TITLE STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES. AND THEIR REDOX REACTIONS.

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STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES AND THEIR REDOX REACTIONS

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
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Dedicated to my parents

and all my tutors.

Declaration

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

D. Baluch

Dosten Baluch

STUDIES OF 1,2-QUINONE MONO-OXIMATO COMPLEXES AND THEIR REDOX REACTIONS.

Abstract

The synthesis of the complexes $Cr(1\text{-nqo})_3$, $Cr(2\text{-nqo})_3$, $Cr(3\text{-Me-5-OHqo})_3$, $Cr(6\text{-Me-5-OHqo})_3$, $Mn(1\text{-nqo})_3$, $Mn(2\text{-nqo})_3$, $Mn(1\text{-nqo})_2$, and $Mn(2\text{-nqo})_2$ has been systematically examined (1-nqoH = 1,2-naphthoquinone 1-oxime, 2-nqoH = 1,2-naphthoquinone 2-oxime, 3-Me-5-OHqoH = 3-methyl-5-hydroxy-1,2-benzoquinone 2-oxime, 6-Me-5-OHqoH = 6-methyl-5-hydroxy-1,2-benzoquinone 2-oxime). Reactions of $Cr(1\text{-nqo})_3$ and $Cr(2\text{-nqo})_3$ with $Cr(CO)_6$ led to $[Cr(1\text{-nqo})_2]_2O$ and $[Cr(2\text{-nqo})_2]_2O$. The chromium(III) and manganese(III) trischelates are monomeric and have normal magnetic moments. In contrast, the aforementioned u-oxo complexes, $Mn(1\text{-nqo})_2$, and $Mn(2\text{-nqo})_2$ have sub-normal magnetic moments. Variable temperature magnetic studies on the manganese(II) complexes have indicated antiferromagnetic interactions which have been rationalised in terms of polymeric structures.

A comparative study on the behaviour of the complexes $M(1\text{-nqo})_3$, $M(2\text{-nqo})_3$ (M = Cr, Mn, Fe), and $M(1\text{-nqo})_2$, $M(2\text{-nqo})_2$ (M = Mn, Cu or Ni), towards Lewis base solvents has been carried out. The complexes $M(1\text{-nqo})_2$ and $M(2\text{-nqo})_3$ give internal redox reactions with pyridine at room temperature. In contrast, the complexes $M(nqo)_n$ (M = Cr, n = 3; M = Mn, Cu, or Ni, n = 2) did not undergo internal redox reactions with any of the Lewis base solvents. It has been demonstrated that the reactivity of Lewis base solvents towards $Mn(2\text{-nqo})_3$ is a function of the Lewis base strength.

An intermediate product, $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (2-nqiH = 1,2-naphthoquinone 2-imine), was isolated from the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine. The corresponding reactions of $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ afforded $[Mn(1\text{-nqo})_2]_2O$ and $[Mn(2\text{-nqo})_2]_2O$. In addition, the reactions involving $Mn(2\text{-nqo})_3$ and $Cr(2\text{-nqo})_3$ led to 5-hydroxy-dibenzo[b,i]phenazin-12-(6H)-one and 2-amino-N-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine arising from reactions of the deoxygenated ligand molecule. $[Mn(2\text{-nqo})_2]_2O$ reacted further with triphenylphosphine to give $[Mn(2\text{-nqi})_2]_2O$. Acidification of this complex afforded 1,2-naphthoquinone 2-imine. The greater reactivity of 1,2-naphthoquinone 2-oxime and its metal complexes towards triphenylphosphine and pyridine has been correlated with ligand stereochemistry. Mechanisms have been proposed, based on kinetic studies, for the reactions involving triphenylphosphine and the complexes $M(2\text{-nqo})_3$ (M = Cr or Mn).

Aerobic oxidation of methyl oleate, styrene, cyclohexene, and 1-octene catalysed by the complexes $Mn(nqo)_n$ led to the corresponding epoxides in better yields than previously reported. The reactions have been mechanistically assesed and high-valent oxo-manganese species have been proposed as the active catalysts.

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Abbreviations

acridine	6-Hydroxydibenzo[b,kl]acridin-8-one
acacH	Acetylacetone
4-ClqoH	4-Chloro-1,2-benzoquinone 2-oxime
edtc	Diethyldithiocarbamate
3-imine	2-Imino-N^3-(1-quinone-2-naphthyl)-1,3-3-imine
4-imine	2-Amino-N^4-(1-hydroxy-2-naphthyl)-1, naphthoquinone 4-imine
imid	Imidazole
i.r.	Infra-red
3-Me-5-OHqoH	3-Methyl-5-hydroxy-1,2-benzoquinone 2-oxime
6-Me-5-OHqoH	6-Methyl-5-hydroxy-1,2-benzoquinone 2-oxime
MO	Methyl oleate
2-nqiH	1,2-Naphthoquinone 2-imine
1-nqoH	1,2-Naphthoquinone 1-oxime
2-nqoH	1,2-Naphthoquinone 2-oxime
OAc	Acetate anion
5-OMeqoH	5-Methoxy-1,2-benzoquinone 2-oxime
Ph_3P	Triphenylphosphine
Ph_3PO	Triphenylphosphine oxide
phenazinone	5-Hydroxy-dibenzo[b,i]phenazin-12(6H)one
py	Pyridine
qoH	1,2-Quinone mono-oxime
salenH	Salicylaldimine
t.l.c.	Thin layer chromatography

tropH	Tropolone
u.v./vis.	Ultra-violet/visible

CONTENTS

CHAPTER ONE

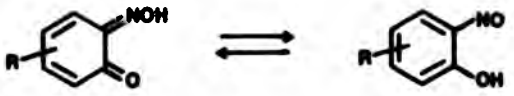
1,2-QUINONE MONO-OXIMES AND THEIR METAL COMPLEXES

These compounds have attracted considerable attention because of their potential in synthesis, catalysis, and medicine. Thus, dimethylacetylenedicarboxylate reacts with $Cu(1\text{-nqo})_2$, $Cu(2\text{-nqo})_2$, and $Cu(5\text{-OMeqo})_2$ to give, in each case, the respective benzoxazine in high yield.[1] Benzylamine is converted to N-benzylidenebenzylamine when heated at 70 °C with $Cu(4\text{-Clqo})_2$ in catalytic amounts.[2] The complexes $Mn(1\text{-nqo})_n$ and $Mn(2\text{-nqo})_n$ (n = 2 or 3) catalyse the aerobic oxidation of unsaturated organic compounds (see Chapter 6). 1,2-Quinone mono-oximes also have considerable potential in the treatment of disorders resulting from iron overload in the human body.[3]

1.1 Structure

1,2-Quinone mono-oximes (1.1) can exist in a tautomeric equilibrium with their nitrosophenolic forms (1.2) (Figure 1.1).

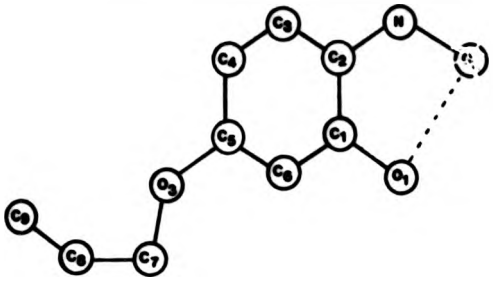
Figure 1.1 Tautomerism of 1,2-quinone mono-oximes



1.1 1.2

Traditionally, these compounds were named as 2-nitrosophenols. In this thesis, however, they will be referred to as 1,2-quinone mono-oximes. This is because all the compounds studied todate, by X-ray diffraction crystallography, have the oximic form. Thus, β-5-n-propoxy-2-nitrosophenol is oximic with the NOH group bent towards the carbonyl oxygen, syn form (Figure 1.2).[4] α-5-(2-Chloroethoxy)-2-nitrosophenol is also oximic with the NOH group bent away from the carbonyl group, anti form (Figure 1.3).[5] The oximic nature is indicated by: (1) two short and four long carbon to carbon bonds in the six-membered carbon ring, (2) the short carbon to oxygen and carbon to nitrogen bond lengths relative to the corresponding bonds in phenols[6] and nitrosobenzene.[7] The oximic nature of the protonated ligands is unperturbed by

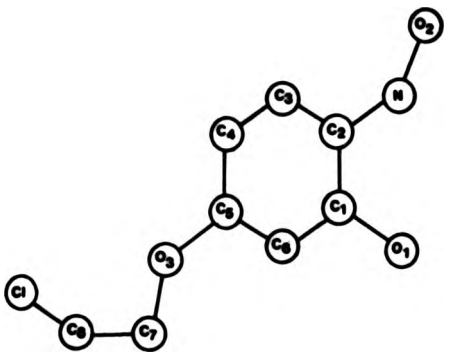
Figure 1.2 Structure of β-5-n-propoxy-1,2-benzoquinone 2-oxime.



Bond lengths in Å.

C_1-C_2 1.482, C_2-C_3 1.442, C_3-C_4 1.344, C_4-C_5 1.458,
C_5-C_6 1.357, C_1-O_1 1.270, C_2-N 1.319, N-O_2 1.353,
C_5-O_3 1.344, O_3-C_7 1.451, C_7-C_8 1.511, C_8-C_9 1.523.

Figure 1.3 Structure of α-5-(2-chloroethoxy)-1,2-benzoquinone 2-oxime.

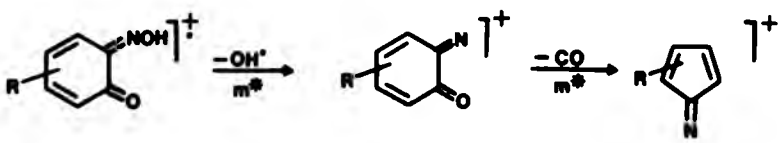


Bond lengths in Å.

C_1-C_2 1.502, C_2-C_3 1.435, C_3-C_4 1.345, C_4-C_5 1.457,
C_5-C_6 1.358, C_1-O_1 1.253, C_2-N 1.306, N-O_2 1.365,
C_5-O_3 1.343, O_3-C_7 1.448, C_7-C_8 1.501, C_8-C_1 1.792.

replacement of the acidic proton with a metal cation. Thus, the coordinated anionic ligands in copper(II),[8] uranium(VI),[9] and lithium(I)[10] complexes of 1-nqoH and 2-nqoH are oximic. I.r. studies have indicated the oximic nature of the protonated ligands and their metal complexes in solution. Thus, the C=O band frequencies of the protonated ligands are comparable to those of quinones.[11] The C=O bands shift to lower frequencies upon chelation as a result of reduction in C=O bond orders. Electron impact mass spectrometric studies have suggested the dominance of the oximic form in the vapour state. The molecular ion ($M^{+\cdot}$) mainly fragments by successive loss of OH$^{\cdot}$ and CO. These metastable supported reactions have been accounted for in terms of a quinoneoximic $M^{+\cdot}$ (Scheme 1.1). This type of fragmentation is comparable to the fragmentation of various oximes.[12]

Scheme 1.1 Electron impact induced fragmentation of 1,2-quinone mono-oximes.



X-ray diffraction studies have also shown that in transition metal complexes chelation occurs through the oximic nitrogen and the carbonyl oxygen (Figure 1.4).[8] In contrast, in the actinide complexes $UO_2(1\text{-nqo})_2(H_2O)_2.2CHCl_3$ and $UO_2(2\text{-nqo})_2(H_2O)_2.2CHCl_3$, only the oxime group is involved in bonding (Figure 1.5).[9]

Figure 1.4 Mode of chelation in transition metal complexes of 1,2-quinone mono-oximes.

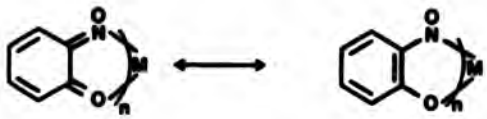
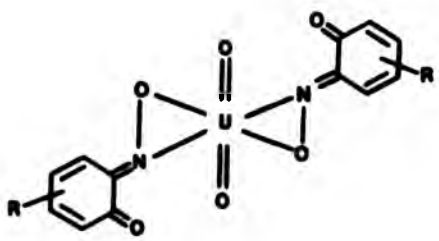
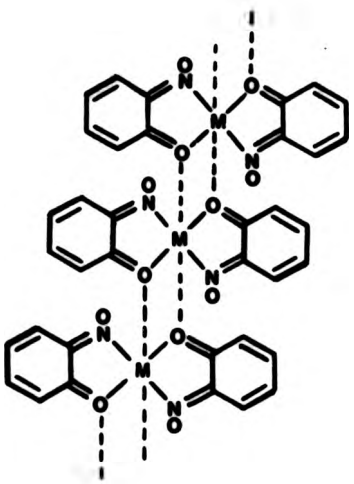


Figure 1.5 Mode of bonding in uranium(VI) complexes of 1,2-quinone mono-oximes.



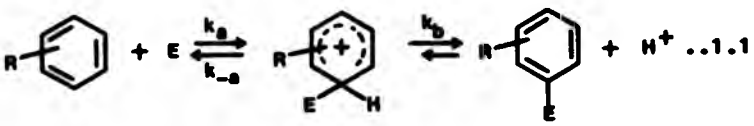
In transition metal bis-chelates of type $M(qo)_2$, coordination number of six is attained by oligomerisation (Figure 1.6). This leads to subnormal magnetic moments and antiferromagnetic behaviour.[13]

Figure 1.6 Oligomerisation in transition metal chelates of type $M(qo)_2$.



1.2 Synthesis

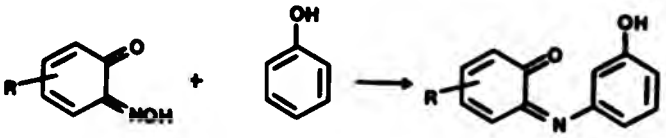
Mechanistic studies have shown that an unusual feature of aromatic nitrosations, compared with other A-S_E2 reactions is that proton loss from the Wheland intermediate (Step k_b) is rate limiting (Reaction 1.1). This difference has been attributed to the relative stability of the nitrosonium ion (NO^+) in acid solutions, promoting the k_{-a} step.[14] Consequently, ring nitrosation of aromatic compounds is difficult unless highly activating groups are attached to the aromatic ring, for example, hydroxy or amino. Studies with benzene, for example, have indicated that NO^+ is at least 10^{14} times less effective at electrophilic substitution than the nitronium ion (NO_2^+).



..1.1

A hydroxy group is a strong ortho/para director and can overwhelm the directing effects of any other substituents attached to the aromatic ring. Nitrosation of phenols should, therefore, yield mixtures of 2- and 4-isomers in roughly equal proportions. The 4-isomer, however, is usually the dominant product as the 2-isomer is labile with

respect to further reactions. Thus, under the oxidative influence of nitrous acid, conversion to 2-nitrophenol takes place. 1,2-Quinone mono-oximes can also react with any unreacted phenol present in the reaction mixture to give indophenols (Reaction 1.2).[15] Consequently, only a small number of 1,2-quinone mono-oximes have been isolated.



..1.2

The direct and the nitrosation methods provide the main synthetic routes to 1,2-quinone mono-oximato complexes.

1.2.1 The direct method

This involves the reaction between a protonated ligand and metal salt (Reaction 1.3)[16] or metal carbonyl (Reaction 1.4).[17]

$$n(qoH) + MX_n \longrightarrow M(qo)_n + nHX \qquad ..1.3$$

(X = Cl^- or NO_3^-)

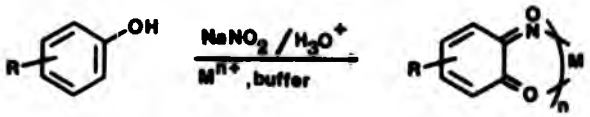
$$n(qoH) + M(CO)_n \longrightarrow M(qo)_n + nCO \qquad ..1.4$$

Reaction 1.3 can be used with all metals whereas reaction 1.4 can only be used with metals which have

stable metal carbonyls. The applicability of the direct method is limited owing to the small number of 1,2-quinone mono-oximes available.

1.2.3 The nitrosation method

This involves the nitrosation of a phenol using sodium nitrite/acetic acid in the presence of a metal salt.[13] The 1,2-quinone mono-oxime ligand is generated in situ and immediately forms a complex with the metal ion (Reaction 1.5). This stabilizes the protonated ligand by preventing it from undergoing further reactions. The nitrosation method is more applicable than the direct method and has been used for the synthesis of a number of complexes of type $M(qo)_n$ (M = V,[18] Fe,[19] Ni,[13] Cu,[13] Co,[20]).



..1.5

During the course of this work the synthetic routes were extended to ligand exchange reactions of $Mn(acac)_3$ with 1-nqoH or 2-nqoH (Reaction 1.5).

$$Mn(acac)_3 + 3nqoH \longrightarrow Mn(nqo)_3 + 3acacH \qquad ..1.6$$

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CHAPTER TWO

COMPLEXES OF CHROMIUM WITH 1,2-QUINONE MONO-OXIMES

Complexes of type $Cr(qo)_3$ have been prepared, where qoH is 1,2-naphthoquinone 1-oxime (1-nqoH), 1,2-naphthoquinone 2-oxime (2-nqoH), 3-methyl-5-hydroxy-1,2-benzoquinone 2-oxime (3-Me-5-OHqoH), and 6-methyl-5-hydroxy-1,2-benzoquinone 2-oxime (6-Me-5-OHqoH). Reactions of $Cr(CO)_6$ with 1-nqoH and 2-nqoH led to the corresponding chromium(III) tris-chelates in addition to organic products. Oxo-bridged complexes of type $[Cr(nqo)_2]_2O$ were obtained in quantitative yield from the reactions of the complexes $Cr(nqo)_3$ with $Cr(CO)_6$. The complexes have been investigated by elemental analysis, relative molecular mass determinations, magnetic susceptibility measurements, i.r. and u.v./vis. spectroscopy.

2.1 Introduction

The study of chromium complexes derived from 1,2-quinone mono-oximes has received very limited attention. Although, i.r. and u.v./vis. data for tris(1,2-naphthoquinone 1-oximato)chromium(III) has been reported, no details have been presented with regard to the preparation and characterisation of the complex.[1]

Chromium has an extensive coordination chemistry. Under aerobic conditions, the metal exists in an oxidation state of III. Many chromium(III) chelates of anionic chelating ligands are known (Table 2.1). In all such chelates, the metal has a coordination number of six and octahedral geometry. The usual starting material in the synthesis of chromium(III) complexes is chromium(III) chloride hexahydrate. In aqueous solutions, chromium(III) exists as the aquo cation $[Cr(H_2O)_6]^{3+}$. Complexation with bidentate anionic chelating ligands involves replacement of the aquo ligands (Scheme 2.1).

Scheme 2.1 Replacement of aquo ligands by a bidentate chelating ligand

$$[Cr(H_2O)_6]^{3+} \xrightarrow[-2H_2O]{+chel^-} [Cr(H_2O)_4(chel)]^{2+} \xrightarrow[-2H_2O]{+chel^-} [Cr(H_2O)_2(chel)_2]^{+} \xrightarrow[-2H_2O]{+chel^-} [Cr(chel)_3]$$

Table 2.1 Neutral chromium chelates of anionic ligands

Complex[h]	Oxidation state	C.N.	Method of preparation	Refs.
$Cr(acac)_3$	+3	6	a,d	2
$Cr(dtba)_3$	+3	6	a,e	3
$Cr(dtpa)_3$	+3	6	a,e	3
$Cr(2\text{-}Meox)_3$	+3	6	a,d	4
$Cr(acht)_3$	+3	6	b,f	5
$Cr(pak)_3$	+3	6	b,c,d	6
$Cr(acac)(tfac)_2$	+3	6	b,c,d	7
$Cr(acac)_2(tfac)$	+3	6	b,c,g	7

Key to Table 2.1

[a] aerobic conditions. [b] Anaerobic conditions. [c] Anhydrous conditions. [d] Reaction of $CrCl_3.6H_2O$ with the protonated ligand in the presence of a base or buffer. [e] Reaction of the ligand sodium salt with $CrCl_3.6H_2O$. [f] Reaction of $Cr(CO)_6$ with the protonated ligand; [g] Ligand exchange. [h] dtbaH = dithiobenzoic acid, dtpaH = dithiophenylacetic acid, 2-MeoxH = 2-methyloxine, achtH = N,N'-disubstituted--1-amino-7-imino-1,3,5-cycloheptatriene, pakH = pentane--2-alkylimine-4-ketone.

Complications can arise in the preparation of chromium complexes in aqueous media because of the tendency of chromium to undergo hydrolysis, olation and oxolation reactions.[8] These reactions are highly likely in neutral and basic solutions, and possible in slightly acidic solutions. Furthermore, the use of a base or buffer to neutralize the acid formed can cause the equilibrium in Reaction 2.1 to shift to the right and enhance hydrolysis.

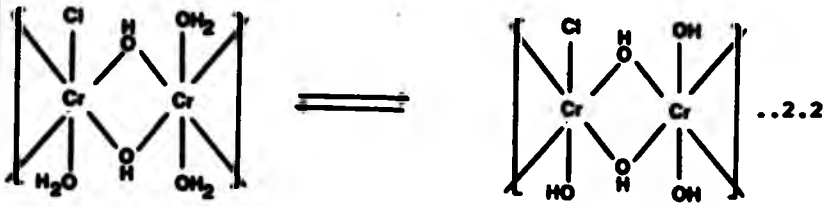
$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H_3O^+ \qquad ..2.1$$

Olation can follow hydrolysis, resulting in the formation of polynuclear complexes. The first steps in this process may be represented as shown below.

$$[Cr(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_5Cr\overset{H}{O}Cr(H_2O)_5]^{5+} + H_2O$$

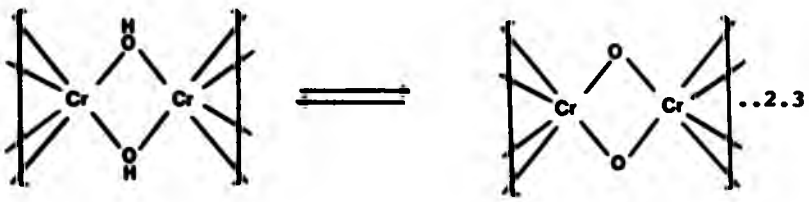
$$2[Cr(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4Cr\overset{H}{O}\overset{H}{O}Cr(H_2O)_4]^{4+} + 2H_2O$$

The diol can undergo further olation by releasing hydrogen ions and leaving coordinated OH groups (Reaction 2.2).



..2.2

Ultimately such a process can lead to the precipitation of 'chromium hydroxide', the hydrate $Cr(OH)_3.xH_2O$. Thus, making chromium unavailable for complexation. Oxolation may follow olation, particularly if the reaction mixture is heated, to give polynuclear oxo-bridged complexes (Reaction 2.3).



..2.3

Polynuclear chromium compounds with hydroxy- and oxo-bridges have been reported.[9] To avoid problems associated with hydrolysis, olation and oxolation reactions, preparation of chromium complexes has been attempted under anhydrous conditions. Thus, complexes of type CrL_3 (e.g. LH = pentane-2-alkylimine-4-ketone) have been prepared by the reaction of $CrCl_3.3thf$ with the ligand using non-aqueous conditions.[6]

2.2 Synthetic Studies

The following synthetic methods were investigated in this study.

1. Nitrosation of phenols and naphthols in the presence of chromium(III) chloride hexahydrate.
2. Reaction of Na[1-nqo] or Na[2-nqo] with chromium(III) chloride hexahydrate.
3. Reaction of 1-nqoH or 2-nqoH with chromium(III) chloride hexahydrate in the presence or absence of a buffer.
4. Ligand exchange between $Cr(acac)_3$ and 1-nqoH or 2-nqoH.
5. Reaction of hexacarbonylchromium(0) with 1-nqoH or 2-nqoH.

Nitrosation of 1-naphthol or 2-naphthol, in the presence of chromium(III) chloride hexahydrate, led to tris(1,2-naphthoquinone 2-oximato)chromium(III) and tris-(1,2-naphthoquinone 1-oximato)chromium(III), respectively, in good yield.

In marked contrast to the behaviour of the naphthols, nitrosation of 4-methylphenol, 4-chlorophenol, or 4-t-butylphenol in the presence of chromium(III) chloride hexahydrate did not lead to the respective chromium(III) tris-chelate. Instead, complex mixtures of organic products were formed. These results suggest that the preparation of $Cr(qo)_3$ complexes by means of the nitrosation method, is only applicable for phenols

which give stable and isolable 1,2-quinone mono-oximes. In order to check this hypothesis, 2-methyl-3-hydroxyphenol and 3-methyl-5-hydroxyphenol were nitrosated in the presence of chromium(III) chloride hexahydrate. This led to tris(6-methyl-5-hydroxy-1,2-benzoquinone 2-oximato)chromium(III) and tris-(3-methyl-5-hydroxy-1,2-benzoquinone 2-oximato)chromium-(III), respectively, in good yield. The protonated ligands 6-Me-5-OHqoH and 3-Me-5-OHqoH are stable and their preparation by the nitrosation method has been described.[10]

The reactions of Na[1-nqo] and Na[2-nqo] with chromium(III) chloride hexahydrate afforded the respective chromium tris-chelates in satisfactory yields.

