2O (X = H, 6-Et, 6-Cl or 5-Me) and Cu(X-dnr)py (X = H, 6-Et or 6-Cl) were measured at room temperature and the calculated magnetic moments are given in Table 1. The magnetic moments at room temperature for both the hydrates and the pyridine adducts of Cu(X-dnr) studied fall in a range (1.0–1.6 BM) which is well below the limits expected for magnetically dilute copper(II) complexes. Generally, copper complexes have moments in the range 1.8–2.1 BM, independent of the co-ordination number.[6] A deviation from simple paramagnetic behaviour therefore is indicated for these copper complexes. A variable-temperature study of magnetic moments was carried out on Cu(6-Cldnr)·py. The decreasing magnetic moment with temperature (Table 3) and the negative Weiss constant observed for the complex suggests antiferromagnetic behaviour. This may arise either through the bridging X-dnr^{2-} ligand or through association involving copper atoms in different chains of the polymer (3). The latter possibility is less likely because: (i) antiferromagnetic behaviour is also shown by the corresponding six-coordinate nickel(II) complexes Ni(X-dnr)·$2H_2O$ which have X-dnr bridges, and (ii) the pyridine adducts of analogous copper(II) complexes of 2-nitrosophenols are known to exhibit five-co-ordination.[7,8]

The relatively low magnetic moment of Cu(2-Memnr)$_2$·$4H_2O$ would suggest some association between Cu(2-Memnr)$_2$ units as found in related nickel complexes.[10]

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Paper presented at the XXIV International Conference on Coordination Chemistry, 1986, Book of Abstracts, p. 512.

INTERNAL REDOX REACTIONS OF METAL COMPLEXES

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Reactions of metal complexes of 1,2-quinone mono-oximes (qoH) with Lewis bases can lead to (i) adduct formation, (ii) another complex arising from the reaction of the coordinated quinone mono-oxime ligand with the Lewis base, or (iii) internal redox behaviour of the metal quinone oximic complex. The latter type of reaction is of considerable value in synthesis, catalysis and in biologically important processes.

We have examined the reaction of several metal quinone oximic and related complexes with various Lewis bases (e.g. pyridine, 2,2'-dipyridyl, triphenylphosphine, acetonitrile, propan-2-ol), and report on the factors which favour the occurrence of internal redox reactions.

Mechanistic appraisals of the internal redox reactions shown by the systems involving complexes of the type $M(qo)_3$ (M = Fe, Co or Cr) based on product and intermediate characterisation, and kinetic studies are presented. These reactions can proceed by reduction of the metal accompanied by either loss of a ligand radical or retention of the radical as a coordinated species to the metal. In either case the radical formed reacts further to give products which are otherwise difficult to obtain.

TITLE STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES AND OF THEIR OXIDATION OF AMINES

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INSTITUTION and DATE NORTH LONDON POLYTECHNIC 1988

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