The interaction of 1-nqoH and 2-nqoH with chromium(III) chloride hexahydrate, in the presence of a buffer, gave the corresponding chromium tris-chelates in reasonable yields. In contrast, in the absence of a buffer the analogous reactions gave the complexes in poor yield.

The synthesis of $Cr(nqo)_3$ was also attempted using the ligand exchange method. Previously, Palmer et al. had satisfactorily used this method to prepare mixed ligand complexes of type $Co(tfac)_n(acac)_{3-n}$ from $Co(acac)_3$.[7] In this study ligand exchange was attempted between $Cr(acac)_3$ and 1,2-naphthoquinone mono-oximes (Reaction

2.4). Reaction between $Cr(acac)_3$ (1 mol eq.) and 1-nqoH or 2-nqoH (3 mol eq.) did not occur under ambient or reflux conditions in toluene.

$$Cr(acac)_3 + 3(nqoH) \longrightarrow Cr(nqo)_3 + 3acacH \quad ..2.4$$

Synthesis of $Cr(nqo)_3$ complexes was then investigated through the reaction of hexacarbonylchromium(0) with 1-nqoH or 2-nqoH (Reaction 2.5).

$$Cr(CO)_6 + 3nqoH \longrightarrow Cr(nqo)_3 + 6CO \quad ..2.5$$

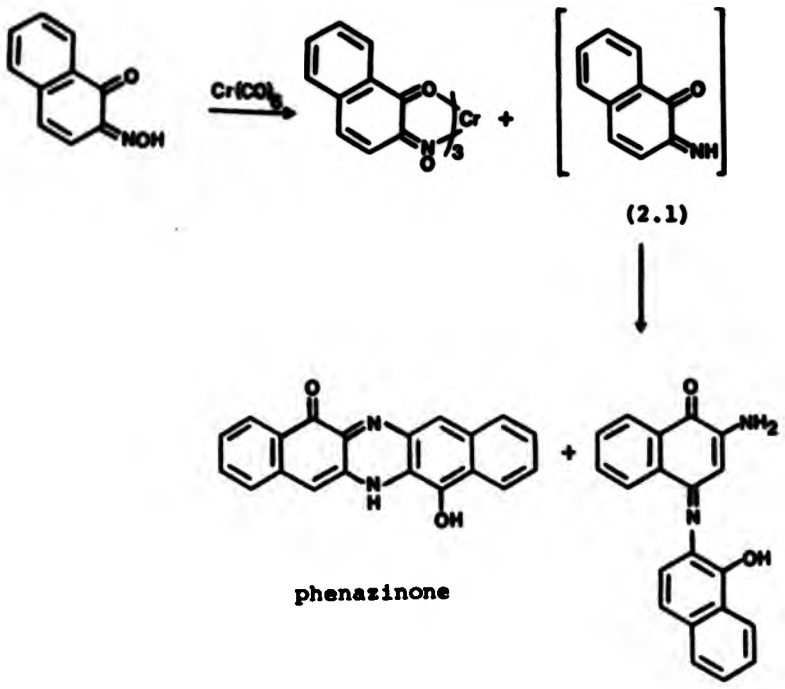
Transition metal carbonyls have been used in the preparation of a wide range of complexes which result from the replacement of carbonyl groups by neutral ligands. In addition, investigations into the use of metal carbonyls for the preparation of complexes by oxidative decarbonylation have been carried out, particularly for transition metal chelates of carboxylic acids, β-diketones, thio-ligands, Schiff bases, and porphyrins.[11] For example, hexacarbonylchromium(0) and hexacarbonylmolybdenum(0) react with N-methylsalicylideneimine to give the corresponding tris-chelates of chromium(III) and molybdenum(III).[16]

Recent work has shown that the reactions of pentacarbonyliron(0) with 1-nqoH and 2-nqoH in refluxing tetrahydrofuran afford, in each case, mainly the corresponding iron(II) bis-chelates and a mixture of small amounts of organic products.[12] In the case of the

reaction involving 2-nqoH, 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine and 5-hydroxy-dibenzo-[b,i]phenazin-12(6H)-one have been identified as the main organic products.

In contrast to pentacarbonyliron(0), hexacarbonylchromium(0) did not react with 1-nqoH or 2-nqoH in refluxing tetrahydrofuran. However, reactions did occur in refluxing toluene to give, in each case, the corresponding chromium(III) tris-chelate, $Cr(nqo)_3$, in poor yield together with relatively large amounts of organic products. In addition, in the case of 1-nqoH, a chromium-containing by-product of indefinite composition was obtained. The organic products, from the reaction of 2-nqoH, included 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4--naphthoquinone 4-imine and 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one. The complexity of the reaction mixture, from the interaction involving 1-nqoH, hindered separation and characterisation of the organic products. The organic products obtained from these reactions parallel those arising from the reactions of pentacarbonyliron(0) with the free ligands[12] and of the complexes Cu(nqo)2 with triphenylphosphine[13] or aniline.[14] They can be accounted for in terms of deoxygenation of the protonated ligands to give the quinoneimine/nitrene (2.1) followed by hydrogen abstraction and/or coupling reactions (e.g. Scheme 2.2).

Scheme 2.2 Deoxygenation of protonated ligands



phenazinone

4-imine

The large amount of organic products formed in these reactions can be ascribed to the high reaction temperature. Pyrolysis of aromatic nitrogen compounds frequently leads to phenazine type end-products.[15] Indeed, 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one and 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine were obtained when 2-nqoH was refluxed in toluene. The corresponding reaction involving 1-nqoH afforded a black tar. On the basis of these observations, the poor yields of $Cr(qo)_3$ complexes, in

the reactions of $Cr(CO)_6$ with 1-nqoH or 2-nqoH, can also be ascribed to ligand decomposition in refluxing toluene.

The complexes $Fe(qo)_3$ (qoH = 1,2-naphthoquinone 1-oxime, and 1,2-naphthoquinone 2-oxime, and 5-methoxy--1,2-benzoquinone 2-oxime) react with pentacarbonyliron-(0) to give the respective $Fe(qo)_2$ complexes in quantitative yield. Organic products are not formed in these reactions.[12] In contrast, the complexes $Cr(nqo)_3$ reacted with hexacarbonylchromium(0) to give oxo-bridged complexes of type $[Cr(nqo)_2]_2O$ in quantitative yield. No organic products were formed. The complexes $[Cr(1\text{-}nqo)_2]_2O$ and $[Cr(2\text{-}nqo)_2]_2O$ had well defined i.r. spectra (Figures 2.1 and 2.2) and, in both cases, analytical results were in accord with the formulations. Both complexes were sparingly soluble in dichloromethane, toluene, and pyridine at room temperature. Analogous complexes have previously been observed. Thus, it has been reported that the reaction of Hg(salen) [salen = N,N'-ethylenebis(salicylidene-iminate)] with hexacarbonylchromium(0) leads to $[Cr(salen)]_2O$.[16] The room temperature magnetic moment of this complex is 2.20 B.M. per chromium atom. Room temperature magnetic moments of other typical chromium(III) oxo-bridged complexes range from 0 to 2.3 B.M. The complexes $[Cr(1\text{-}nqo)_2]_2O$ and $[Cr(2\text{-}nqo)_2]_2O$ had room temperature magnetic moments of 2.24 and 2.36 B.M. per chromium repectively, which clearly lie in the region expected for oxo-bridged complexes of chromium(III).

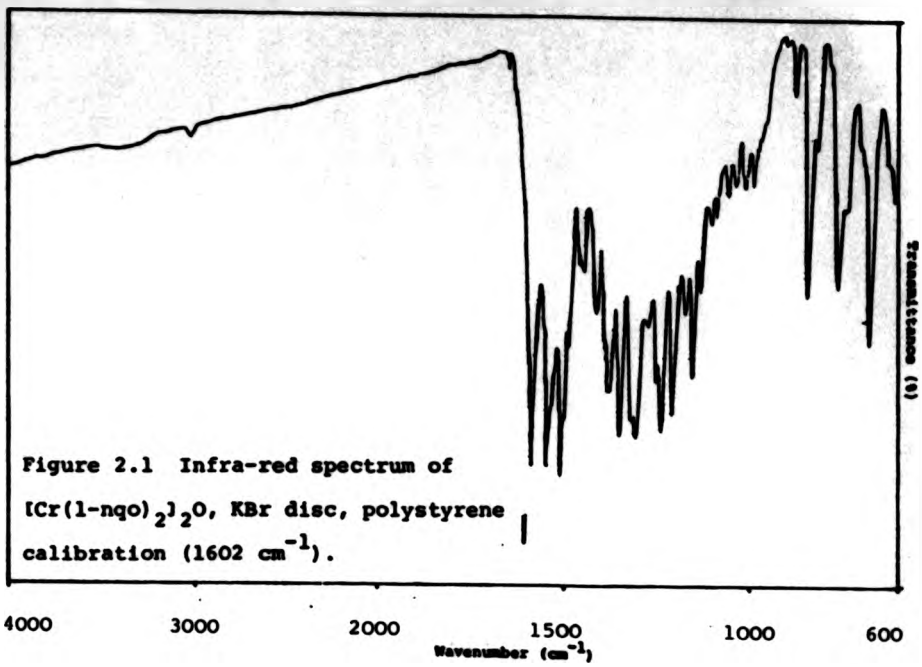


Figure 2.1 Infra-red spectrum of $[Cr(1\text{-nqo})_2]_2O$, KBr disc, polystyrene calibration (1602 cm^{-1}).

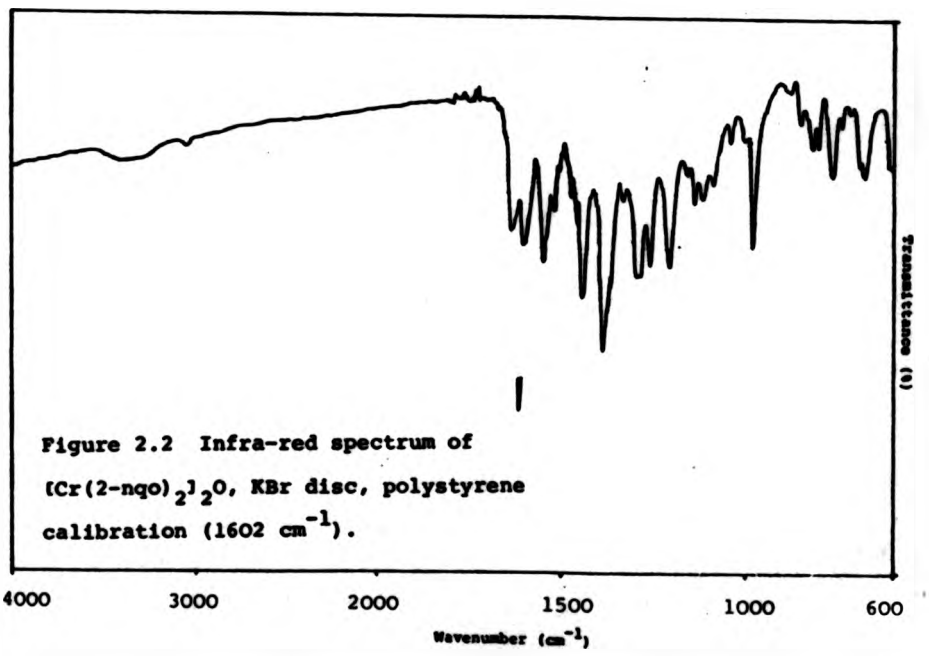


Figure 2.2 Infra-red spectrum of $[Cr(2\text{-nqo})_2]_2O$, KBr disc, polystyrene calibration (1602 cm^{-1}).

2.3 Structural studies

Elemental analysis of the chromium complexes indicated that they have formulations of type $Cr(qo)_3$ (qoH = 1-nqoH, 2-nqoH, 3-Me-5-OHqoH, and 6-Me-5-OHqoH). Magnetic moment measurements (Table 2.2) showed that the metal has an oxidation state of III in all the complexes. The spin-only value for chromium(III) (d^3) is 3.87 B.M. Magnetic moments somewhat lower than the spin-only value are usual for octahedral d^3 configurations, for example, the room temperature magnetic moment of tris(N-methylsalicylidene-iminato)molybdenum(III) is 3.66 B.M.[16] As expected for coordinately saturated chromium(III) tris-chelates, relative molecular mass determinations suggested that the complexes are monomeric in solution.

Table 2.2 Magnetic and relative molecular mass determination results for the complexes $Cr(qo)_3$

Complex	μ_{eff}/B.M. (295 °K)	Molecular weight Found	Calculated
$Cr(1\text{-nqo})_3$	3.64	570 ± 20[a]	568
$Cr(2\text{-nqo})_3$	3.72	564 ± 20[a]	568
$Cr(3\text{-Me-5-OHqo})_3$	3.73	480 ± 20[b]	508
$Cr(6\text{-Me-5-OHqo})_3$	3.56	485 ± 20[b]	508

Key to Table 2.2

[a] Toluene solution; [b] methanol solution.

As noted in Chapter 1, X-ray diffraction studies have established two modes of coordination of 1,2-quinone mono-oximate ligands. In transition metal complexes, chelation occurs through the quinone oxygen and the oximic nitrogen.[17] In contrast in the actinide complexes $UO_2(1\text{-nqo})_2(H_2O)_2.2CHCl_3$ and $UO_2(2\text{-nqo})_2(H_2O)_2.2CHCl_3$ bonding involves the oximic group only.[18] In the i.r. spectra of $Cr(1\text{-nqo})_3$ (Figure 2.3) and $Cr(2\text{-nqo})_3$ (Figure 2.5) the C=O absorptions occur at 1602 and 1615 cm^{-1}. The corresponding absorptions in the spectra of 1-nqoH (Figure 2.4) and 2-nqoH (Figure 2.6) occur at 1618 and 1668 cm^{-1} respectively. The complexes $Cr(6\text{-Me-5-OHqo})_3$ and $Cr(3\text{-Me-5-OHqo})_3$ show similar behaviour. Lowering of the C=O frequency upon coordination is indicative of the involvement of the quinone oxygen in chelation. This suggests that bonding of the ligands in the complexes $Cr(qo)_3$ is similar to that found in other transition metal chelates of 1,2-quinone mono-oximes.

The electronic absorption spectra of the complexes $Cr(qo)_3$ were studied in order to determine crystal field parameters. Previous workers had found that the electronic absorption spectra of transition metal chelates of type $M(qo)_n$ exhibit intense ligand bands which tail into the visible region. Consequently, detection and interpretation of d-d transitions had proved difficult.[19] Comparison between the spectra of the complexes $Cr(qo)_3$ and their respective protonated ligands (e.g. Figures 2.7 and 2.8) also showed the dominance of ligand bands. Molar absorptivities of $Cr(2\text{-nqo})_3$, $Cr(1\text{-nqo})_3$, $Cr(3\text{-Me-5-OHqo})_3$,

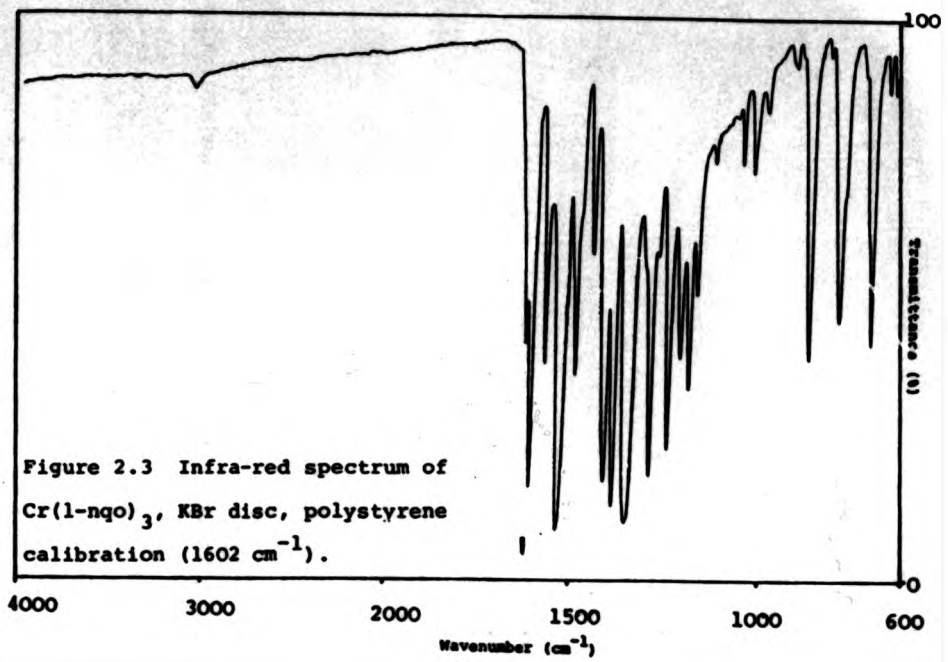


Figure 2.3 Infra-red spectrum of $Cr(1\text{-nqo})_3$, KBr disc, polystyrene calibration (1602 cm^{-1}).

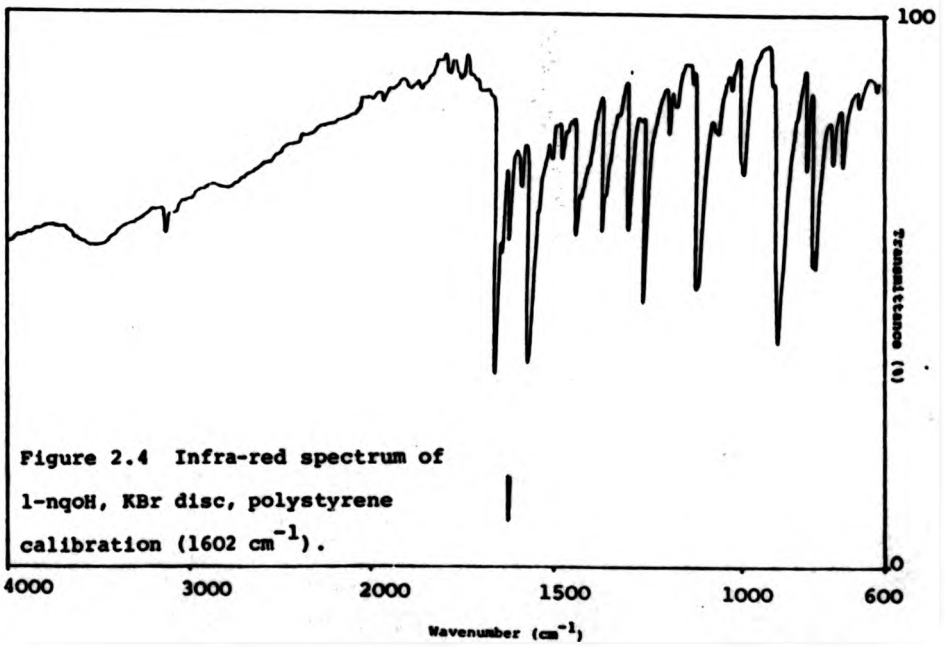


Figure 2.4 Infra-red spectrum of 1-nqoH, KBr disc, polystyrene calibration (1602 cm^{-1}).

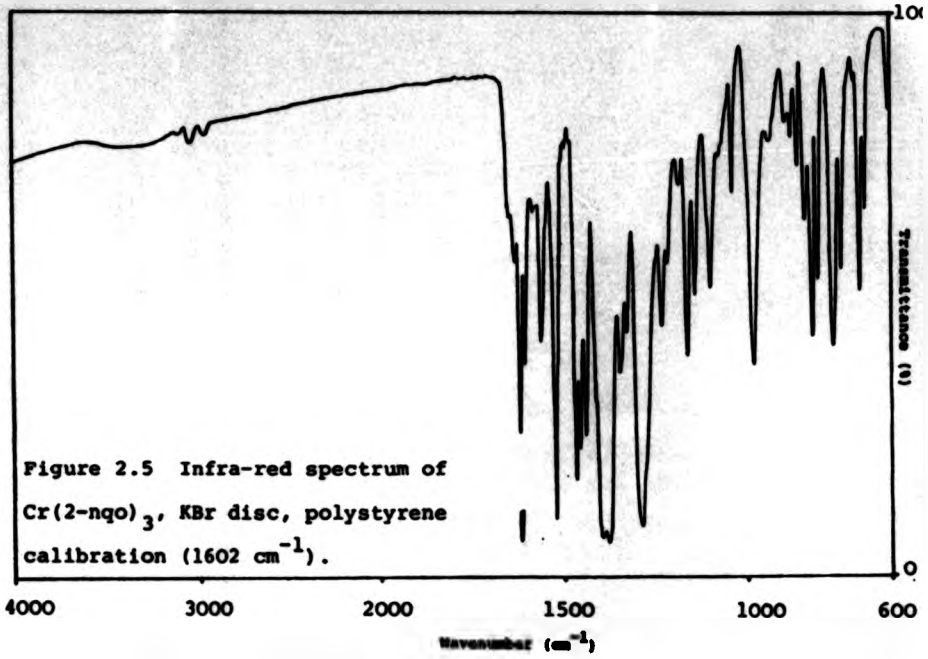


Figure 2.5 Infra-red spectrum of $Cr(2\text{-nqo})_3$, KBr disc, polystyrene calibration (1602 cm^{-1}).

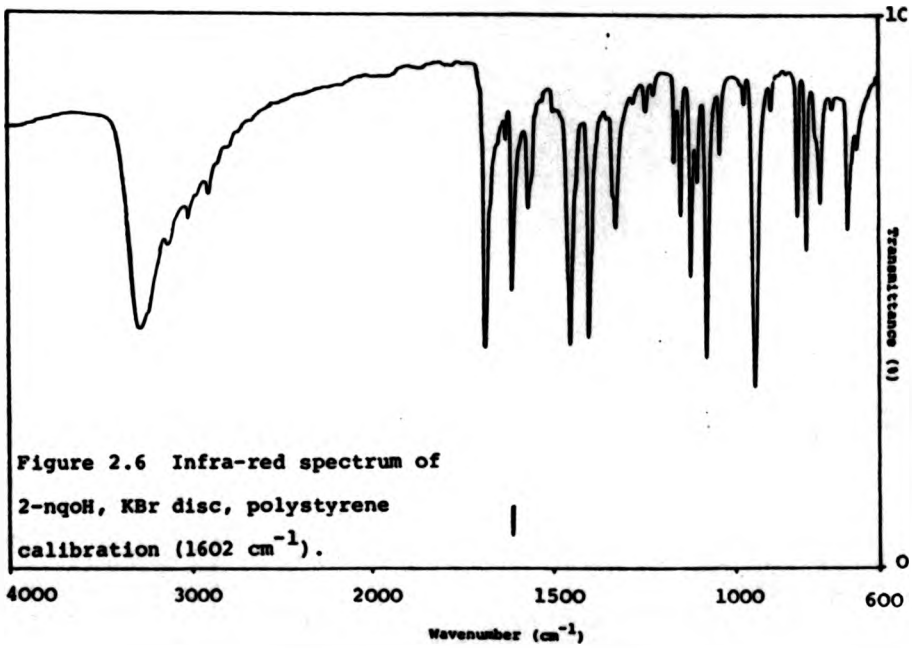


Figure 2.6 Infra-red spectrum of 2-nqoH, KBr disc, polystyrene calibration (1602 cm^{-1}).

$Cr(6\text{-Me-5-OHqo})_3$, and their protonated ligands are given in Table 2.3.

Examination of the spectra of $Cr(2\text{-nqo})_3$ and 2-nqoH indicated the presence of three d-d bands in the spectrum of the chelate (Figures 2.7 and 2.8). These bands were assigned as follows.

ν_1 = 275 nm = 36364 cm^{-1}	$^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$
ν_2 = 452 nm = 22124 cm^{-1}	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
ν_3 = 582 nm = 17182 cm^{-1}	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$

Using the ratio ν_1/ν_3 of 2.12 and the appropriate Tanabe-Sugano diagram,[20] it was found that 10Dq = 17200 cm^{-1} and the Racah parameter B = 621 cm^{-1}. A check on the internal consistency of the interpretation predicted the $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$ transition to occur at 22356 cm^{-1}, which was found to be in good agreement with the band observed at 22124 cm^{-1}. The B value of $Cr(2\text{-nqo})_3$ was 60% of the free ion value for Cr^{3+} (1030 cm^{-1}). This lowering of the B value indicates that bonding in $Cr(2\text{-nqo})_3$ is not purely ionic.[20]

In the past, similarity in the d-d spectra of $[Ni(H_2O)_6]^{2+}$ and $Ni(acac)_2$ has been used as evidence of octahedral geometry in the latter compound.[22] The d-d bands reported for $[Cr(H_2O)_6]^{3+}$ are listed below.[21]

ν_1 17000 cm^{-1}	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
ν_2 24000 cm^{-1}	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$

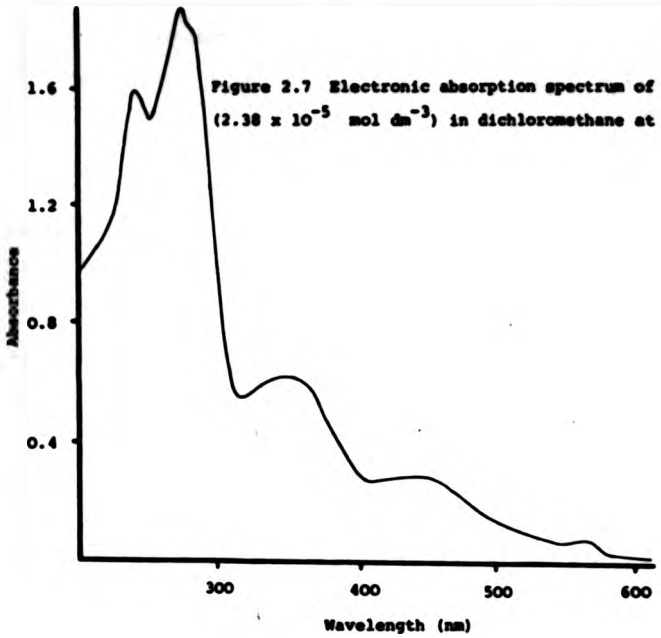


Figure 2.7 Electronic absorption spectrum of $Cr(2\text{-nqo})_3$ (2.38×10^{-5} mol dm^{-3}) in dichloromethane at 30.0 ± 0.3 °C.

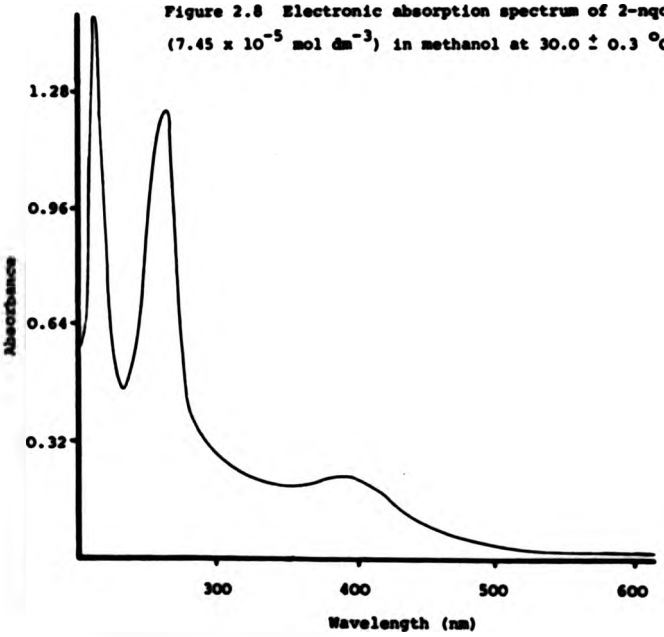


Figure 2.8 Electronic absorption spectrum of 2-nqoH (7.45×10^{-5} mol dm^{-3}) in methanol at 30.0 ± 0.3 °C.

Table 2.3 Electronic absorption results for the complexes $Cr(qo)_3$ at 30.0 ± 0.3 °C.

Compound/ concentration (mol dm^{-3})/ solvent	λ_{max} (nm)	ϵ (m^2 mol^{-1})
$Cr(2\text{-nqo})_3$	582	117
2.38×10^{-5}	452	820
dichloromethane	353	1876
	275	5275
	265	5698
	233	4854
2-nqoH	387	300
7.45×10^{-5}	258	1703
methanol	203	2059
$Cr(1\text{-nqo})_3$	470	1754
1.71×10^{-5}	411	1987
dichloromethane	274	5562
	231	6994
1-nqoH	387	300
3.40×10^{-5}	258	1703
methanol	203	2060

Table 2.3 (continued)

$Cr(3\text{-Me-5-OHqo})_3$	310	135
2.55×10^{-5}		
water		
3-Me-5-OHqoH	415	184
5.24×10^{-5}	306	877
water	289	853
$Cr(6\text{-Me-5-OHqo})_3$	350	100
2.73×10^{-5}		
water		
6-Me-5-OHqoH	385	184
5.71×10^{-5}	325	398
water	235	318

ν_3 37000 cm^{-1} $\quad {}^4T_{1g}(P) \longleftarrow {}^4A_{2g}(F)$

These bands compare well with those observed in the spectrum of $Cr(2\text{-nqo})_3$. This can be taken as a confirmation of the expected octahedral geometry in $Cr(2\text{-nqo})_3$.

Only one d-d band was detectable in the spectrum of $Cr(1\text{-nqo})_3$ (Figure 2.9). The other d-d bands are masked by the intense ligand bands (Figure 2.10). The spectra of the complexes $Cr(6\text{-Me-5-OHqo})_3$ and $Cr(3\text{-Me-5-OHqo})_3$ exhibited ligand bands only. Comparison between the spectra of the latter complexes and their protonated ligands indicated that the ligand bands shift to shorter wavelengths upon coordination (a hypsochromic or blue shift). Peaks associated with $n \longrightarrow \pi^*$ transitions and in some cases $\pi \longrightarrow \pi^*$ transitions, in the electronic absorption spectra of organic compounds, are generally shifted to shorter wavelengths with increasing polarity of the solvent. This has been attributed to a lowering in energy of the non-bonding orbital as a result of hydrogen bond formation between the solvent protons and the non-bonded electron pair of the organic compound.[23] By analogy, it is proposed that the energy of the ligand non-bonding orbital is lowered as a result of electron donation from the ligand to the metal. Consequently, a blue shift is observed upon coordination.

Figure 2.9 Electronic absorption spectrum of $Cr(1\text{-nqo})_3$ (1.71×10^{-5} mol dm^{-3}) in dichloromethane at 30.0 ± 0.3 °C.

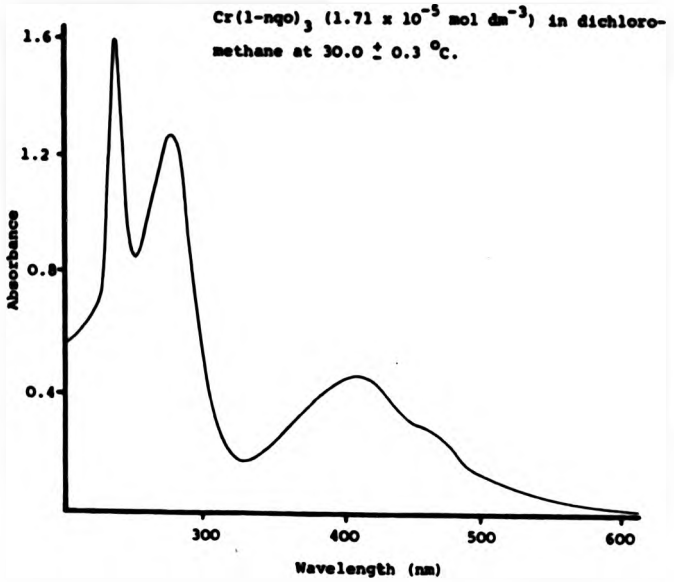
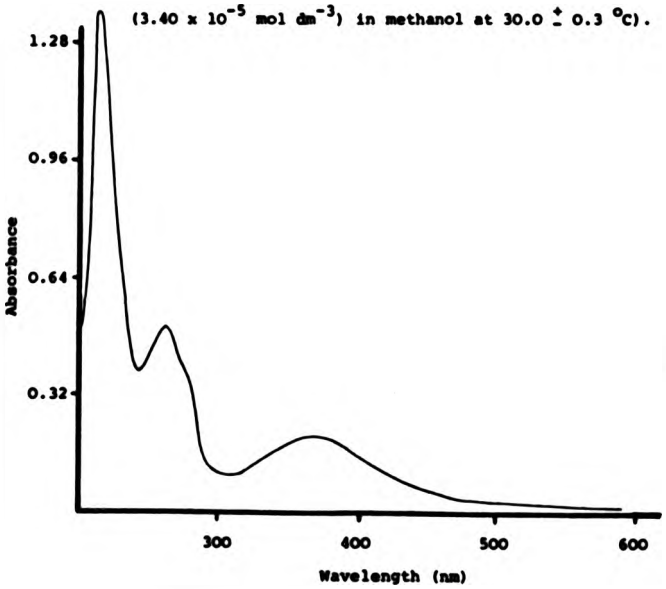


Figure 2.10 Electronic absorption spectrum of 1-nqoH (3.40×10^{-5} mol dm^{-3}) in methanol at 30.0 ± 0.3 °C).



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CHAPTER THREE

COMPLEXES OF MANGANESE WITH 1,2-QUINONE MONO-OXIMES

Manganese complexes of type $Mn(qo)_2$ and $Mn(qo)_3$ have been prepared, where qoH is 1,2-naphthoquinone 1-oxime (1-nqoH) or 1,2-naphthoquinone 2-oxime (2-nqoH). The complexes have been studied by elemental analysis, variable temperature magnetic studies, i.r. and u.v./vis. spectroscopy. Their reactions with hydrochloric acid have been investigated.

3.1 Introduction

The study of manganese complexes derived from 1,2-quinone mono-oximes has received limited attention. Gurrieri and Siracusa reported the synthesis of $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$ without full characterisation of the complexes.[1] The only other paper to be published on the subject has reported the synthesis of $Mn(1\text{-nqo})_2(OAc)$ and

$Mn(2\text{-nqo})_2(OAc)$.[2]

Manganese, with seven valency electrons, shows the widest variety of oxidation states in the first transition series.[3] Although, under aerobic conditions, manganese(II) (d^5) is the most stable oxidation state, manganese(III) (d^4) complexes are also known (Table 3.1). Indeed, one of the difficulties in the synthesis of manganese(II) complexes is the oxidation of manganese(II) to manganese(III). Thus, the reaction of manganese(II) chloride with N,N'-disubstituted aminotroponimines leads to a mixture of manganese(II) and manganese(III) chelates.[10] Manganese(II) chelates of 2-aminobenzenethiol[8] and salicylaldimines[4] are prepared under anaerobic conditions to avoid formation of manganese(III) products. Coordination numbers of four, five, and six have been observed for neutral manganese(II) chelates of anionic ligands. In contrast, most of the manganese(III) chelates are hexa-coordinate.

Manganese(II) chloride tetrahydrate and manganese(II) acetate tetrahydrate are the usual starting materials in the synthesis of neutral manganese(II) chelates. Manganese(III) chelates may be prepared by oxidation of manganese(II) chelates or by using manganese(III) acetate dihydrate as the starting material. When manganese(II) chloride tetrahydrate is used, the presence of a base or buffer is necessary to neutralize the hydrochloric acid formed (Reaction 3.1). However when manganese(II) acetate tetrahydrate is used, acetic acid is formed and

Table 3.1 Neutral manganese(II) and manganese(III) chelates of anionic ligands.

Complex[j]	Oxidation state	C.N.	Method of preparation	Refs.
$Mn(Me\text{-}sal)_2$	+2	5	b,d	4
$Mn(salen)_2$	+2	4	a,d	5
$Mn(trop)_2$	+2	6	a,d	6,7
$Mn(abt)_2$	+2	4	b,d	8
$Mn(acac)_2.2H_2O$	+2	6	a,d	9
$Mn(dati)_2$	+2	4	b,c,f	10
$Mn(OAc)(salen)_2$	+3	6	d	5
$Mn(trop)_3$	+3	6	b,c,d	6,7
$Mn(tbd)_3$	+3	6	b,c,e	11
$Mn(tftbd)_3$	+3	6	b,c,e	11
$Mn(acac)_3$	+3	6	a,i	12
$Mn(dati)_3$	+3	6	b,c,f	10
$Mn(acac)(dati)_2$	+3	6	a,j	10
$Mn(edtc)_3$	+3	6	a,k	13
$Mn(edtc)_2$	+2	6	b,k	13

[a] aerobic conditions. [b] anaerobic conditions. [c] Anhydrous conditions. [d] Reaction of $Mn(OAc)_2$ with the protonated ligand. [e] Reaction of $Mn(OAc)_3$ with the protonated ligand. [f] Reaction of anhydrous $MnCl_2$ with datiH and also by the reaction of $Mn_2(CO)_{10}$ with datiH. [g] Oxidation of Mn(acac)2 with $KMnO_4$ in the presence of acacH. [h] Ligand exchange between $Mn(acac)_3$ and datiH. [i] Reaction of $MnCl_2.4H_2O$ with Na[edtc]. [j] Me-salH = N-methylsalicylaldimine, abtH = 2-aminobenzenethiol, datiH = N,N'-disubstituted aminotroponimines, tbdH = 1-(2-thienyl)-1,3-butanedione, tftbd = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione.

neutralization is not neccessary.

$$MnCl_2.4H_2O + 2LH \longrightarrow MnL_2 + 4H_2O + 2HCl \qquad ..3.1$$

3.2 Synthetic studies

The following synthetic methods were investigated.

1. Nitrosation of naphthols or phenols in the presence of manganese(II) chloride tetrahydrate.
2. Reactions of 1-nqoH or 2-nqoH with manganese(II) chloride tetrahydrate or manganese(II) acetate tetrahydrate.
3. Reaction of Na[1-nqo] or Na[2-nqo] with manganese(II) chloride tetrahydrate.
4. Ligand exchange between $Mn(acac)_3$ and 1-nqoH or 2-nqoH.
5. Reactions of decacarbonyldimanganese(0) with 1-nqoH or 2-nqoH.

Previous studies had shown that the reaction of cobalt(II) chloride with 1-nqoH or 2-nqoH leads to the respective cobalt(III) tris-chelates.[14] Similarly the reaction of iron(II) chloride with 1-nqoH or 2-nqoH, and the nitrosation of 1-naphthol or 2-naphthol in the presence of an iron(II) salt, leads to a mixture of iron(II) and iron(III) chelates.[15] Not unexpectedly, nitrosations of 1-naphthol and 2-naphthol, in the presence of manganese(II) chloride tetrahydrate, led to tris(1,2-naphthoquinone 2-oximato)manganese(III) and tris-(1,2-naphthoquinone 1-oximato)manganese(III) respectively, in good yield. In marked contrast to the behaviour of the

naphthols, nitrosation of 4-methylphenol, 4-chlorophenol, or 4-t-butylphenol in the presence of manganese(II) chloride tetrahydrate did not lead to the respective manganese bis- or tris-chelates. Instead, complex mixtures of organic products were formed.

The reaction of Na[1-nqo] with manganese(II) chloride tetrahydrate afforded bis(1,2-naphthoquinone 1-oximato)manganese(II) in good yield. Similarly the corresponding reaction involving Na[2-nqo] led to bis(1,2-naphthoquinone 2-oximato)manganese(II) in satisfactory yield. The reaction of manganese(II) acetate tetrahydrate with 1,2-naphthoquinone 1-oxime, 1,2-naphthoquinone 2-oxime, or their sodium salts, gave the corresponding manganese(II) bis-chelate in satisfactory yield. In contrast, reactions of manganese(II) chloride tetrahydrate with the protonated ligands led to manganese-containing products which were ill-defined by i.r.

Neutral complexes of manganese(III) with anionic chelating ligands have previously been prepared in satisfactory yield by the ligand exchange method. For example, the reaction of $Mn(acac)_3$ with datiH (datiH = N,N'-disubstituted aminotroponimines) leads to $Mn(acac)(dati)_2$.[10] It has also been reported that $Ru(acac)_3$ undergoes reductive ligand exchange with 1-nqoH to give $Ru(1\text{-nqo})_2$.[16] The reactions of $Mn(acac)_3$ (1 mol eq.) with 1-nqoH and 2-nqoH (3 mol eq.) led to tris(1,2-naphthoquinone 1-oximato)manganese(III) and tris-(1,2-naphthoquinone 2-oximato)manganese(III), respectively,

in good yield. This is the first reported instance of ligand exchange between a first series transition metal chelate of an anionic ligand and a 1,2-quinone mono-oxime and provides a convenient route to complexes of type $Mn(qo)_3$.

As noted in Chapter two, $Fe(1\text{-}nqo)_2$ and $Fe(2\text{-}nqo)_2$ can be prepared by the reaction of $Fe(CO)_5$ with 1-nqoH or 2-nqoH respectively. Similarly, the synthesis of $Mn(dati)_3$ by the reaction of datiH with $Mn_2(CO)_{10}$ has been reported (Table 3.1). The reaction of $Mn_2(CO)_{10}$ (1 mol eq.) with 1-nqoH or 2-nqoH (6 mol eq.), however, led to thermal decomposition of the protonated ligands (see Chapter 2) instead of manganese(II) or manganese(III) complexes.

It has previously been reported that the reaction of $Fe(qo)_3$ (1 mol eq.) (qoH = 1-nqoH, 2-nqoH, or 5-OMeqoH) with hydrochloric acid (6M) leads to $Fe(qo)_2Cl$ (1 mol eq.) and qoH (1 mol eq.).[17] However, when the complexes $Fe(qo)_3$ were stirred with hydrochloric acid (6M) in this study, iron-containing products of indefinite composition and qoH (trace) were obtained. In contrast, $Mn(1\text{-}nqo)_3$ or $Mn(2\text{-}nqo)_3$ (1 mol eq.) reacted smoothly with hydrochloric acid (6M) to give 1-nqoH and 2-nqoH (3 mol eq.) respectively.

3.3 Structural studies

Elemental analysis of manganese(II) and manganese(III) complexes prepared in this study showed their formulations to be $Mn(nqo)_2$ and $Mn(nqo)_3$ respectively. Relative molecular mass measurements could not be carried out due to insolubility of the manganese(II) complexes and decomposition of the manganese(III) complexes in solvents suitable for such measurements.

I.r. studies indicated that the C=O vibrations in $Mn(1\text{-}nqo)_2$ (Figure 3.1) $Mn(2\text{-}nqo)_2$ (Figure 3.2), $Mn(1\text{-}nqo)_3$ (Figure 3.3), and $Mn(2\text{-}nqo)_3$ (Figure 3.4) occur at 1610, 1615, 1605, and 1625 cm^{-1} respectively. As noted in Chapter 2, the C=O frequencies of 1-nqoH and 2-nqoH are 1618 and 1668 cm^{-1}, respectively. This lowering of the C=O frequency upon complexation indicates the involvement of the carbonyl group in chelation.

The electronic absorption spectra of $Mn(1\text{-}nqo)_3$ and $Mn(2\text{-}nqo)_3$ were investigated in order to determine crystal field parameters. The configuration d^4, manganese(III), can lead to either a quintet (^5E_g) or a triplet ($^3T_{1g}$) ground state.[18] Several spin-allowed bands are possible for the triplet ground state. In contrast, the ^5E_g ground state can give rise to only one spin-allowed transition. The spectrum of $Mn(2\text{-}nqo)_3$ exhibited three d-d bands at 775, 590, and 475 nm and an intense ligand band at 338 nm (Figure 3.5). The spectrum of Mn(1-nqo)3 consisted of an intense ligand band at 412 nm and a d-d band at 825 nm

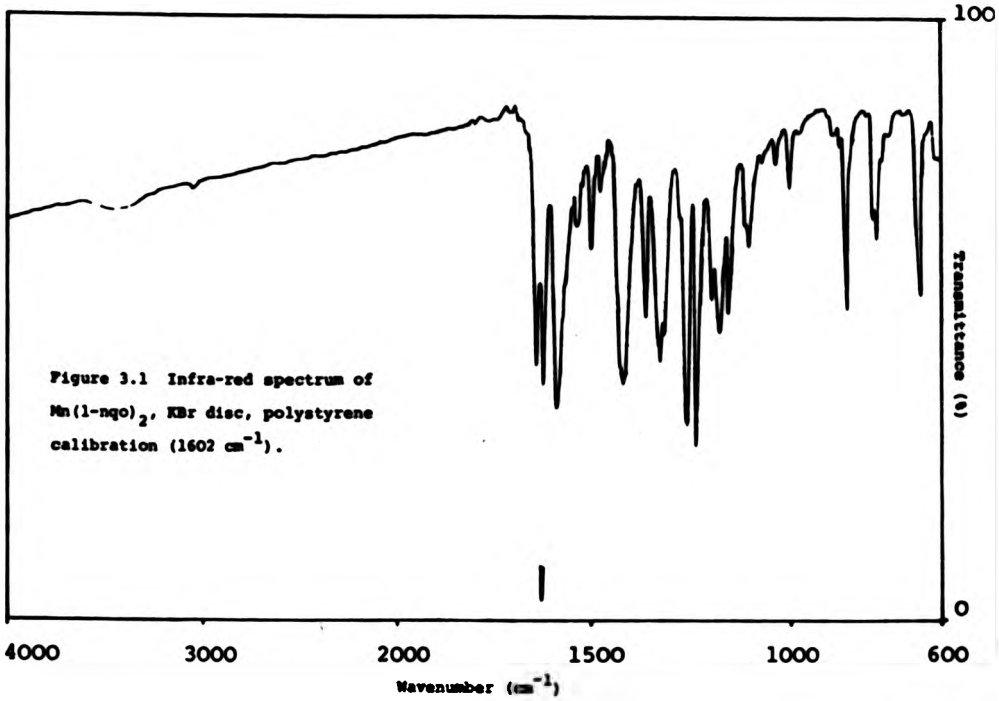


Figure 3.1 Infra-red spectrum of $Mn(1\text{-nqo})_2$, KBr disc, polystyrene calibration (1602 cm^{-1}).

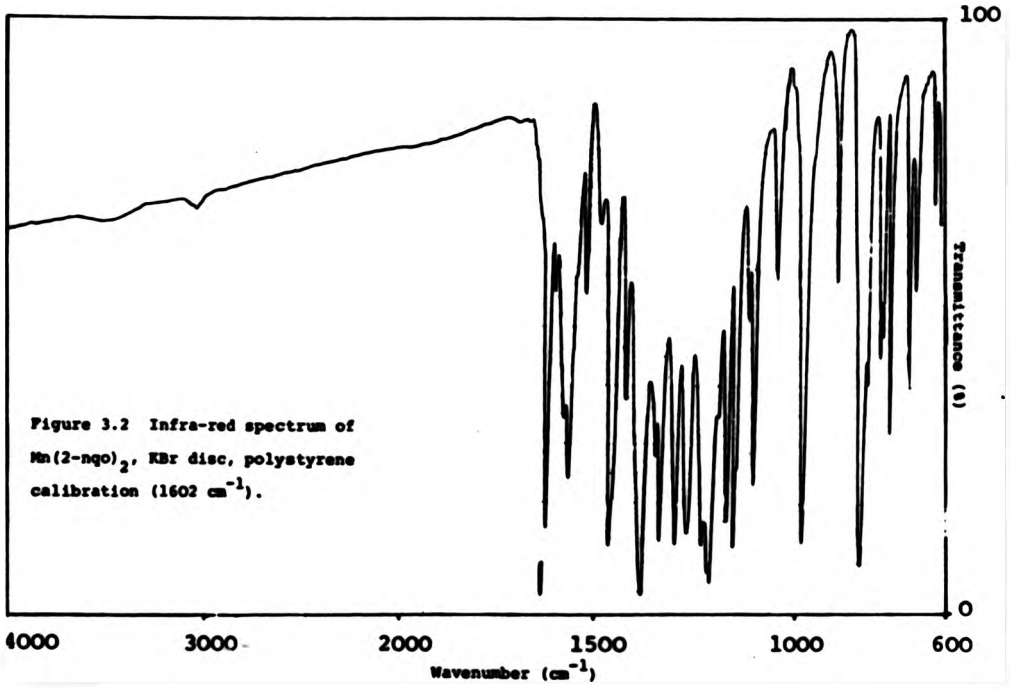


Figure 3.2 Infra-red spectrum of $Mn(2\text{-nqo})_2$, KBr disc, polystyrene calibration (1602 cm^{-1}).

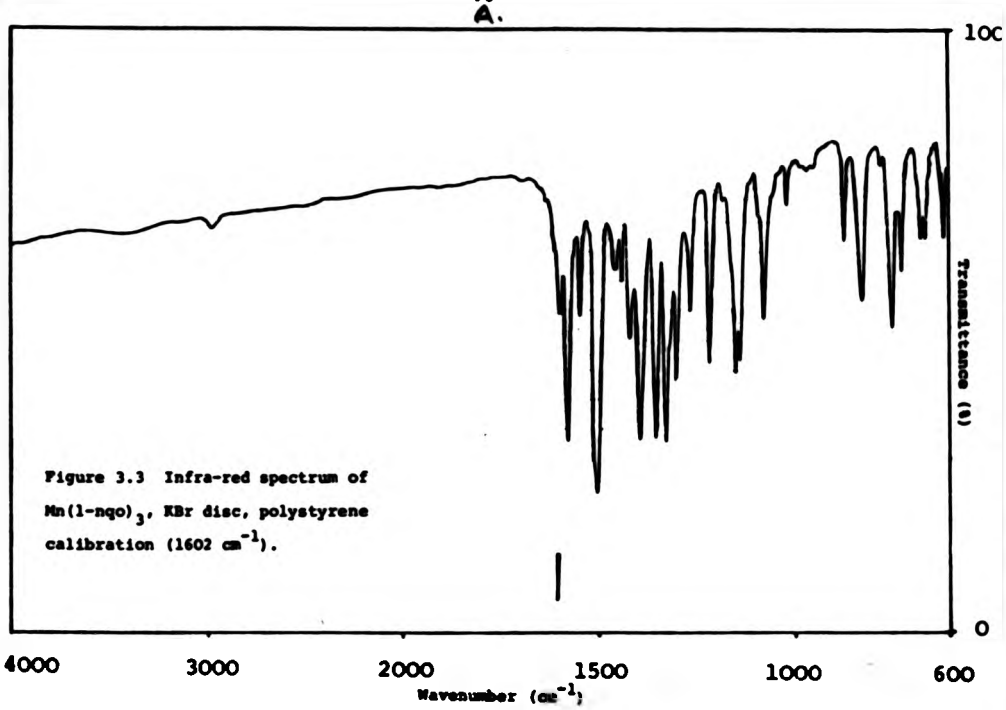


Figure 3.3 Infra-red spectrum of $Mn(1\text{-nqo})_3$, KBr disc, polystyrene calibration (1602 cm^{-1}).

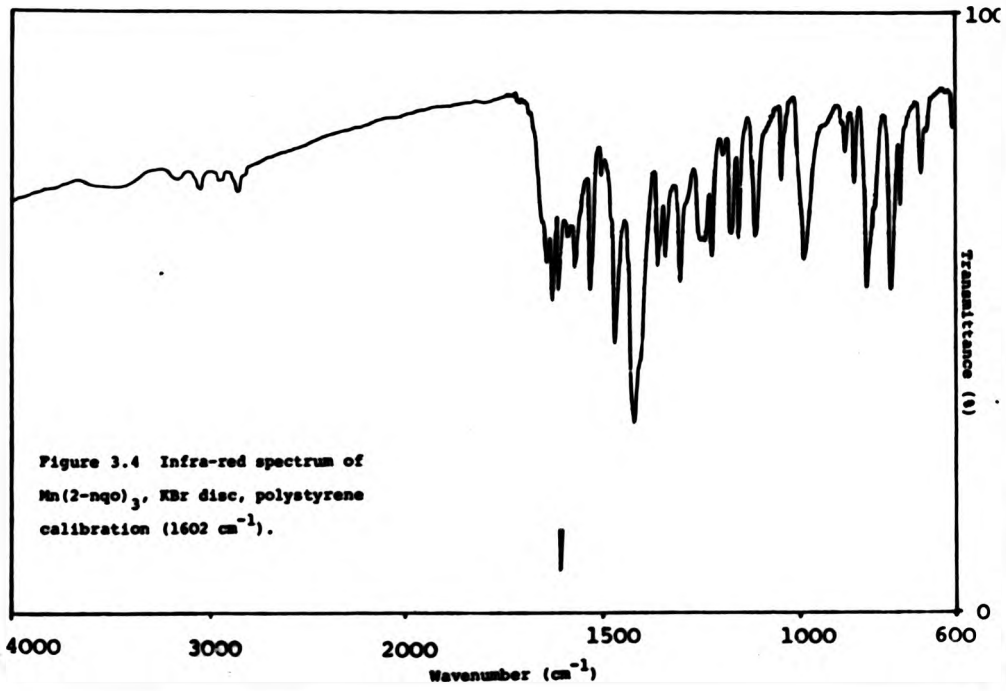


Figure 3.4 Infra-red spectrum of $Mn(2\text{-nqo})_3$, KBr disc, polystyrene calibration (1602 cm^{-1}).

(Figure 3.6). It is likely that the d-d spectrum of $Mn(1\text{-nqo})_3$ is obscured by the ligand band. Assignment of the d-d spectrum of $Mn(2\text{-nqo})_3$ was not possible and crystal field parameters could not be determined. The number of d-d bands observed, however, pointed towards the triplet ground state ($^3T_{1g}$). Molar absorptivities of $Mn(2\text{-nqo})_3$ and $Mn(1\text{-nqo})_3$ are given in Table 3.2.

Table 3.2 Electronic absorption results for the complexes $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ in acetone at 30.0 ± 0.3 °C.

Compound/ concentration mol dm^{-3}	λ_{max} nm	ϵ m^2 mol^{-1}
$Mn(2\text{-nqo})_3$	775	298
2.28×10^{-5}	590	243
	475	606
	338	2450
$Mn(1\text{-nqo})_3$	825	725
1.60×10^{-5}	412	2950

The room temperature magnetic moments of the complexes $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ were found to be 2.75 and 2.70 B.M. respectively. These values are close to the spin-only magnetic moment expected for spin-paired manganese(III) (2.83 B.M.) and indicate a triplet ground state ($^3T_{1g}$). Spin-paired manganese(III) complexes are not common.

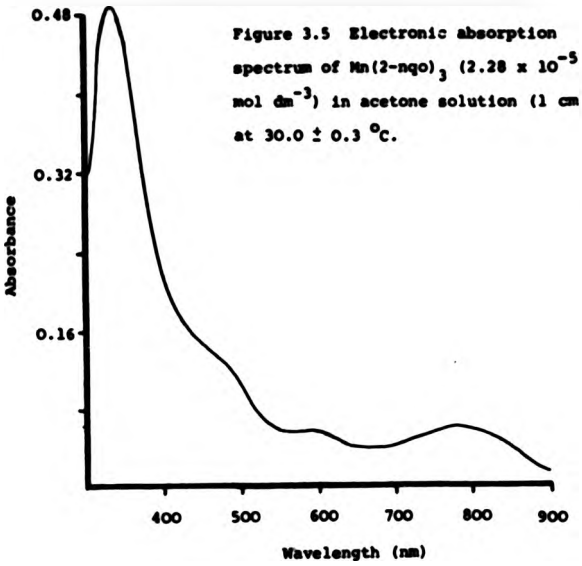


Figure 3.5 Electronic absorption spectrum of $Mn(2\text{-nqo})_3$ (2.28×10^{-5} mol dm^{-3}) in acetone solution (1 cm cell) at 30.0 ± 0.3 °C.

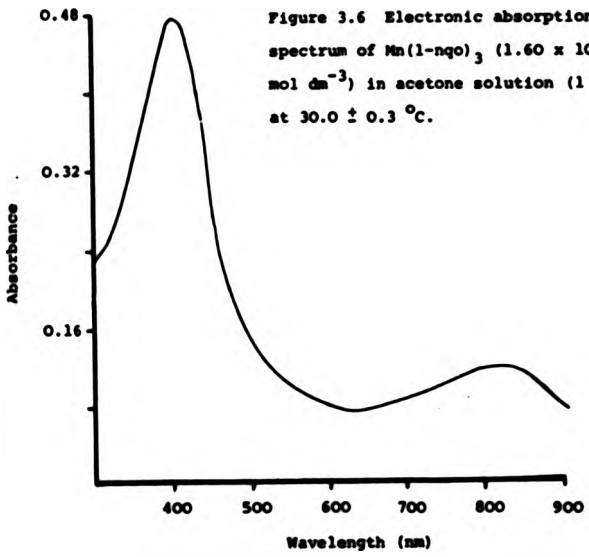


Figure 3.6 Electronic absorption spectrum of $Mn(1\text{-nqo})_3$ (1.60×10^{-5} mol dm^{-3}) in acetone solution (1 cm cell) at 30.0 ± 0.3 °C.

Usually manganese(III) complexes are spin-free and their room temperature magnetic moments lie in the range 4.85 - 5.10 B.M. Thus, $Mn(acac)_3$ and mixed ligand complexes of type $Mn(acac)(dati)_2$ are all spin-free.[10] The dithiocarbamate ligands can induce intermediate and spin-paired behaviour in iron(III),[19] but manganese(III) is the only case with a possible choice of spin states for which all the tris-dithiocarbamato complexes reported to-date are spin-free.[20] Amongst the few spin-paired manganese(III) complexes is tris(dimethylaminotroponiminato)manganese(III), for which the room temperature magnetic moment is 3.12 B.M.[10] Manganese(III) spin crossover has been reported in M(taa) ($taaH_3$ = tris[1-(2-azolyl)-2-azabuten-4-yl]amine).[21] In this complex, the room temperature magnetic moment falls from 4.9 to 3.2 B.M. corresponding to a change from four to two unpaired electrons. $TaaH_3$ is a strong-field ligand and so are 1,2-quinone mono-oximes. For example, $Fe(1\text{-nqo})_3$ and $Fe(2\text{-nqo})_3$ are spin-paired complexes.[22] Thus, the spin-paired configurations of $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ are not surprising.

The room temperature magnetic moments of $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$ were 5.51 and 5.50 B.M., respectively. An octahedral or tetrahedral spin-free mono-nuclear manganese(II) complex has a $^6A_1$ ground state ($^6A_{1g}$ for octahedral) and a spin-only magnetic moment of 5.92 B.M. which is independent of temperature.[23] If the symmetry of the manganese(II) complexes is lower than cubic, the $^6A_1$ term can be split to some extent by 'mixing in', via spin

orbit coupling, the split components of a high-lying $^4T_1$ term. If this zero field splitting becomes of the order of several wavenumbers, then departures from the spin-only value of the magnetic moment and from Curie law behaviour can be expected. Thus, for spin-free square planar or five coordinate manganese(II) complexes the observed magnetic moments may be lower than the spin-only value and could depend on temperature. This is not a necessary consequence of these stereochemistries as magnetic properties will depend not only on the magnitude of the splitting of the $^4T_1$ level but also on the energy seperation from the ground term.

Furthermore any significant antiferromagnetic interaction between the manganese ions may give a measureable decrease in the room temperature magnetic moment and cause it to vary significantly with temperature. Indeed, previous studies have shown that magnetic moments of the complexes $Ni(qo)_2$ decrease with temperature and have negative Weiss constants.[24] This antiferromagnetic interaction between the metal atoms has been rationalised in terms of association of $M(qo)_2$ units. Results of variable temperature magnetic studies on $Mn(1\text{-}nqo)_2$ and $Mn(2\text{-}nqo)_2$ are presented in Table 3.3. The measurements were carried out at various field strengths. The susceptibility values have been corrected for diamagnetism.

Table 3.3 Variable temperature magnetic study of $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$

$Mn(1\text{-nqo})_2$						
T (^oK)	295.1	273.0	240.0	202.1	153.0	93.2
$10^6 X_A$	12860	13670	15504	18018	22330	31420
μ_{eff} (B.M.)	5.51	5.47	5.46	5.40	5.22	4.84
$Mn(2\text{-nqo})_2$						
T (^oK)	295.3	273.0	240.3	202.1	153.0	93.2
$10^6 X_A$	13260	14184	15625	18349	22472	31746
μ_{eff} (B.M.)	5.60	5.57	5.48	5.45	5.25	4.87

The susceptibilities of the complexes $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$ are independent of the field strength used and follow the Curie-Weiss law with negative Weiss constants of 45^o and 51 ^oK respectively (Figures 3.7 & 3.8). This suggests antiferromagnetic interaction between adjacent manganese ions and association of $Mn(nqo)_2$ units. This type of behaviour has previously been reported for manganese(II) Schiff base complexes and accounted for by assuming either a binuclear or a long linear chain structure.[23] The antiferromagnetic behaviour of the complexes $Mn(nqo)_2$, their extreme insolubility, and their stability towards Lewis bases (see Chapters 4 and 5) indicates that these complexes are also long chain polymers (Figure 3.9). This type of infinite chain polymeric structure has previously been reported for $Mn(edtc)_2$.[13]

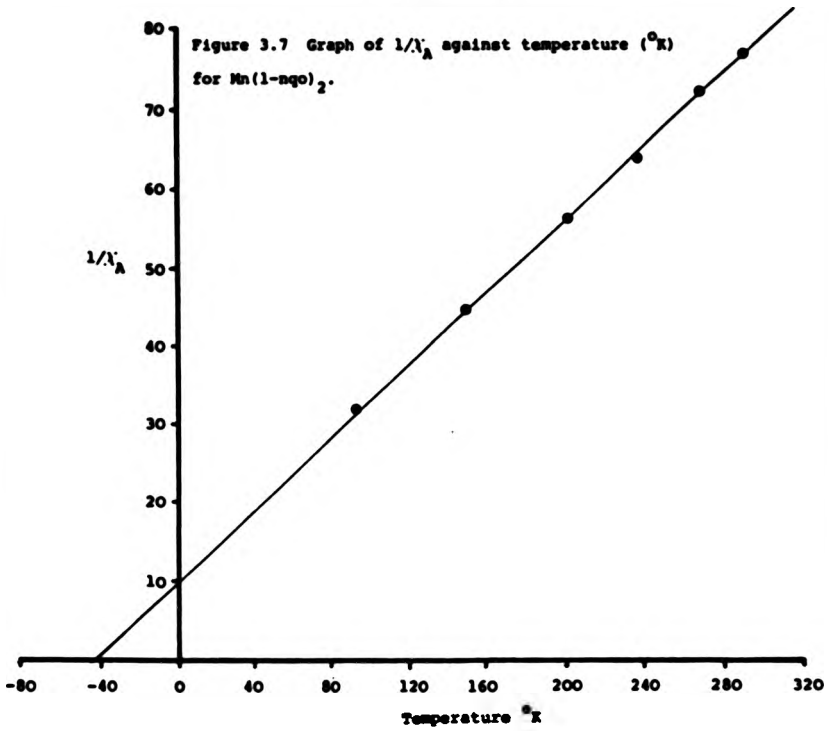


Figure 3.7 Graph of $1/\chi_A$ against temperature (^{o}K) for $Mn(1\text{-nqo})_2$.

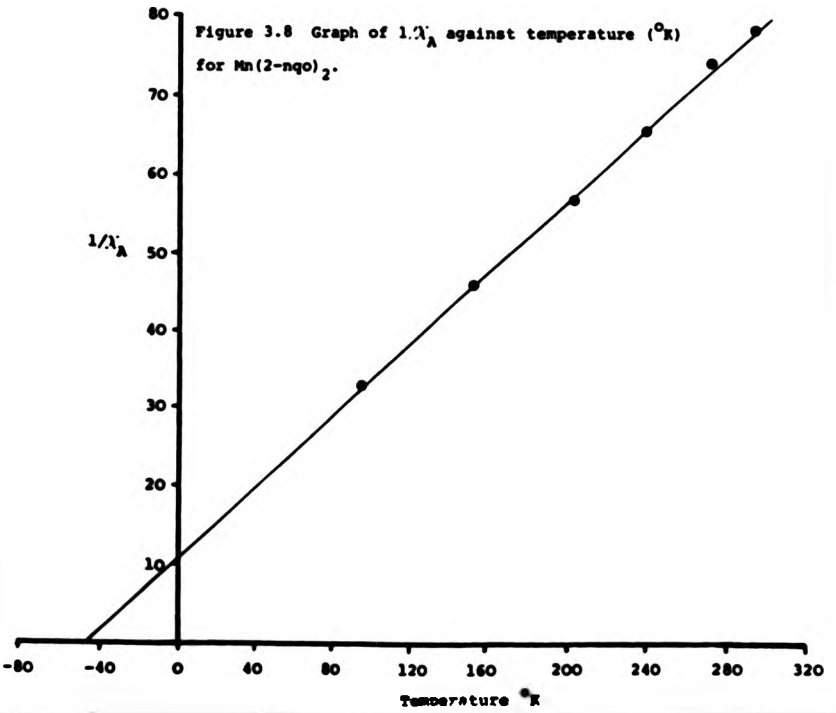
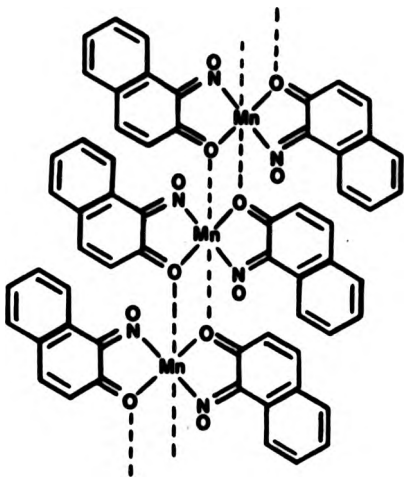


Figure 3.8 Graph of $1/\chi_A$ against temperature (^{o}K) for $Mn(2\text{-nqo})_2$.

Figure 3.9 Polymeric structure of $Mn(1\text{-nqo})_2$.



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CHAPTER FOUR

INTERNAL REDOX REACTIONS OF CHROMIUM AND MANGANESE COMPLEXES OF 1,2-QUINONE MONO-OXIMES

A study has been made of Lewis base induced internal redox reactions of the complexes $M(qo)_n$ (qoH = 1,2-naphthoquinone 1-oxime or 1,2-naphthoquinone 2-oxime, n = 3, M = Cr; n = 2 or 3, M = Mn). The Lewis bases used were triphenylphosphine, dimethyl sulphoxide, tetrahydrofuran, acetone, methyl cyanide, and benzene.

4.1 Nature and importance of internal redox reactions

Past studies have shown that neutral transition metal chelates of anionic ligands undergo three main types of reaction with Lewis bases. These are : (1) adduct for-

mation, (2) reaction with the coordinated ligand and, (3) internal redox reaction. The former two types of reaction occur in the case of complexes in which the metal is not easily reduced. They lead to products in which the oxidation state of the metal remains unchanged. An essential requirement of an internal redox reaction is the presence of an easily reducible metal in the complex. Generally, this type of reaction leads to products which contain the metal in a reduced oxidation state.

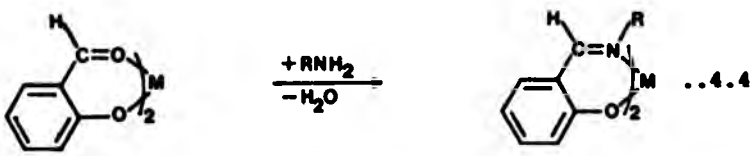
In adduct formation, a coordinate bond is formed between the metal and the Lewis base (Reactions 4.1,[1-4] 4.2,[5,6] 4.3[7]).

$$Cu(edtc)_2 + 2Ph_3P \longrightarrow Cu(edtc)_2(Ph_3P)_2 \qquad ..4.1$$

$$Ni(Sacac)_2 + 2py \longrightarrow Ni(Sacac)_2(py)_2 \qquad ..4.2$$

$$Cu(qo)_2 + imid \longrightarrow Cu(qo)_2(imid) \qquad ..4.3$$

Reactions involving the coordinated ligands are typified by the condensation of primary amines with transition metal chelates of salicylaldehyde (Reaction 4.4).[6]

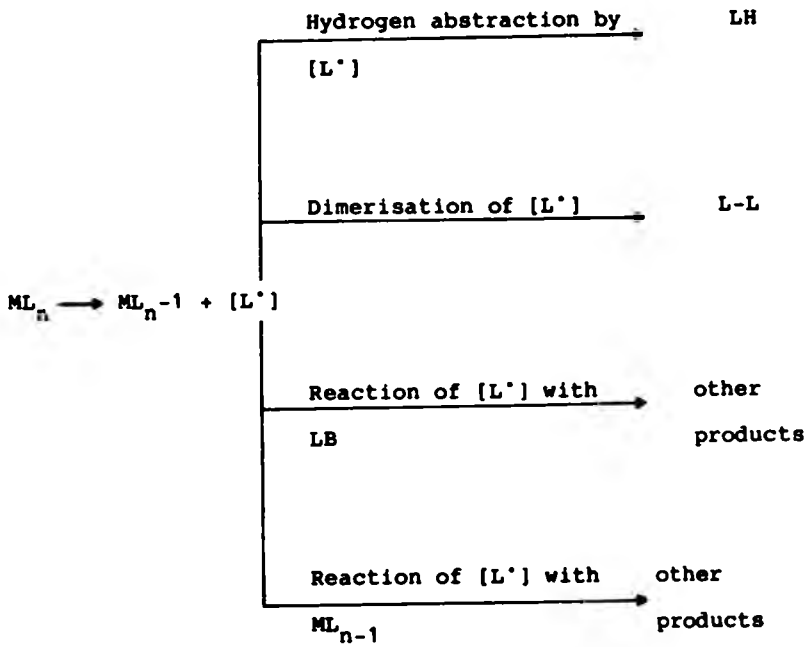


..4.4

Internal redox reactions occur by the homolytic cleavage of the M-L bond to give a reduced metal species and a ligand radical (Reaction 4.5). The various types of reaction which the ligand radical can undergo have been recently discussed (Sceheme 4.1).[8]

$$L_xM^n\underline{\frown\!\!\!\frown}L \longrightarrow L_xM^{n-1} + [L^\cdot] \qquad ..4.5$$

Scheme 4.1 Typical reactions of ligand radicals arising from internal redox reactions



In addition to the metal, the occurrence of an internal redox reactions is also dependent upon the Lewis base and the ligand. Thus, $Cu(qo)_2$ complexes

react with Lewis bases to give stable 1:1 adducts (LB= pyridine, imidazole and pyrazole).[7,9] In contrast, these complexes undergo internal redox reactions with primary amines[10] and triphenylphosphine.[11] Internal redox reactions are favoured by Lewis bases capable of stabilizing metals in low oxidation states (e.g. triphenylphosphine[8]). This is also true of ligands which can stabilize low oxidation states by means of their strong ligand field effects (e.g. 1,2-quinone mono-oximate and dithiocarbamate anions[8]).

Internal redox reactions are important in synthesis and catalysis. Their synthetic uses include the manganese(III) oxidation of aromatic hydrocarbons.[12] The first step in this oxidation involves an internal redox reaction (Scheme 4.2). The catalytic importance is shown by the metal catalysed epoxidation of olefins (Scheme 4.3)[13] and the addition of organic polyhalides to olefins (Scheme 4.4).[14-16]

Scheme 4.4 Catalytic addition of organic polyhalides to olefins

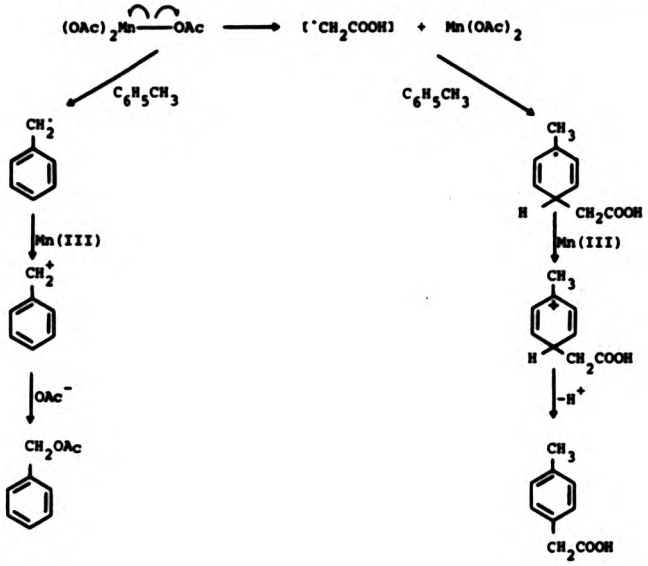
(1) $CuCl + CCl_4 \longrightarrow CuCl_2 + [CCl_3^{\bullet}]$

(2) $[CCl_3^{\bullet}] + R\text{-}CH{=}CHR \longrightarrow [CCl_3\text{-}CHR\text{-}CHR^{\bullet}]$

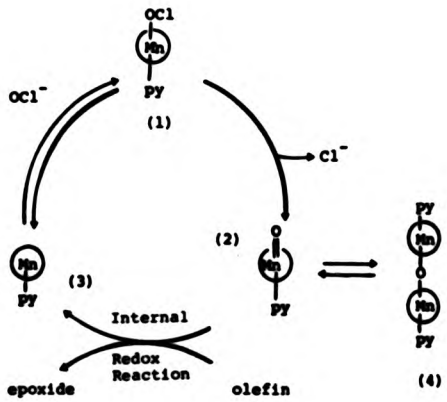
(3) $[CCl_3\text{-}CHR\text{-}CHR^{\bullet}] + ClCu^{II}Cl \longrightarrow CCl_3\text{-}CHR\text{-}CHRCl + CuCl$

Internal redox reations are also important in a number of biological systems. This is examplified by the role of copper in oxygenases. These enzymes are capable of opening oxidatively the aromatic rings of

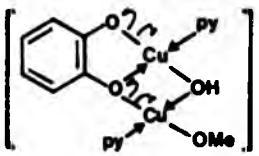
Scheme 4.2 Manganese(III) oxidation of aromatic hydrocarbons



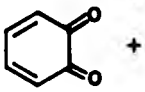
Scheme 4.3 Olefin epoxidation by the mono-oxygenase model (tetraphenylporphinato)manganese(III) acetate/ sodium hypochlorite.



phenols and catechols by inserting both atoms of an oxygen molecule into the substrate. It has been shown by means of model reactions that for the oxygenation of catechols, in the presence of pyridine and methanol, the oxidising species is a copper(II) complex.[17] Although these systems are complex it has been established that the initial stages of oxidation involve complex formation between catechol and the copper(II) species. Subsequently, copper(II) is reduced to copper(I) and benzoquinone is produced during a step which involves an internal redox reaction (Reaction 4.6).



..4.6



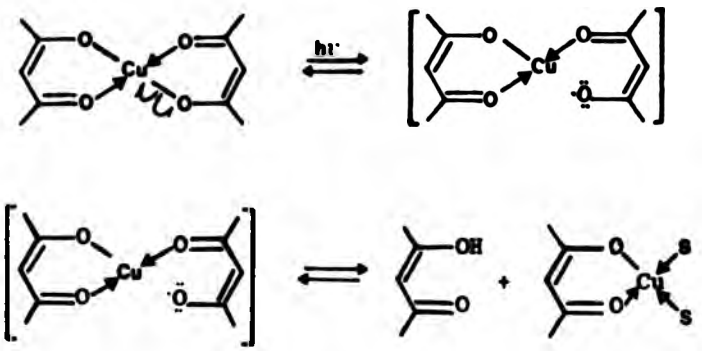
+ Cu(I) product

4.2 General assesment of the behaviour of metal complexes of 1,2-quinone mono-oximes towards Lewis base solvents

A number of internal redox reactions of first row transition metal complexes have been reported to be induced by irradiation,[18-20] thermolysis,[22] and Lewis base reagents.[10,11] In all cases, the reactions were

investigated in Lewis base solvents but the role of the solvent was not considered. For example, metal β-diketonate complexes are reported to undergo reduction upon irradiation in Lewis base solvents (Scheme 4.5)[18-20]. These reductions have been accounted for solely in terms of irradiation but it is likely that the solvent has also an effect.

Scheme 4.5 Reduction of bis(acetylacetonato)copper(II)



S = solvent molecule

Internal redox reactions of $Cu(qo)_2$ complexes with triphenylphosphine had previously been investigated in refluxing pyridine (qoH= 5-hydroxy-1,2-benzoquinone 2-oxime and 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime).[22] In these cases it is also likely that, in addition to triphenylphosphine, the reactions are induced to some extent by pyridine. Indeed, recent work has shown that $Cu(nqo)_2$ complexes undergo internal redox reactions with refluxing pyridine, in the absence

of triphenylphosphine.[23] Thus, knowledge concerning the behaviour of a Lewis base solvent towards a metal complex is important. Consequently, in this study the behaviour of chromium and manganese complexes derived from the mono-oximes of 1,2-naphthoquinones towards a number of Lewis base solvents has been investigated and compared with the analogous behaviour of other complexes (Table 4.1).

Previous studies have shown that the complexes $Cu(cup)_2$ and $Fe(nqo)_3$ do not undergo internal redox reactions with triphenylphosphine in aprotic solvents.[8,24] Similarly, none of the metal complexes investigated in this study show internal redox behaviour towards trichlorotrifluoroethane. These observations strongly indicate that proton abstraction is a crucial step in an internal redox reaction.

Interaction of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with pyridine led to internal redox reactions at room temperature. Iron(III) was reduced to iron(II) and the released ligand radicals afforded the protonated ligands by hydrogen abstraction (Reaction 4.7). Although less readily than with pyridine, the iron(III) chelates react similarly with other Lewis base solvents (Ref. 8 and Table 4.1).

$$Fe(nqo)_3 \xrightarrow{py} Fe(nqo)_2(py)_2 + [nqo^{\bullet}] \qquad ..4.7$$

$$[nqo^{\bullet}] \xrightarrow{H\text{-abstraction}} nqoH$$

Table 4.1 Behaviour of metal complexes derived from the mono-oximes of 1,2-naphthoquinones towards Lewis base solvents.

	Lewis base[a]							
	1	2	3	4	5	6	7	8
Complex								
$Fe(1\text{-nqo})_3$	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	NR
$Fe(2\text{-nqo})_3$	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	NR
$Co(1\text{-nqo})_3$	NR	NR	NR	NR	NR	NR	NR	NR
$Co(2\text{-nqo})_3$	NR	NR	NR	NR	NR	NR	NR	NR
$Cr(1\text{-nqo})_3$	IR[c]	NR	NR	NR	NR	NR	NR	NR
$Cr(2\text{-nqo})_3$	IR[c]	NR	NR	NR	NR	NR	NR	NR
$Mn(1\text{-nqo})_3$	IR[b]	NR	NR	NR	NR	NR	NR	NR
$Mn(2\text{-nqo})_3$	IR[b]	IR[b]	IR[b]	IR[b]	IR[b]	NR	IR[b]	NR
$Mn(1\text{-nqo})_2$	IR[d]	NR	NR	NR	NR	NR	NR	NR
$Mn(2\text{-nqo})_2$	IR[d]	NR	NR	NR	NR	NR	NR	NR
$Fe(1\text{-nqo})_2$	AF[b]	NR	NR	NR	NR	NR	NR	NR
$Fe(2\text{-nqo})_2$	AF[b]	NR	NR	NR	NR	NR	NR	NR
$Cu(1\text{-nqo})_2$	AF[b]	IR[c]	AF[c]	AF[c]	IR[c]	NR	NR	NR
$Cu(2\text{-nqo})_2$	AF[b]	IR[c]	AF[c]	AF[c]	IR[c]	NR	NR	NR
$Ni(1\text{-nqo})_2$	AF[d]	NR	NR	NR	NR	NR	NR	NR
$Ni(2\text{-nqo})_2$	AF[d]	NR	NR	NR	NR	NR	NR	NR

IR = internal redox reaction of $M(nqo)_n$ with Lewis base. AF = adduct formation of $M(nqo)_n$ with Lewis base. NR = no reaction of $M(nqo)_n$ with Lewis base solvent under ambient or reflux conditions. [a] 1 = Pyridine, 2 = dimethyl sulfoxide, 3 = tetrahydrofuran, 4 = acetone, 5 = methylcyanide, 6 = methanol, 7 = benzene, and 8 = trichlorotrifluoroethane. [b] Reaction of $M(nqo)_n$ upon stirring at 20 °C in neat Lewis base. [c] Reaction of $M(nqo)_n$ under reflux conditions in neat Lewis base. [d] Reaction of $M(nqo)_n$ under reflux conditions in a mixture of pyridine and acetone.

In contrast, the corresponding cobalt(III) chelates did not react with pyridine or any other Lewis base solvent at room temperature. This can be rationalised on the basis of crystal field stabilization energy (CFSE).[25] Reduction of spin-paired iron(III) (d^5) complexes to spin-paired iron(II) (d^6) complexes is favoured on CFSE grounds. In contrast, reduction of spin-paired cobalt(III) (d^6) complexes to spin-paired cobalt(II) (d^7) complexes is not favoured.

Like the cobalt(III) tris-chelates, the complexes $Cr(1\text{-nqo})_3$ or $Cr(2\text{-nqo})_3$ did not react with any of the Lewis base solvents under ambient conditions.

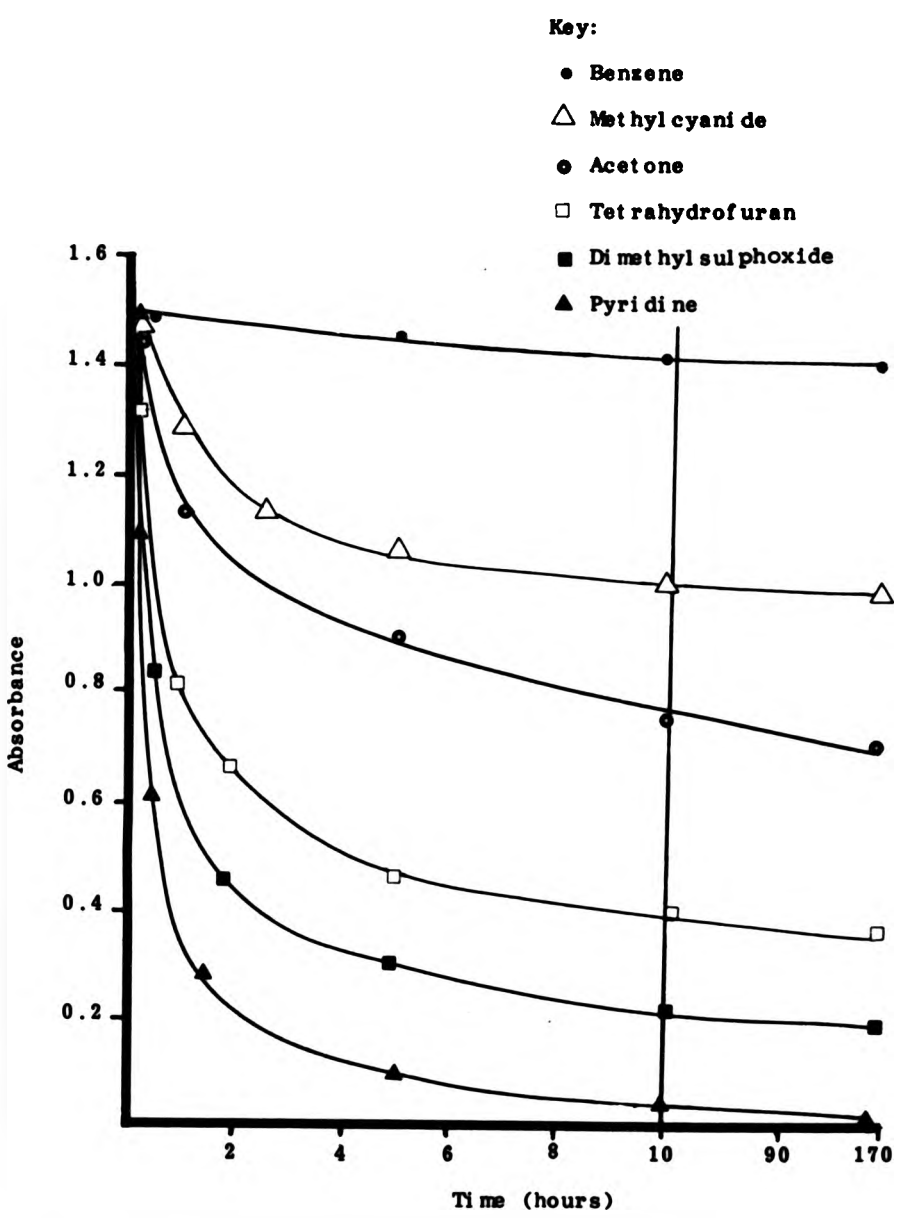
The complexes $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ were less reactive towards Lewis base solvents than the corresponding iron(III) complexes. Apart from pyridine, $Mn(1\text{-nqo})_3$ did not react with any of the Lewis base solvents after 168 hours of stirring at room temperature. In the reaction involving pyridine, the bulk of the tris-chelate was recovered unreacted (85% recovery).

The reactivity of $Mn(2\text{-nqo})_3$ towards Lewis base solvents was greater than that of $Mn(1\text{-nqo})_3$. Thus, $Mn(2\text{-nqo})_3$ gives an internal redox reaction with benzene, methyl cyanide, acetone, tetrahydrofuran, pyridine, or dimethyl sulphoxide. Apart from pyridine, none of the Lewis bases lead to complete consumption of $Mn(2\text{-nqo})_3$. The chelate was recovered in amounts ranging from 25%

to 80% after 168 hours of stirring at room temperature. Reaction of $Mn(2\text{-nqo})_3$ with pyridine afforded μ-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese-(III) (for characterisation of the μ-oxo complex see Chapter 5), 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (henceforth designated as phenazinone), and 2-nqoH. The lower reactivity of $Mn(1\text{-nqo})_3$ relative to $Mn(2\text{-nqo})_3$ follows the trend shown by these quinone mono-oximes and their metal complexes. 1,2-Naphthoquinone 2-oxime and its metal complexes are generally more reactive (see Chapter 5).

In order to correlate the rate of reaction of $Mn(2\text{-nqo})_3$ with Lewis base reactivity, the reactions of $Mn(2\text{-nqo})_3$ with the Lewis bases were followed spectrophotometrically. In a typical experiment, the absorbance at 780 nm of a 5×10^{-4} mol dm^{-3} solution of $Mn(2\text{-nqo})_3$ was monitored at 30.0 ± 0.3 °C. The reaction was considered complete when no significant change in the absorbance could be detected. Results are displayed in Figure 4.1. Lewis base reactivity towards $Mn(2\text{-nqo})_3$ follows the order pyridine > dimethyl sulphoxide > tetrahydrofuran > acetone > methyl cyanide > benzene. This is also the order of reactivity of these Lewis bases in the donor number (DN) approach of V. Gutmann.[26] The DN approach is an empirical method of predicting Lewis base reactivity. Donor 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,

Figure 4.1 Graph showing changes in the absorbance of $Mn(2\text{-nqo})_3$ (5.01×10^{-4} mol dm^{-3}) at 780 nm with time in selected Lewis base solvents at 30.0 $\pm$ 0.3 ^{o}C.



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 acid. For Gutmann's scale the reference acid is $SbCl_5$, and the negative of the heat of reaction of a dilute solution of the solvent with $SbCl_5$ in 1,2-dichloroethane is called the DN or donicity of the solvent. It is assumed that the entropy effects are constant and that 1:1 adducts are formed so that the DN is reflection of the inherent solvent to $SbCl_5$ bond strength. The most important assumption of the DN approach, however, is that the order of base strengths established by the $SbCl_5$ scale remains constant for all other acids.

The fact that the order of reactivity of the Lewis base solvents towards $Mn(2\text{-nqo})_3$ is same as their order of reactivity in the DN approach, indicates that the DN scale can be used for predicting the reactivity of other Lewis base solvents towards $Mn(2\text{-nqo})_3$.

The complexes $Cr(1\text{-nqo})_3$ and $Cr(2\text{-nqo})_3$ reacted with pyridine at 115 ^{o}C to give chromium-containing products whose elemental composition corresponded to $Cr(2\text{-nqo})_2$. However, these products were ill-defined by i.r. and they did not give nqoH on treatment with concentrated hydrochloric acid. In addition, the reaction involving $Cr(1\text{-nqo})_3$ afforded 6-hydroxydibenzo[b,kl]acridin-8-one and 1-nitro-2-naphthol. Phenazinone and 2-nitro-1-naphthol were obtained from the reaction of $Cr(2\text{-nqo})_3$. In

each of the above cases, the loss of one mole of ligand per mole of complex was indicated by the amount of organic products formed. This is indicative of an internal redox reaction (Reaction 4.8).

$$(nqo)_2Cr\overset{O}{\frown}nqo \longrightarrow Cr(nqo)_2 + [nqo^{\bullet}] \quad ..4.8$$

$[nqo^{\bullet}] \downarrow$ other products

$Cr(1\text{-}nqo)_3$ and $Cr(2\text{-}nqo)_3$ do not undergo internal redox reactions in pyridine at ambient temperature or when refluxed in neat toluene. Thus, pyridine and heat are essential for these reactions.

As stated in Chapter 2, 2-nqoH undergoes deoxygenation in refluxing pyridine or toluene to give the phenazinone. In contrast, 1-nqoH does not yield the acridine under identical conditions. This indicates that in the case of 2-nqoH mere heat is sufficient to cause deoxygenation. Whereas in the case of 1-nqoH deoxygenation is influenced by the metal. To conclude, in the systems $Cr(1\text{-}nqo)_3$/pyridine and $Cr(2\text{-}nqo)_3$/pyridine: (1) the internal redox reactions are initiated by pyridine/heat, and (2) the metal and heat are jointly responsible for ligand deoxygenation.

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CHAPTER FIVE

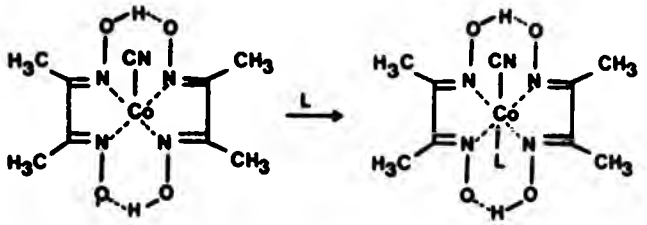
Triphenylphosphine induced internal redox reactions of chromium and manganese complexes of 1,2-quinone mono-oximes

Reactions involving triphenylphosphine and the complexes $M(qo)_n$ have been studied (qoH = 1,2-naphthoquinone 1-oxime, 1,2-naphthoquinone 2-oxime, 3-methyl-5-hydroxy-1,2-benzoquinone 2-oxime, or 6-methyl-5-hydroxy-1,2-benzoquinone 2-oxime, n = 3, M = Cr; qoH = 1,2-naphthoquinone 1-oxime or 1,2-naphthoquinone 2-oxime, n = 2 or 3, M = Mn). Reaction mechanisms have been proposed on the basis of the reaction products obtained and kinetic studies. The greater reactivity of 1,2-naphthoquinone 2-oxime and its metal complexes towards triphenylphosphine has been rationalised in terms of ligand stereochemistry.

5.1 Introduction

As a Lewis base, triphenylphosphine can take part in adduct formation reactions,[1] reactions with the coordinated ligands,[2] and internal redox reactions[3] with transition metal complexes.

Thus, the reaction of triphenylphosphine with cobaloximes leads to 1:1 adducts (Reaction 5.1a).[1] Tri-



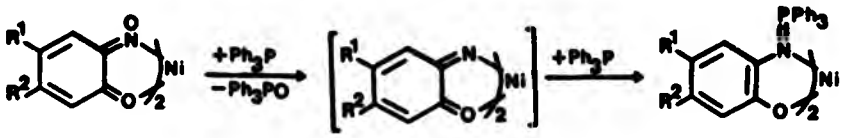
..5.1a

L = Ph_3P

phenylphosphine acts as a deoxygenating agent in reactions with the coordinated ligands. For example, the reaction of triphenylphosphine with $Ni(qo)_2$ or $Zn(qo)_2$ results in deoxygenation of the oximic group and formation of triphenyl-(2-hydroxyphenylimino)phosphorane complexes (Scheme 5.1).[2] The major impetus behind deoxygenation reactions comes from the great strength of the P=O bond formed.[4]

The occurrence of deoxygenation is indicated by the formation of triphenylphosphine oxide, but the involvement of nitrene intermediates has not been directly established. However, there is a plethora of indirect evidence from the deoxygenation of related

Scheme 5.1 Deoxygenation of nickel(II) complexes of 1,2-quinone mono-oximes by triphenylphosphine

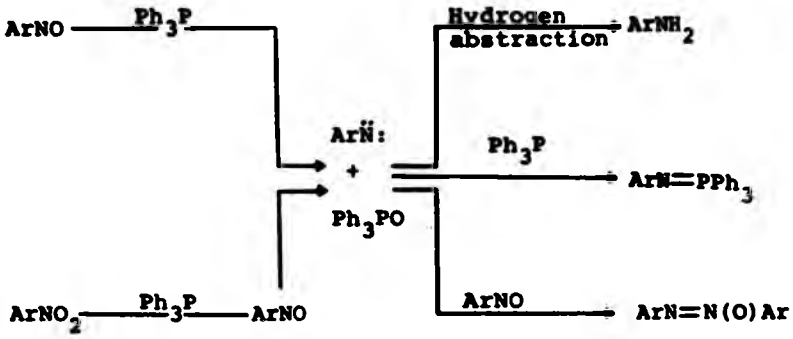


(R^2 = H, R^1 = Cl, Br, Me, H; R^2 =, OMe, R^1 = H)

nitroso and nitro compounds which indicates the involvement of nitrenes. Thus a large number of reactions are known in which aromatic nitroso and nitro derivatives are deoxygenated by tervalent phosphorus compounds to give various organic products and pentavalent phosphorus oxo compounds.[5-18] It has been suggested that these reactions proceed via nitrene intermediates.[19-30] These can react to give amines, N-aryliminophosphoranes and azoxy compounds (Scheme 5.2).

Complexes containing metals which are easily reducible, such as copper(II)[31] and iron(III),[10] undergo internal redox reactions with triphenylphosphine. These reactions are characterized by the formation of metal-containing products in which the metal has a reduced oxidation state. In addition to organic products arising by the loss of ligand species from the metal complex. Internal redox reactions may be preceded by adduct formation and/or reaction with the coordinated ligands. Thus, the

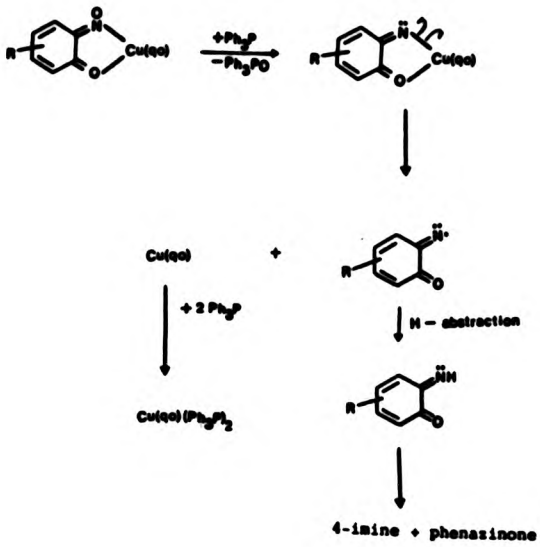
Scheme 5.2 Deoxygenation of aromatic nitro and nitroso compounds by triphenylphosphine



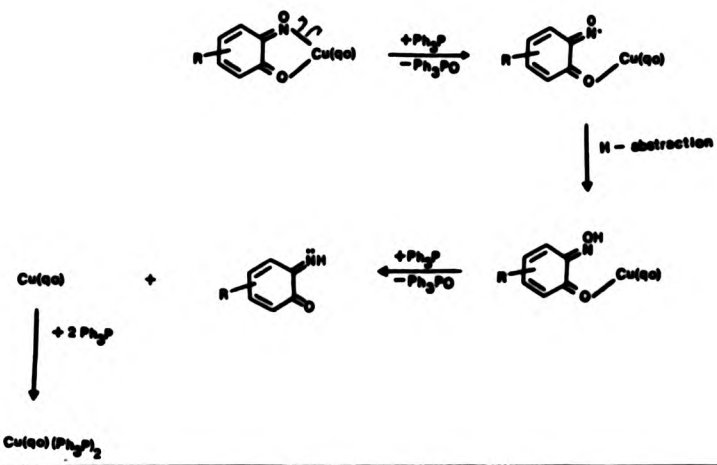
reaction of triphenylphosphine with $Cu(1\text{-nqo})_2$ gives $Cu(1\text{-nqo})(PPh_3)_2$, 1-phenylamino-2-naphthol, 1-amino-2--naphthol, and 6-hydroxydibenzo[b,kl]acridin-8-one. Similarly, the reaction of $Cu(2\text{-nqo})_2$ with triphenylphosphine leads to $Cu(2\text{-nqo})(PPh_3)_2$, 2-amino-$N^4$(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (henceforth designated as 4-imine), and phenazinone.

Two mechanisms have previously been proposed on the reaction of triphenylphosphine with $Cu(1\text{-nqo})_2$ or $Cu(2\text{-nqo})_2$. The mechanism outlined in Scheme 5.3, involves deoxygenation of the coordinated ligand followed by an internal redox reaction. In the mechanism shown in Scheme 5.4, internal redox reaction precedes deoxygenation. Recently, it was proposed on the basis of kinetic evidence that the reaction of triphenylphosphine with $Fe(1\text{-nqo})_3$ or $Fe(2\text{-nqo})_3$ is

Scheme 5.3 Reaction of the complexes $Cu(nqo)_2$ with triphenylphosphine - Internal redox reaction preceded by deoxygenation.



Scheme 5.4 Reaction of the complexes $Cu(nqo)_2$ with triphenylphosphine - Deoxygenation preceded by internal redox reaction.



dependent on the solvent (Reaction 5.1b).

$$Fe(nqo)_3 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(nqo)_3.S] \rightleftharpoons \text{products} \quad ..5.1b$$

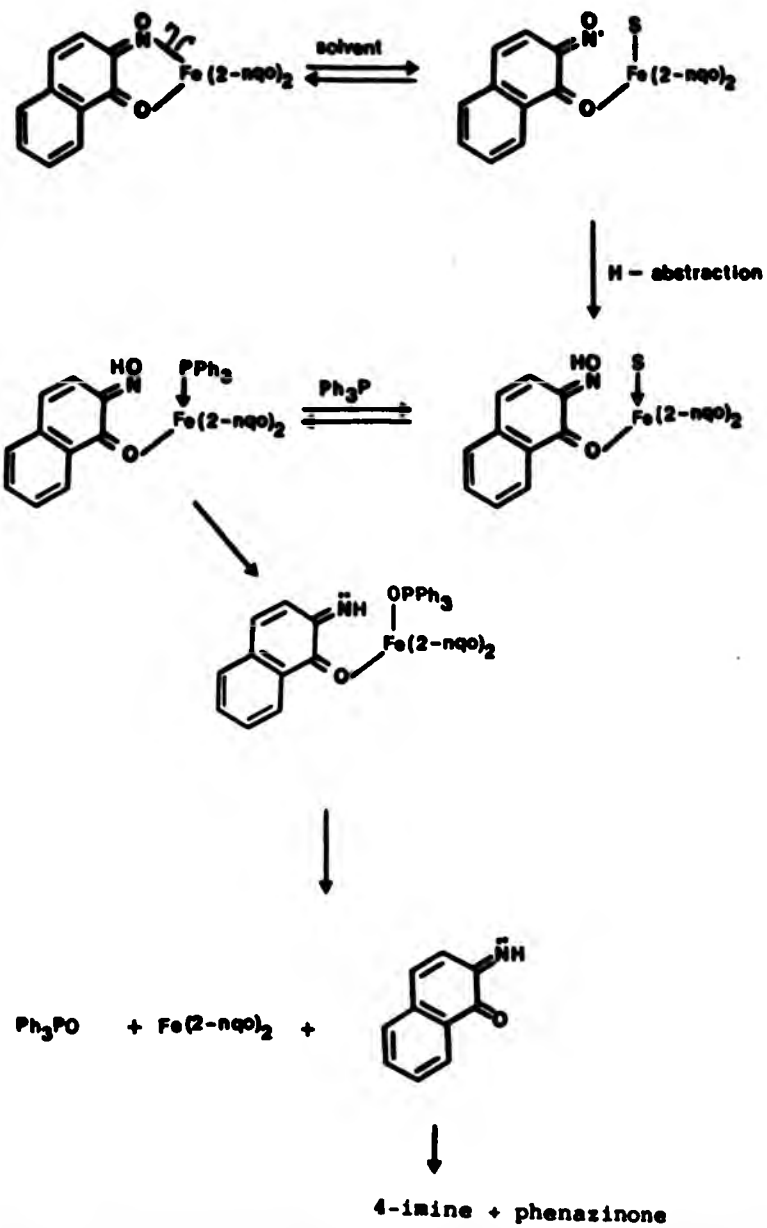
These reactions lead to intermediates of type $[Fe(nqo)_2(nqiH)(OPPh_3)]$. This indicates that, for reactions involving the iron(III) complexes, deoxygenation of the ligand molecule occurs whilst it is coordinated to the metal (Scheme 5.5).

5.2 Reaction of tris(1,2-naphthoquinone 1-oximato)-chromium(III) and tris(1,2-naphthoquinone 2-oximato)-chromium(III) with triphenylphosphine

A reaction did not occur when $Cr(1\text{-}nqo)_3$ (1 mol eq.) and triphenylphosphine (3 mol eq.) were stirred in acetone at room temperature for one month. In contrast, when $Cr(2\text{-}nqo)_3$ (1 mol eq.) was stirred with triphenylphosphine (3 mol eq.) in acetone at room temperature, a chromium-containing product '$Cr(2\text{-}nqo)_2$' (1 mol eq.), phenazinone (0.3 mol eq.), 4-imine (0.1 mol eq.), triphenylphospohine oxide (1 mol eq.), and unreacted triphenylphosphine (2 mol eq.) were obtained.

Elemental analysis of '$Cr(2\text{-}nqo)_2$' gave an empirical formula of $C_{20}H_{12}CrN_2O_4$ which indicates the presence of

Scheme 5.5 Reaction of Fe(2-nqo)2 with triphenylphosphine.



two ligand residues per chromium. However, the compound had an ill-defined i.r. spectrum and it did not react with concentrated hydrochloric acid. Normally the reaction of a metal complex, derived from 1,2-quinone mono-oximes, and hydrochloric acid leads to the protonated ligand. These results indicate that '$Cr(2\text{-nqo})_2$' is not a 1,2-quinone mono-oximato complex. The room temperature effective magnetic moment of '$Cr(2\text{-nqo})_2$' was 2.65 B.M., which is in the region expected for oxo-bridged multinuclear chromium(III) complexes.[32]

When the reaction of $Cr(2\text{-nqo})_3$ (1 mol eq.) with triphenylphosphine (3 mol eq.) in acetone was stopped after one hour of stirring at room temperature, bis(1,2-naphthoquinone 2-imine)tetrakis(1,2-naphthoquinone 2-oximato)dichromium(II) (0.3 mol eq.), '$Cr(2\text{-nqo})_2$', phenazinone (0.3 mol eq.), 4-imine (0.1 mol eq.), triphenylphosphine oxide(1 mol eq.), and unreacted triphenylphosphine (2 mol eq.) were obtained.

The i.r. spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was well-defined and exhibited a peak at 3120 cm^{-1} which may be attributed to N-H stretching (Figure 5.1). Elemental analysis of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was in accord with the formulation. Deoxygenation of one mole equivalent of 2-nqoH per mole equivalent of $Cr(2\text{-nqo})_3$ was indicated by the consumption of one mole equivalent of triphenylphosphine and by the formation of one mole equivalent of triphenylphosphine oxide.

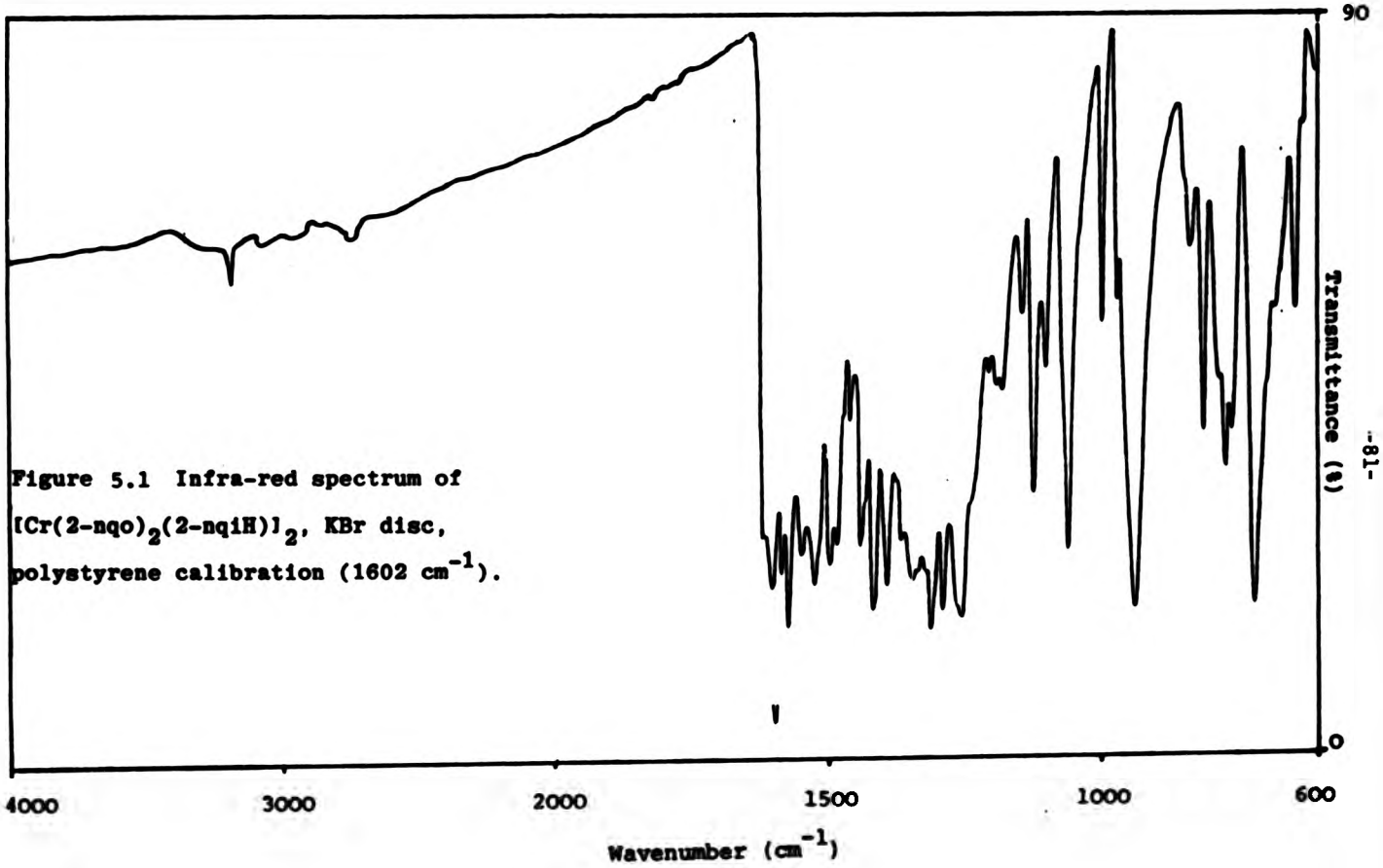


Figure 5.1 Infra-red spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$, KBr disc, polystyrene calibration (1602 cm^{-1}).

Attempts were made to crystallize $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ so that its structure could be determined directly by X-ray diffraction. These efforts, however, led either to decomposition in solution or to flaky crystals not suitable for X-ray diffraction studies. Thus, the chemical reactivity of the complex towards hydrochloric acid and pyridine was examined to gain further information on its structure. It was hoped that decomposition of the complex would occur to yield the ligands bonded to chromium.

When $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (1 mol eq.) was stirred with 6M hydrochloric acid at room temperature, phenazinone (0.6 mol eq.), 4-imine (0.1 mol eq.), 2-nqoH (trace), and '$Cr(2\text{-nqo})_2$' were obtained. In contrast, the complexes $Cr(nqo)_3$, $Mn(nqo)_3$, and $Fe(nqo)_3$ react with 6M hydrochloric acid to give nqoH as the only organic product. Furthermore, 2-nqoH does not react with 6M hydrochloric acid at room temperature. These results support the presence of the reactive nitrene/quinoneimine moeity in $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$. The nitrene/quinoneimine, liberated upon acidification of the dichromium complex, can lead to phenazinone and 4-imine by dimerisation.

When $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (1 mol eq.) was stirred with pyridine at room temperature, phenazinone (1 mol eq.) and '$Cr(2\text{-nqo})_2$' were obtained. In contrast, phenazinone was not obtained when 2-nqoH was stirred

with pyridine under identical conditions. This indicates the presence of 2-nqiH in $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (Reaction 5.2).

$$[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2 \xrightarrow{py} [2\text{-nqiH}] + \text{'}Cr(2\text{-nqo})_2\text{'} \quad 5.2$$

$$\downarrow$$

phenazinone + 4-imine

Room temperature magnetic susceptibility measurements showed that $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was diamagnetic. A likely explanation is metal-to-metal interactions. Chromium(II) and chromium(III) complexes with Cr--Cr interactions can have exceptionally low magnetic moments and can also exhibit diamagnetism.[32] The room temperature effective magnetic moments of $[Cr(salen)]_2O$[32a] and $\{[Cr(NH_3)_5]_2O\}Br_4$[32b] are 2.2 and 1.29 B.M. respectively, per chromium.

The electronic absorption spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was studied in order to enable a distinction to be made between chromium(III) (d^3) and chromium(II) (d^4). For a d^3 configuration in an octahedral crystal field, three spin allowed transitions are possible. In Chapter 2, the u.v./vis. spectrum of $Cr(2\text{-nqo})_3$ was rationalised in terms of these transitions. The d^4 configuration can lead to either a quintet (^5E_g) ground state or a triplet ($^3T_{1g}$) ground state.[33] For the triplet ground state, several spin allowed bands are possible because there

is more than one triplet excited state. But for the quintet ground state the only other quintet state is $^5T_{2g}$, so the spectrum is expected to exhibit only one d-d transition. The u.v./vis. spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was recorded in acetone solution (Figure 5.2) . Four bands ν_1 (708 nm), ν_2 (630 nm), ν_3 (520 nm) and ν_4 (473 nm) were found in the region 440-900 nm. They were assumed to be d-d transitions because: (1) they occur in the visible region, and (2) the ligand bands in the spectra of 1-nqoH, 2-nqoH, and their chromium, manganese, nickel,[34] and copper[34] chelates occur at wavelengths shorter than 440 nm.

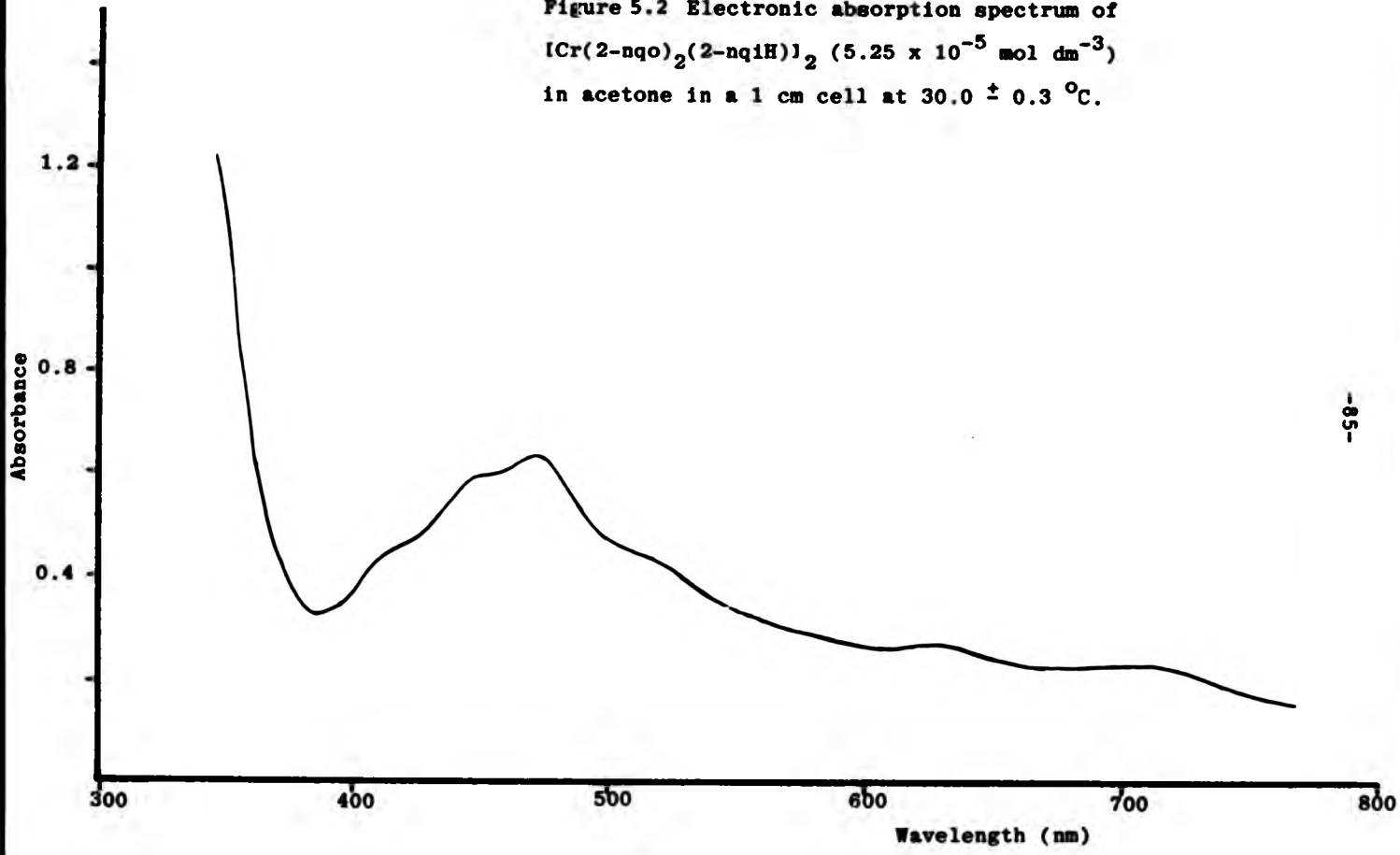
These d-d transitions could not be rationalised in terms of a chromium(III) (d^3) configuration. They could, however, be assigned to the four spin allowed transitions of the d^4 triplet state:

ν_1 $^3T_{1g} \longrightarrow {}^3E_g$
ν_2 $^3T_{1g} \longrightarrow {}^3T_{2g}$
ν_3 $^3T_{1g} \longrightarrow {}^3A_{1g}$
ν_4 $^3T_{1g} \longrightarrow {}^3A_{2g}$

To summerize, the u.v./vis. spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ pointed towards an oxidation state of +2.

1,2-Quinone mono-oximes induce strong ligand fields, for example, tris-chelates of manganese(III) and iron(III) are spin-paired complexes. It is highly

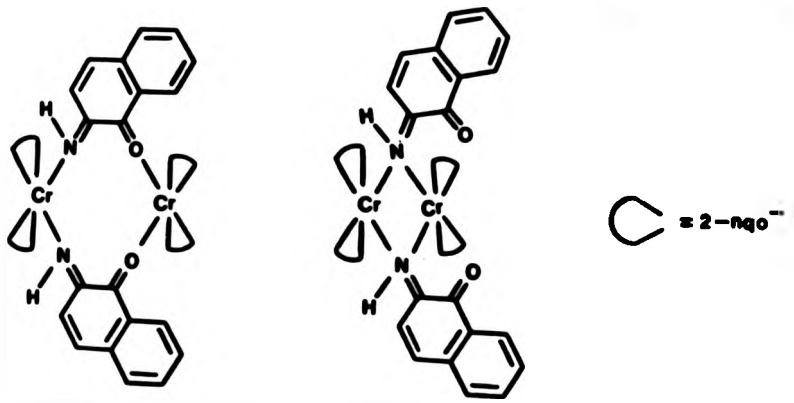
Figure 5.2 Electronic absorption spectrum of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (5.25×10^{-5} mol dm^{-3}) in acetone in a 1 cm cell at 30.0 ± 0.3 °C.



likely, therefore, that $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ is also a spin-paired complex. This would lead to a triplet ground state ($^3T_{1g}$), for a d^4 configuration, in accord with the assignment of the u.v./vis. spectrum. Spin-paired chromium(II) d^4 has a spin only magnetic moment of 2.82 B.M., whereas chromium(III) d^3 has a spin only magnetic moment of 3.87 B.M.[35] It is logical to assume that the probability of a chromium(II) complex being diamagnetic is higher than a chromium(III) complex.

On the basis of the foregoing discussion, two structures are likely for $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (Figure 5.3). Structure B is more probable as it would have a shorter Cr--Cr distance and, hence, greater likelyhood of diamagnetism.

Figure 5.3 Possible structures for $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$



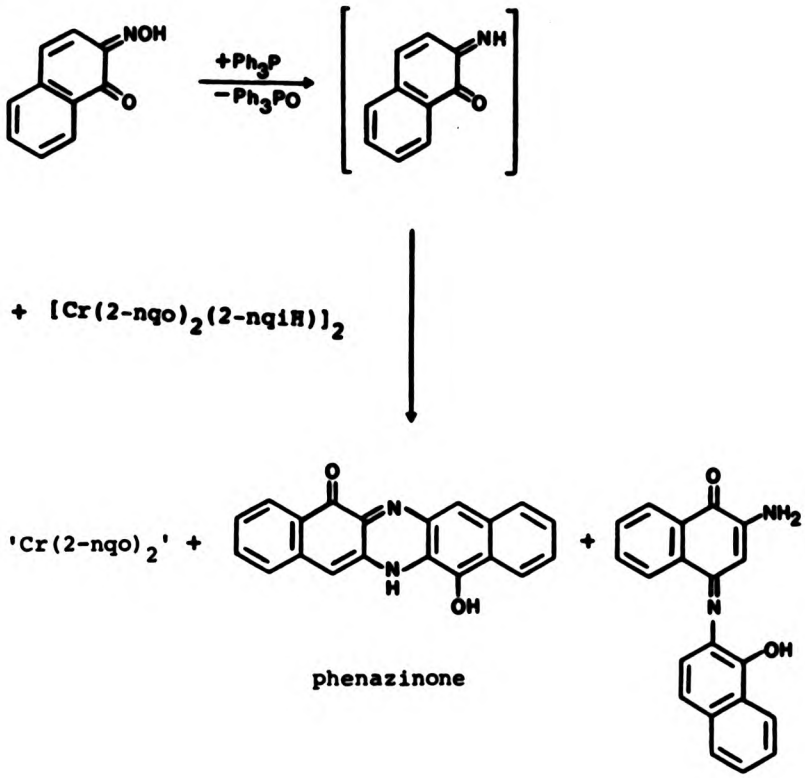
A B

A number of reactions were carried out in order to

determine what causes the decomposition of the intermediate $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ to '$Cr(2\text{-nqo})_2$' during the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine. Thus, $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was stirred at room temperature for twelve days in (1) acetone, (2) acetone/triphenylphosphine, (3) acetone/-phenazinone, (4) acetone/4-imine and, (5) acetone/-/2-nqoH. None of these mixtures, however, led to decomposition of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$.

The organic products obtained in the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine have previously been obtained from the analogous reaction of $Cu(2\text{-nqo})_2$ and rationalised in terms of deoxygenation of the ligand molecules and nitrene intermediates.[36,37] It was thought, therefore, that decomposition of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ could be caused by the reactive nitrene intermediate (2-nqiH) inherent in the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine. Thus, $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (0.5 mol eq.), triphenylphosphine (2.5 mol eq.), and 2-nqoH (2.5 mol eq.) were stirred in acetone at room temperature. It was thought that 2-nqoH would react with triphenylphosphine to generate the nitrene/quinoneimine, which could then react with the coordinated nitrene/quinoneimine in $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ (Scheme 5.6). Significantly, total decomposition of the dichromium complex occurred in twenty four hours to yield '$Cr(2\text{-nqo})_2$', phenazinone (1.2 mol eq.), 4-imine (0.3 mol eq.), and triphenylphosphine oxide (2.5 mol eq.).

Scheme 5.6 Nitrene/quinoneimine induced decomposition of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$.



5.3 Reactions of manganese(II) and manganese(III) complexes of 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime with triphenylphosphine

A reaction did not occur when $Mn(1\text{-nqo})_2$ or $Mn(2\text{-nqo})_2$ (1 mol eq.) was stirred or refluxed with triphenylphosphine (2 mol eq.) in acetone. In marked contrast, $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ reacted readily with triphenylphosphine. The inertness of $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$ towards triphenylphosphine is not entirely unexpected as variable temperature magnetic suceptibility measurements have indicated their polymeric nature (see Chapter 3).

When $Mn(2\text{-nqo})_3$ (1 mol eq.) was stirred with triphenylphosphine (3 mol eq.) in acetone at room temperature for twenty five minutes, μ-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese-(III) (0.5 mol eq.), phenazinone (0.3 mol eq.), 4-imine (0.1 mol eq.), triphenylphosphine oxide (1 mol eq.), and unreacted triphenylphosphine (2 mol eq.) were obtained. The μ-oxo complex was well-defined by i.r. (Figure 5.4) and its elemental analysis was in accord with the formulation. The room temperature effective magnetic moment of 2.61 B.M. per manganese was in the region expected for spin-paired manganese(III).[35] The reaction of $[Mn(2\text{-nqo})_2]_2O$ (1 mol eq.) with 6M hydrochloric acid gave 2-nqoH (4 mol eq.), which supports the formulation of the μ-oxo dimanganese complex.

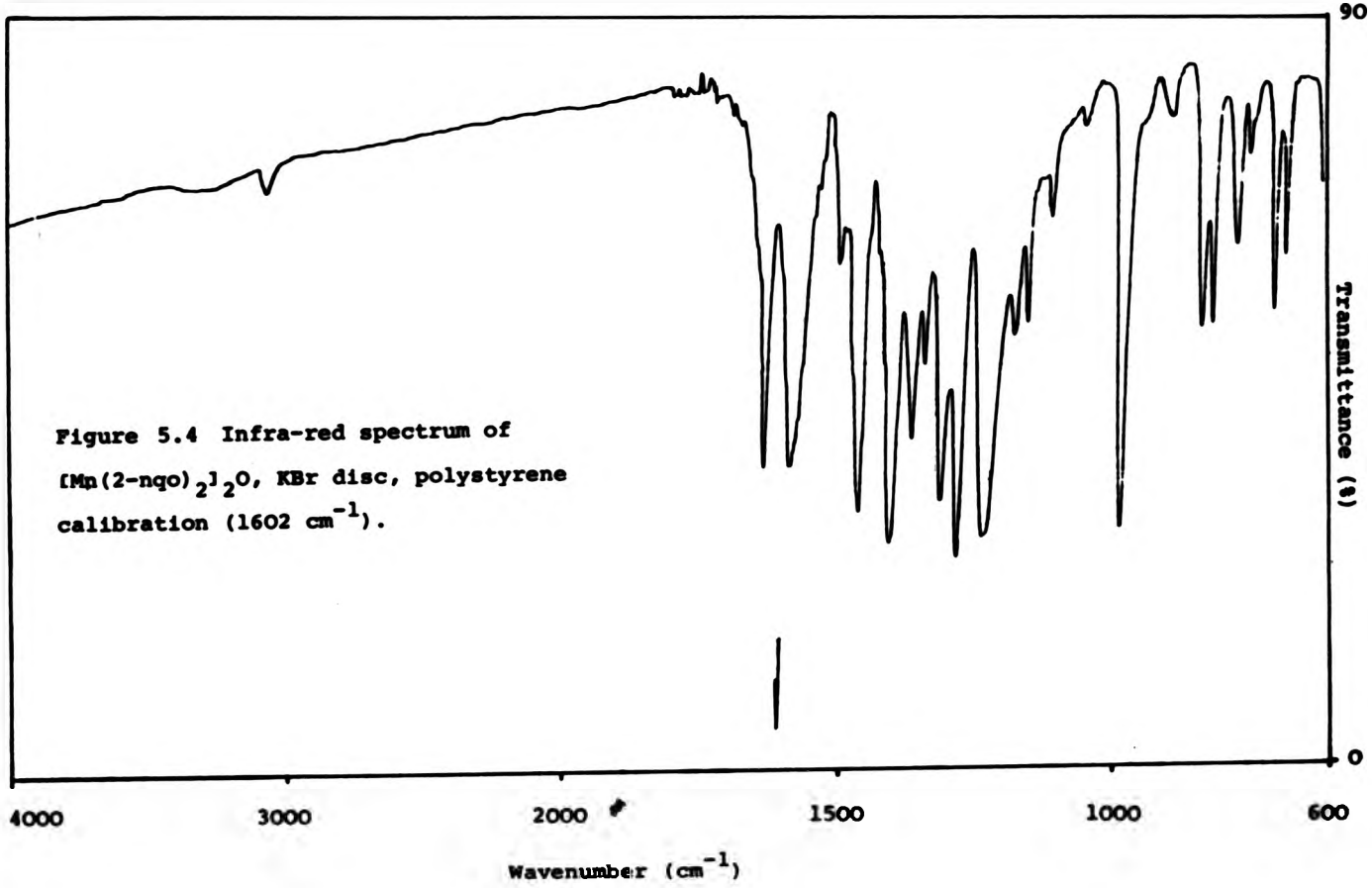


Figure 5.4 Infra-red spectrum of $[Mn(2\text{-nqo})_2]_2O$, KBr disc, polystyrene calibration (1602 cm^{-1}).

The isolated quantities of triphenylphosphine oxide, unreacted triphenylphosphine, and the total quantity of other organic products obtained indicated the deoxygenation and loss of one mole equivalent of 2-nqoH from one mole equivalent of $Mn(2\text{-nqo})_3$ (Reaction 5.3).

$$Mn(2\text{-nqo})_3$$

$$+Ph_3P \downarrow -Ph_3PO \qquad ..5.3$$

$$1/2[Mn(2\text{-nqo})_2]_2 + [2\text{-nqiH}]$$

$$\downarrow$$

$$\text{phenazinone} + \text{4-imine}$$

When $Mn(2\text{-nqo})_3$ (1 mol eq.) and triphenylphosphine (3 mol eq.) were stirred in acetone at room temperature for seven days, μ-oxotetrakis(1,2-naphthoquinone 2-iminato)dimanganese(III) (0.5 mol eq.), phenazinone (0.3 mol eq.), 4-imine (0.1 mol eq.), and triphenylphosphine oxide (3 mol eq.) were obtained. The complex, $[Mn(2\text{-nqi})_2]_2O$, was well-defined by i.r. (Figure 5.5) and elemental analysis was in accord with the formulation. The room temperature effective magnetic moment of 3.01 B.M. per manganese was in the region expected for spin-paired manganese(III).[35] The reaction of $[Mn(2\text{-nqi})_2]_2O$ (1 mol eq.), with 6M hydrochloric acid gave 1,2-naphthoquinone 2-imine (4 mol eq.). This result supports the presence of coordinated nitrene/quinoneimine in the complex.

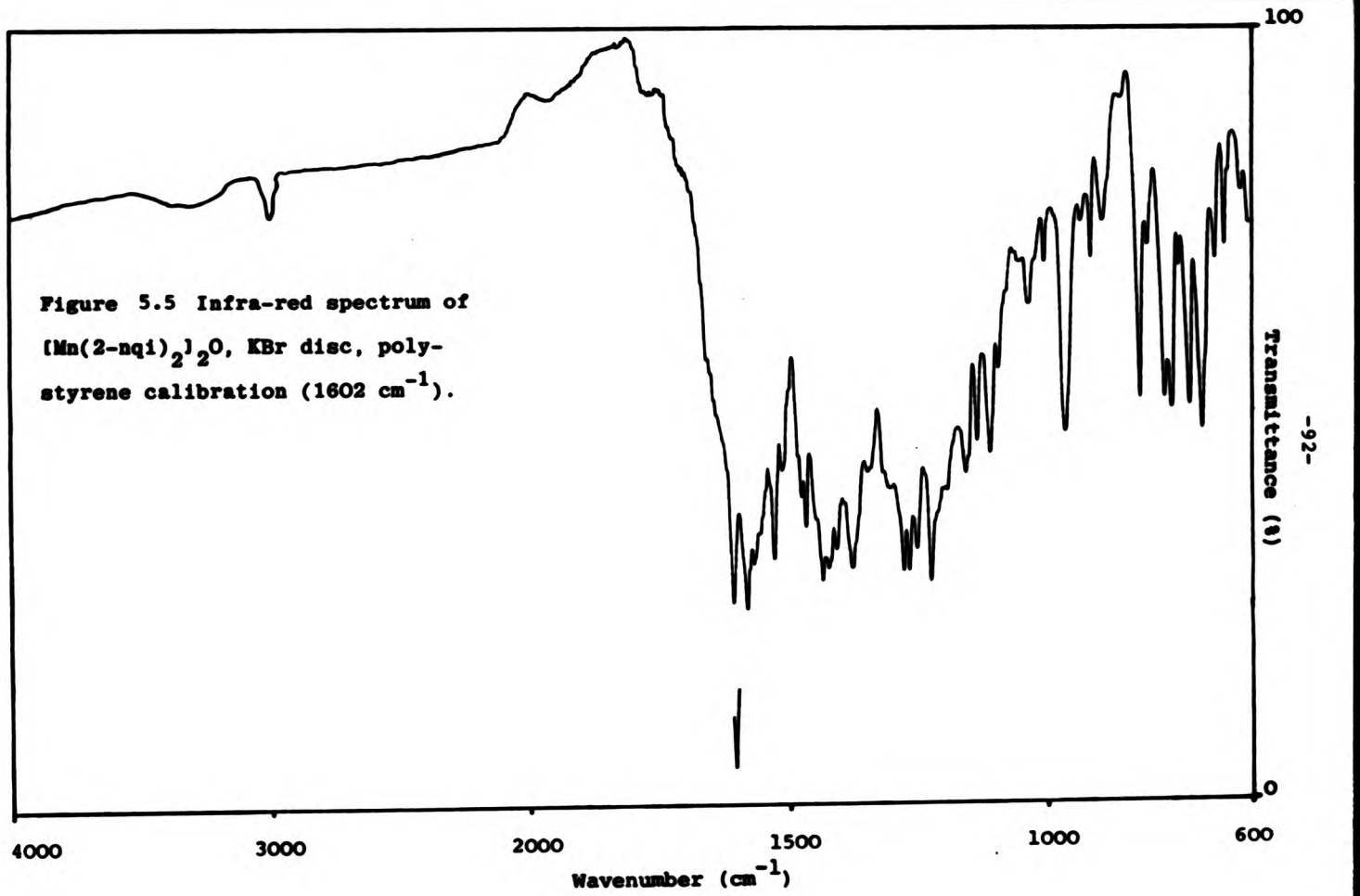


Figure 5.5 Infra-red spectrum of $[Mn(2\text{-nqi})_2]_2O$, KBr disc, polystyrene calibration (1602 cm^{-1}).

The amount of triphenylphosphine used-up in the reaction, and the quantities of products obtained, indicated the deoxygenation of three mole equivalents of 2-nqoH per mole equivalent of $Mn(2\text{-nqo})_3$ (Reaction 5.4).

$$Mn(2\text{-nqo})_3$$

$$+3Ph_3P \downarrow -3Ph_3PO \qquad ..5.4$$

$$1/2[Mn(2\text{-nqi})_2]_2O + [2\text{-nqiH}]$$

$$\downarrow$$

$$\text{phenazinone} + \text{4-imine}$$

When $[Mn(2\text{-nqo})_2]_2O$ (1 mol eq.) and triphenylphosphine (4 mol eq.) were stirred at room temperature for seven days, $[Mn(2\text{-nqi})_2]_2O$ was obtained in good yield. This shows that $[Mn(2\text{-nqo})_2]_2O$ is an intermediate in the conversion of $Mn(2\text{-nqo})_3$ to $[Mn(2\text{-nqi})_2]_2O$ as depicted in Scheme 5.7 (organic products are omitted for clarity).

The molecular ion peak (m/e 312) and the fragmentation pattern exhibited by the mass spectrum of mauve 1,2-naphthoquinone 2-imine identified it as the phenazinone. This result was supported by elemental analysis. However, the t.l.c., i.r. spectrum (Figure 5.6), and melting point of the mauve solid (m.p. = 224 - 226 ^{o}C) were different from those of

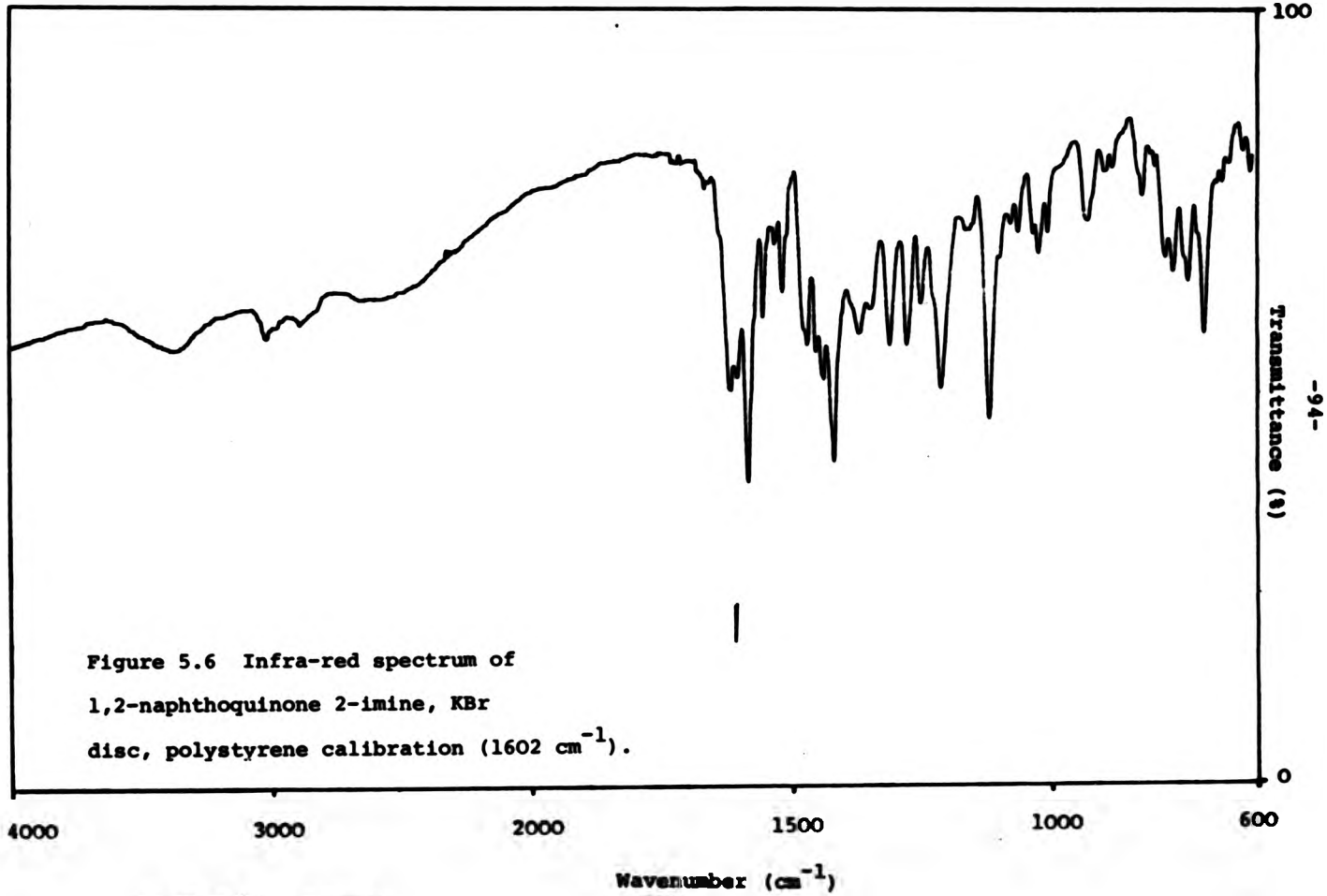
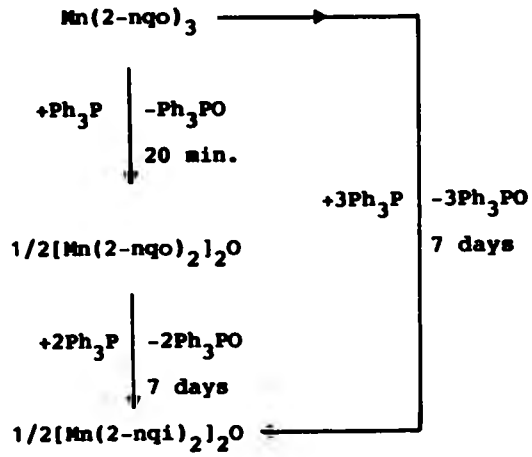


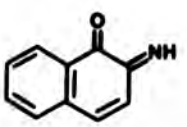
Figure 5.6 Infra-red spectrum of 1,2-naphthoquinone 2-imine, KBr disc, polystyrene calibration (1602 cm^{-1}).

Scheme 5.7 Reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine.

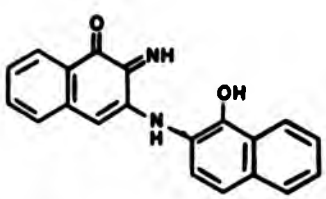


the phenazinone. The imine decomposed on t.l.c. silica plates, in solution, and quantitatively in refluxing ethanol to give the phenazinone. This indicated that the mauve solid was a precursor of the phenazinone. In addition to 1,2-naphthoquinone 2-imine (2-nqiH), 2-imino-N^3-(1-quinone-2-naphthyl)-1,3-naphthoquinone 3-imine (henceforth designated as 3-imine) is also a precursor of the phenazinone (Figure 5.7).

Figure 5.7 Possible phenazinone precursors.



2-nqiH



3-imine

It has been reported that imines can be stabilized as their acetyl derivatives.[38] Thus, it was thought that reaction of the mauve solid with acetic anhydride followed by characterisation of the acetyl derivative(s) could allow distinction between the possible precursors. However, reaction of the mauve solid with acetic anhydride led to 5,12-diacetoxydibenzo[b,i]phenazine as the only product. This shows that decomposition of the mauve solid to phenazinone occurs during the acetylation reaction. The phenazinone then reacts with acetic anhydride to give the diacetoxy derivative.

The reaction of $Mn(1\text{-nqo})_3$ with triphenylphosphine was slower than the corresponding reaction of $Mn(2\text{-nqo})_3$. When $Mn(1\text{-nqo})_3$ (1 mol eq.) and triphenylphosphine (3 mol eq.) were stirred in acetone for twenty four hours, μ-oxotetrakis(1,2-naphthoquinone 1-oximato)dimanganese(III) (0.5 mol eq.), 1-nqoH (0.8 mol eq.), triphenylphosphine oxide (0.4 mol eq.), and unreacted triphenylphosphine (2.5 mol eq.) were obtained. The complex, $[Mn(1\text{-nqo})_2]_2O$, was well defined by i.r. (Figure 5.8) and its elemental analysis was in accord with the formulation. The room temperature effective magnetic moment of 2.72 B.M. was in the region expected for spin-paired manganese-(III).[35] The reaction of $[Mn(1\text{-nqo})_2]_2O$ (1 mol eq.) with 6M hydrochloric acid gave 1-nqoH (4 mol eq.). Attempts to react $[Mn(1\text{-nqo})_2]_2O$ with triphenylphosphine were unsuccessful.

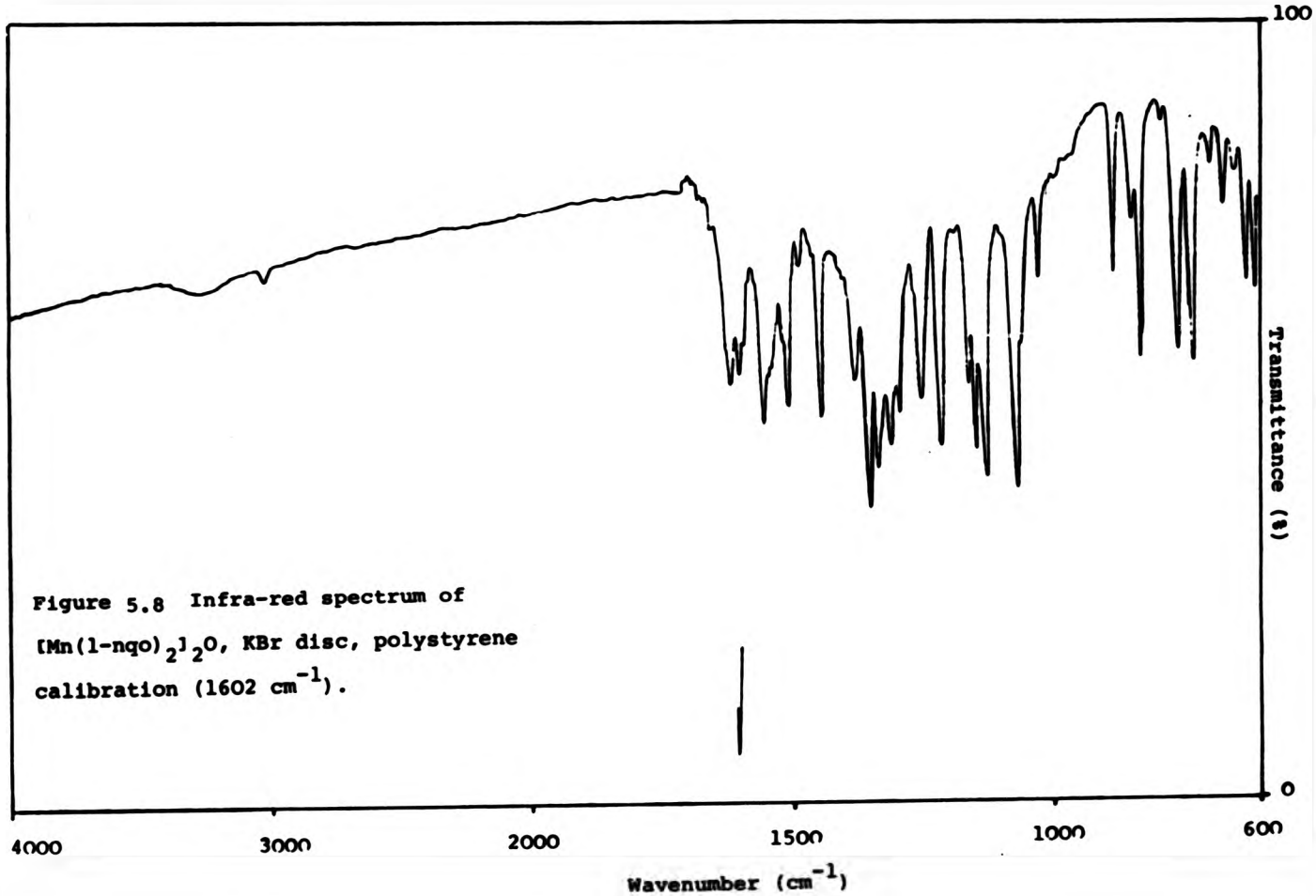


Figure 5.8 Infra-red spectrum of $[Mn(1\text{-nqo})_2]_2O$, KBr disc, polystyrene calibration (1602 cm^{-1}).

5.4 Kinetic studies of the reactions involving triphenylphosphine and $M(2\text{-nqo})_3$ complexes (M = Cr or Mn)

5.4.1 Reaction of tris(1,2-naphthoquinone 2-oximato)-chromium(III) with triphenylphosphine in acetone

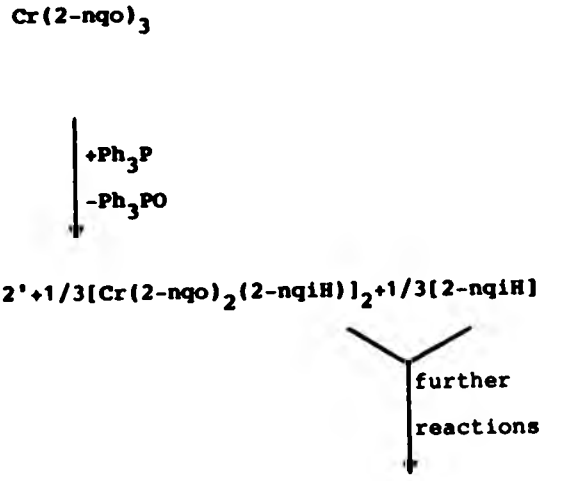
The visible spectra of $Cr(2\text{-nqo})_3$, $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ and '$Cr(2\text{-nqo})_2$' were recorded in acetone solutions at 30.0 ± 0.3 °C as a prelude to the kinetic investigation (Table 5.1). The spectra showed several bands in the visible region. A preliminary u.v./vis. study of the reaction showed that the greatest change in absorbance occurs at 430 nm. This was, therefore, chosen as a suitable wavelength for study. The reaction was studied in a 1 cm cell at 30.0 ± 0.3 °C at concentrations of triphenylphosphine ranging from two-fold to eighty-fold excess. In a typical experiment a freshly made solution of $Cr(2\text{-nqo})_3$ (5.07×10^{-3} mol dm^{-3}) was added to a solution of triphenylphosphine (15.2×10^{-3} mol dm^{-3}) at 30.0 ± 0.3 °C. The reaction was monitored by recording the changes in absorbance at 430 nm corresponding to the formation of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$. The absorbance at 430 nm increased as $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ was formed and then started to decrease as it decomposed. It was assumed that the absorbance at 430 nm was the sum of the absorbances of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ and '$Cr(2\text{-nqo})_2$' because both these complexes are formed in parallel

Table 5.1 Electronic absorption data for tris(1,2-naphthoquinone 2-oximato)chromium(III), bis(1,2-naphthoquinone 2-imine)tetrakis(1,2-naphthoquinone 2-oximato)dichromium(II), and 'Cr(2-nqo)2' in acetone solutions at 30.0 ± 0.3 °C.

Complex	λ_{max} (nm)	ϵ (m^2 mol^{-1})
$Cr(2\text{-nqo})_3$	835	68
	596	578
	534	722
	340	908
$[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$	708	250
	630	320
	524	555
	473	903
	445	832
	430	645
'Cr(2-nqo)2'	608	57
	530	195
	430	275
	400	320

and have absorbances at 430 nm. By using the stoichiometry shown in Scheme 5.9 and the measured molar absorptivities of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ and '$Cr(2\text{-nqo})_2$' at 430 nm, values of absorbances (430 nm) were calculated for each of the complexes. The sum of these values of absorbances was used to process the kinetic data. (Note that the molar absorptivity of '$Cr(2\text{-nqo})_2$' was based on the molarity of chromium because the formulation of the complex is not clear.)

Scheme 5.9 Observed stoichiometry of the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine.



A plot of $\log(A_\infty - A_t)$ against time, for the absorbance at 430 nm, gave a straight line for over one half-life of the reaction (Figure 5.9). When the reaction was studied at other concentrations of triphenylphosphine, the system behaved in an analogous manner. The rate constants for the reaction at different concentrations of phosphine are given in Table 5.2. A plot of k_{obs} versus initial concentration of phosphine gave a straight line which could be extrapolated through zero and which levelled off to a constant value of k_{obs} at an approximate triphenylphosphine concentration of 13.7×10^{-3} mol dm^{-3}, which corresponds to a sixty-fold excess of the phosphine (Figure 5.10).

Figure 5.9 Graph of $\log(A_\infty - A_t)$ against time for the reaction of $Cr(2\text{-nqo})_3$ (5.07×10^{-3} mol dm^{-3}) with triphenylphosphine (15.2×10^{-3} mol dm^{-3}) in acetone at 30 ± 0.3 °C in a 1 cm cell.

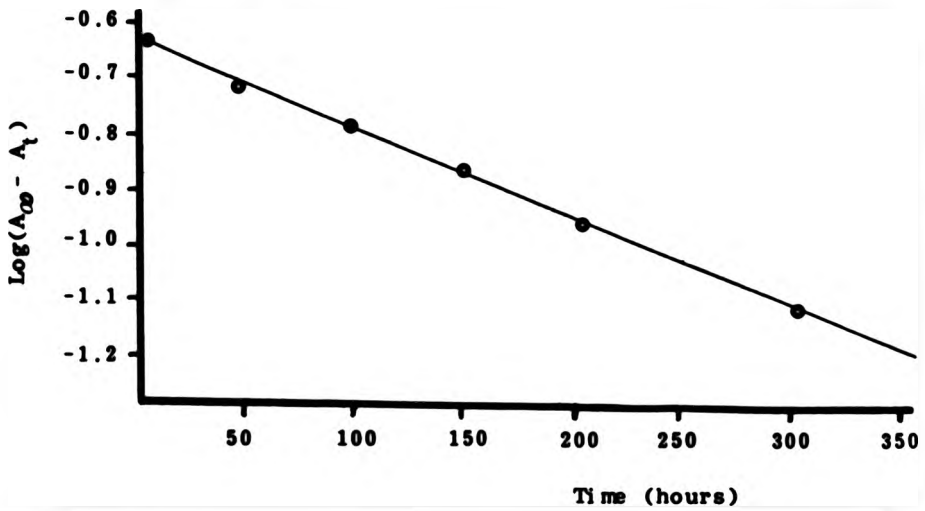
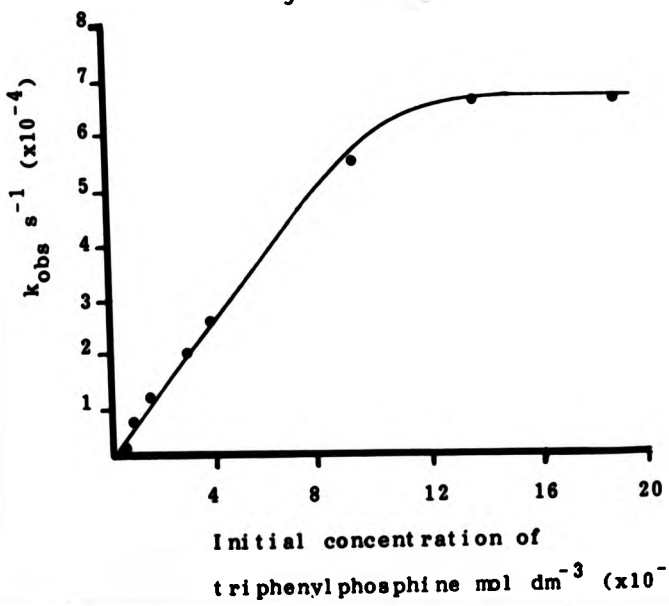


Table 5.2 Variation of rate with initial concentration of triphenylphosphine for the reaction inolving $Cr(2\text{-nqo})_3$ at 30.0 ± 0.3 °C.

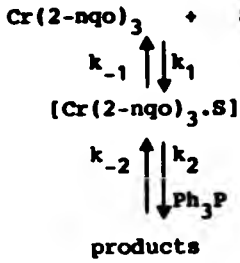
Initial concentration of $Cr(2\text{-nqo})_3$ mol dm^{-3} ($x10^{-4}$)	Initial concentration triphenylphosphine mol dm^{-3} ($x10^{-3}$)	k_{obs} s^{-1} ($x10^{-4}$)
2.30	0.46	0.02
2.33	0.70	0.65
2.36	1.65	1.15
2.06	3.10	1.88
1.95	3.90	2.54
2.28	9.10	5.33
2.31	13.90	6.85
2.30	18.40	6.88

Figure 5.10 Graph of k_{obs} against initial concentration of triphenylphosphine for the reaction involving $Cr(2\text{-nqo})_3$ at 30.0 ± 0.3 °C.



The kinetic results indicate that: (1) the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine is first order with respect to $Cr(2\text{-nqo})_3$ and, (2) although at low concentrations of triphenylphosphine plots of $\log(A_\infty - A_t)$ versus time are linear, the rate constants are dependent on triphenylphosphine concentrations. This type of behaviour is to be expected for cases where the concentration of triphenylphosphine is large in comparison to $Cr(2\text{-nqo})_3$. This is because, in such cases, the concentration of triphenylphosphine effectively remains constant. However, in the reaction involving triphenylphosphine to $Cr(2\text{-nqo})_3$ ratio of 3:1, the excess of triphenylphosphine is quite low. Hence, the reaction should not follow first order kinetics and at the same time have a rate constant dependent on triphenylphosphine concentration.

A likely explanation is that the rate determining step involves a reaction between the phosphine and a species other than $Cr(2\text{-nqo})_3$. This species must be present in a very small amount relative to triphenylphosphine. The concentration of this reactive species must be proportional to the concentration of $Cr(2\text{-nqo})_3$ for the reaction to be first order with respect to $Cr(2\text{-nqo})_3$. Although the nature of the reactive species has not been established, one possibility is that the solvent is involved. The species involving the solvent could then react with triphenylphosphine in a rate determining step (Reaction 5.5).



..5.5

5.4.2 Reaction of tris(1,2-naphthoquinone 2-oximato)-manganese(III) with triphenylphosphine in acetone

Before the kinetic study, the visible spectra of $Mn(2\text{-nqo})_3$, $[Mn(2\text{-nqo})_2]_2O$, and $[Mn(2\text{-nqi})_2]_2O$ were recorded in acetone solutions at 30.0 ± 0.3 ^{o}C (Table 4.4). As noted in Chapter 5, the preparative scale reaction of $Mn(2\text{-nqo})_3$ with triphenylposphine proceeds by two discernable steps. The kinetics of these two steps were investigated separately in this study (Reactions 5.6 and 5.7).

Step One

$$Mn(2\text{-nqo})_3 + PPh_3 \longrightarrow 1/2[Mn(2\text{-nqo})_2]_2O + 2\text{-nqoH} \quad ..5.6$$

Step Two

$$1/2[Mn(2\text{-nqo})_2]_2O + 2PPh_3 \longrightarrow 1/2[Mn(2\text{-nqi})_2]_2O \quad ..5.7$$

Table 5.3 Electronic absorption data for tris(1,2-naphthoquinone 2-oximato)manganese(III), μ-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese-(III), and μ-oxotetrakis(1,2-naphthoquinone 2-iminato)-dimanganese(III) in acetone solutions at 30.0 $\pm$ 0.3 ^{o}C.

Complex	λ_{max} (nm)	ϵ (m^2 mol^{-1})
$Mn(2\text{-nqo})_3$	775	298
	590	243
	475	606
	338	2450
$[Mn(2\text{-nqo})_2]_2O$	800	98
	440	650
$[Mn(2\text{-nqi})_2]_2O$	624	86
	440	895

Kinetic study of the conversion of tris(1,2-naphthoquinone 2-oximato)manganese(III) to μ-oxotetrakis-(1,2-naphthoquinone 2-oximato)dimanganese(III)

The reaction was studied in 1 cm cells at 30 ± 0.3 ^{o}C at concentrations of triphenylphosphine ranging from four-fold to forty-fold excess. In a typical experiment, a freshly made solution of $Mn(2\text{-nqo})_3$ (9.80×10^{-4} mol dm^{-3}) was added to a solution of triphenylphosphine (6.86×10^{-3} mol dm^{-3}) in acetone at 30.0 ± 0.3 ^{o}C. The reaction was monitered by recording the changes in absorbance at 800 nm corresponding to the formation of $[Mn(2\text{-nqo})_2]_2O$. The absorbance at 800 nm increased as $[Mn(2\text{-nqo})_2]_2O$ was formed, and then decreased as it was used up by the second step of the reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine.

In preparative scale investigations, the first step (Reaction 5.6) was the only discernable reaction for the first thirty minutes after mixing $Mn(2\text{-nqo})_3$ and the phosphine. The kinetic data also showed that decomposition of $[Mn(2\text{-nqo})_2]_2O$ did not occur for the initial thirty minutes of the reaction, regardless of the concentration of triphenylphosphine used. This was confirmed by t.l.c. on the reaction solutions which showed no evidence for the presence of $[Mn(2\text{-nqi})_2]_2O$. The visible spectrum of the reaction mixture at this stage was identical to the spectrum of $[Mn(2\text{-nqo})_2]_2O$.

It is likely, however, that after the first thirty minutes of the reaction decomposition of $[Mn(2\text{-nqo})_2]_2O$ starts to occur, i.e. before the first step has gone to completion. Therefore, the value of absorbance observed, i.e. the highest value reached by A_t before it starts to decrease, is not just a function of step one but is also affected by step two. Thus, to investigate the rate and order of step one, a value of absorbance (800 nm) was calculated using the measured molar absorptivity of $[Mn(2\text{-nqo})_2]_2O$ and assuming the stoichiometry given earlier (Reaction 5.6).

$Log(A_\infty - A_t)$ was plotted against time. This gave a straight line for over one half-life of the reaction at all concentrations of triphenylphosphine (Figure 4.13). This indicates step one to be first order with respect to the concentration of $Mn(2\text{-nqo})_3$ because the value of $(A_\infty - A_t)$ at 800 nm is proportional to the concentration of $Mn(2\text{-nqo})_3$. The rate constants for the reaction at different concentrations of triphenylphosphine are given in Table 5.4.

A plot of k_{obs} versus initial concentration of triphenylphosphine gave a straight line which could be extrapolated through zero and which levelled-off to a constant value of k_{obs} at an approximate phosphine concentration of 15.68 mol dm^{-3} corresponding to a sixteen-fold excess of the phosphine (Figure 5.12). As noted earlier, this type of behaviour is not

uncommon when one of the reactants is present in a large excess. The reaction was attempted in a low ratio of phosphine to complex (3:1). It was expected that at such a low ratio, the concentration of triphenylphosphine would not remain constant and a plot of $\log(A_\infty - A_t)$ would be non-linear. However, at this ratio (3:1) the reaction was not amenable to kinetic study.

Figure 5.11 Graph of $\log(A_\infty - A_t)$ against time for step one of the reaction of $Mn(2\text{-nqo})_3$ (9.80 mol dm^{-3}) with triphenylphosphine (15.7 mol dm^{-3}) in acetone at 30.0 ± 0.3 °C.

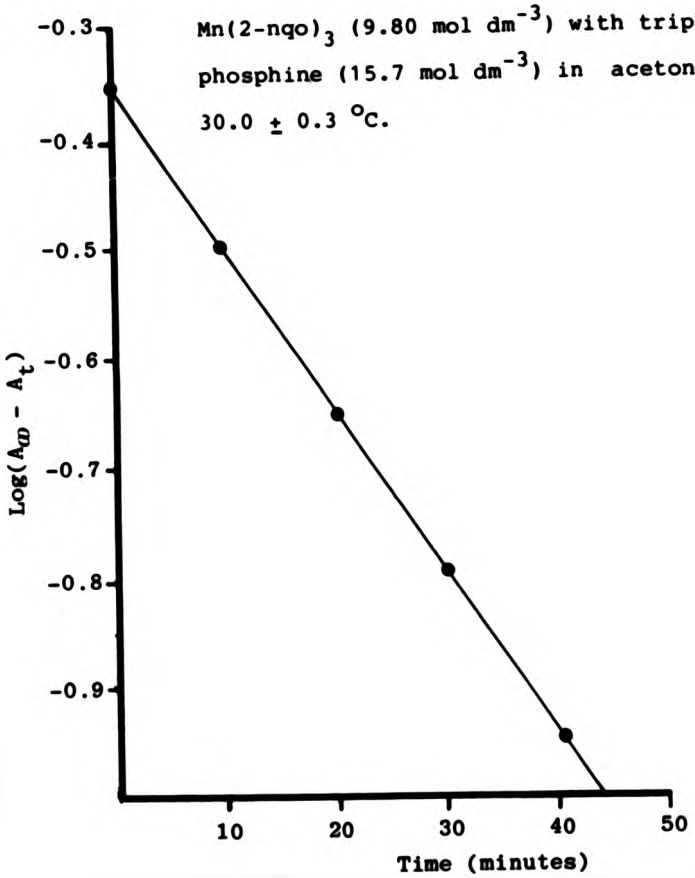
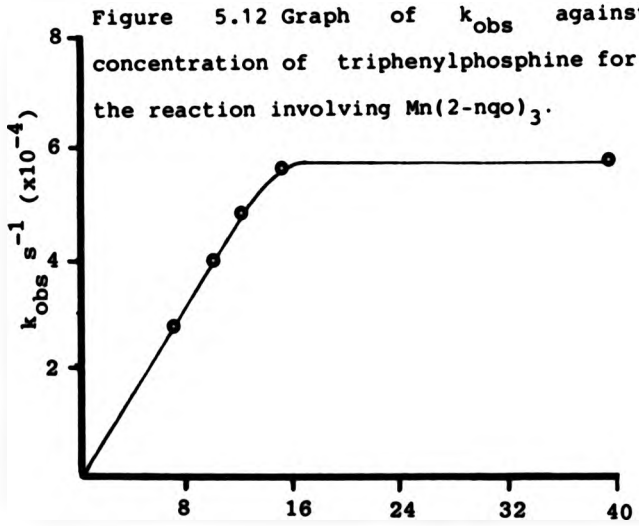


Table 5.4 Variation of rate with initial concentration of triphenylphosphine for the reaction of tris(1,2-naphthoquinone 2-oximato)manganese(III) with the phosphine in acetone at 30.0 ± 0.3 °C.

Initial concentration of $Mn(2\text{-nqo})_3$ mol dm^{-3} ($x10^{-4}$)	Initial concentration of triphenylphosphine mol dm^{-3} ($x10^{-3}$)	k_{obs} s^{-1} ($x10^{-4}$)
9.80	6.86	2.73
9.78	9.78	3.88
9.83	11.79	4.75
9.80	15.68	5.55
9.81	39.20	5.60

Figure 5.12 Graph of k_{obs} against initial concentration of triphenylphosphine for step one of the reaction involving $Mn(2\text{-nqo})_3$.

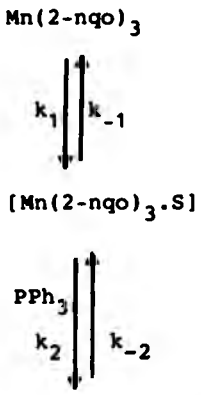


To summerize, the kinetic results indicate that step one is first order with respect to $Mn(2\text{-nqo})_3$ and that triphenylphosphine is involved in the rate determining step. This suggests that triphenylphosphine is reacting with a reactive species other than $Mn(2\text{-nqo})_3$. The reactive species must be present in a small amount so that the phosphine is always in a large excess. The concentration of the reactive species must be proportional to the concentration of $Mn(2\text{-nqo})_3$ in order for the kinetics to be first order with respect to $Mn(2\text{-nqo})_3$. As noted in Chapter 4, $Mn(2\text{-nqo})_3$ reacts with Lewis base solvents, albeit very slowly compared to its reaction with triphenylphosphine. It is possible, therefore, that the reactive species involves the solvent (Scheme 5.10). As long as the amount of $[Mn(2\text{-nqo})_3.S]$, at any time, is small then the phosphine will be in large excess. This can account for the first order rate constants obtained, and formation of $[Mn(2\text{-nqo})_2]_2O$ with a rate determining step dependent on the phosphine.

Kinetic study of the conversion μ-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese(III) to μ-oxotetrakis-(1,2-naphthoquinone 2-iminato)dimanganese(III)

The second step in the reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine was investigated by studying the reaction between $[Mn(2\text{-nqo})_2]_2O$ and triphenylphosphine in 1 cm cells at 30.0 $\pm$ 0.3 ^{o}C at concentrations of

Scheme 5.10 Solvent participation in the reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine



triphenylphosphine ranging from four-fold to forty-fold excess. In a typical experiment a solution of $[Mn(2\text{-nqo})_2]_2O$ (4.43×10^{-4} mol dm^{-3}) was added to a solution of triphenylphosphine (1.77×10^{-3} mol dm^{-3}) in acetone. The reaction was monitored by recording the decrease in absorbance at 800 nm and considered complete when no significant decrease in the absorbance could be detected over a reasonable length of time.

Graphs of $\log(A_t - A_\infty)$ against time for the reactions involving four-, seven-, eight-, and nine-fold excess of triphenylphosphine were not linear.

This suggests that the second step does not involve a solvent dependent equilibrium of the type shown in Scheme 5.10, i.e. the phosphine is reacting directly with $[Mn(2\text{-nqo})_2]_2O$ rather than with an intermediate species present in low concentrations.

The reaction was then studied at higher concentrations of the phosphine, in an attempt to keep the phosphine concentration effectively constant during the reaction. However, the final spectra of the reaction mixtures involving fifteen- to forty-fold excess of triphenylphosphine were different form the spectrum of $[Mn(2\text{-nqi})_2]_2O$. T.l.c. examination of the reaction mixtures showed a different composition to the preparative scale (1:4) reaction of $[Mn(2\text{-nqo})_2]_2O$ with triphenylphosphine. Thus, the kinetic reactions involving fifteen- to forty-fold excess of triphenylphosphine indicated the presence of phenazinone by t.l.c. This shows that reactions other than the expected second step occur at concentrations of triphenylphosphine higher than a nine-fold excess.

Two approaches for analysing the data were then tried in an attempt to draw further conclusions from the kinetic study of the second step. In the first approach, gradients of the tangents to the curves of plots of $(A_t - A_\infty)$ against time, for the reactions involving 1:4, 1:7, 1:8, and 1:9 ratios of $[Mn(2\text{-nqo})_2]_2O$ to triphenylphosphine, were calculated. This gives a measure of the rate of reaction at

various times and provided that the subsequent plots of log(rate) against $\log(A_t - A_\infty)$ are linear, the order of the reaction can be determined by measuring the slope of the straight line. However, plots of log(rate) against $\log(A_t - A_\infty)$ were not linear.

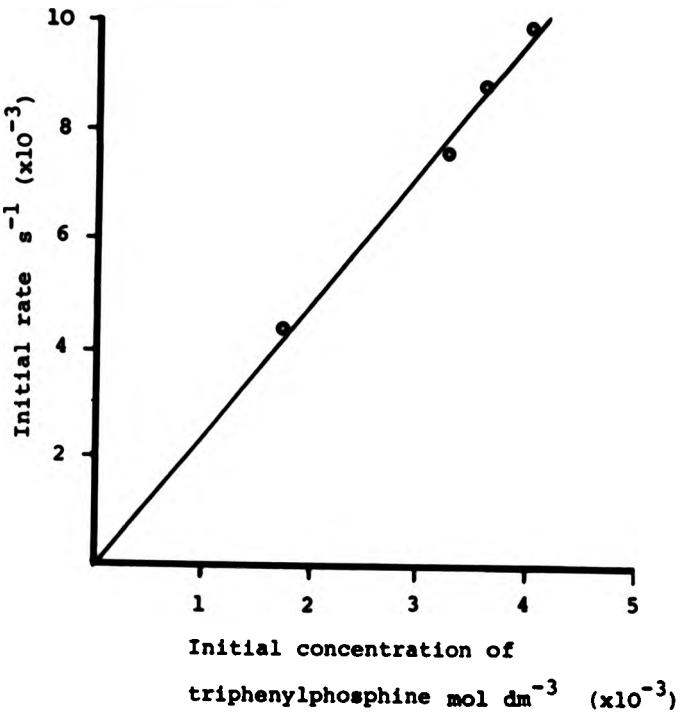
In the second approach to allow for the possibility of reversible reactions creating kinetic difficulties, the initial slopes of plots of $\log(A_t - A_\infty)$ against time, for the reactions involving four- to nine-fold excess of the phosphine, were measured (Table 5.5). A graph of initial rate against initial concentration of triphenylphosphine concentration was then plotted. This gave a straight line which could be extrapolated back through zero (Figure 5.13). The tentative conclusion which may be drawn from these results is that triphenylphosphine reacts directly with $[Mn(2\text{-nqo})_2]_2O$ in a rate determining step. The significant difference between $Mn(2\text{-nqo})_3$ and $[Mn(2\text{-nqo})_2]_2O$ is that in the former complex manganese is coordinatively saturated. Triphenylphosphine cannot, therefore, react directly with $Mn(2\text{-nqo})_3$ until manganese becomes coordinatively unsaturated by means of an internal redox reaction caused by the solvent. In contrast, the phosphine can react directly with $[Mn(2\text{-nqo})_2]_2O$ as, in this complex, manganese is five-coordinate. Involvement of the solvent and an internal redox reaction are, therefore, not necessary. Consequently, the reaction of $[Mn(2\text{-nqo})_2]_2O$ with triphenylphosphine is not first order with respect to

the complex and the rate determining step is dependent on the phosphine concentration.

Table 4.7 Variation of initial rate with initial concentration of triphenylphosphine for the reaction of $[Mn(2\text{-nqo})_2]_2O$ with the phosphine in acetone at 30.0 ± 0.3 °C.

Initial concentration of $[Mn(2\text{-nqo})_2]_2O$ mol dm^{-3} ($x10^{-3}$)	Initial concentration of triphenylphosphine mol dm^{-3} ($x10^{-3}$)	k_{obs} s^{-1} ($x10^{-3}$)
0.443	1.77	4.10
0.443	3.10	7.55
0.443	3.54	9.03
0.443	3.98	9.87

Figure 5.13 Graph of initial rate against initial concentration of triphenylphosphine for the reaction of $[Mn(2\text{-nqo})_2]_2O$ with the phosphine in acetone at 30.0 ± 0.3 °C.

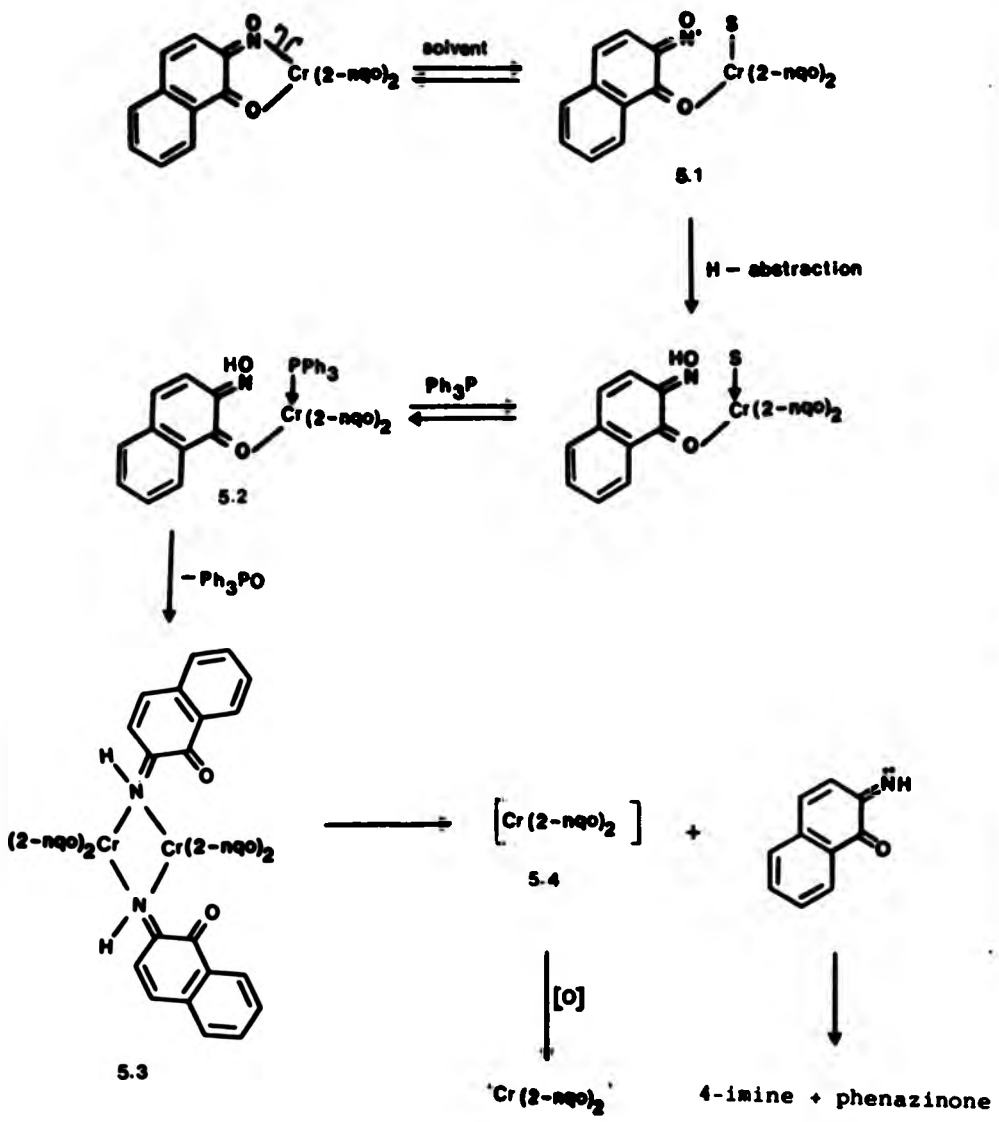


5.5 Mechanistic conclusions

5.5.1 Reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine

Kinetic results and the products obtained in preparative scale studies suggest that the reaction proceeds as outlined in Scheme 5.11. The mechanism is dependent on the solvent interacting with $Cr(2\text{-nqo})_3$ to cause an internal redox reaction. The resultant intermediate 5.1 abstracts an hydrogen from the solvent and then undergoes reversible adduct formation with triphenylphosphine to give 5.2. Deoxygenation of 5.2 by triphenylphosphine followed by dimerisation gives the diamagnetic chromium(II) complex 5.3. Decomposition of 5.3 affords $[Cr(2\text{-nqo})_2]$, 5.4, and 1,2-naphthoquinone 2-imine. Oxidation of 5.4 gives '$Cr(2\text{-nqo})_2$' and the imine reacts with itself to give phenazinone and 4-imine. The mechanism requires a solvent capable of donating a hydrogen atom to a ligand radical. This is substantiated by the fact that $Cr(2\text{-nqo})_3$ (1 mol eq.) and triphenylphosphine (3 mol eq.) do not not react when stirred or heated under reflux in trichlorotrifluoroethane. As depicted in Scheme 5.11, the mechanism involves deoxygenation of a coordinated monodentate 2-nqoH ligand. This mode of deoxygenation is corroborated by the isolation of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$, i.e. a complex containing a coordinated 1,2-naphthoquinone 2-imine ligand. Deoxygenation of a coordinated 2-nqoH ligand is also supported by the absence of 2-nqoH amongst the

Scheme 5.11 Reaction of Cr(2-nqo)3 with triphenylphosphine.



products of the reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine.

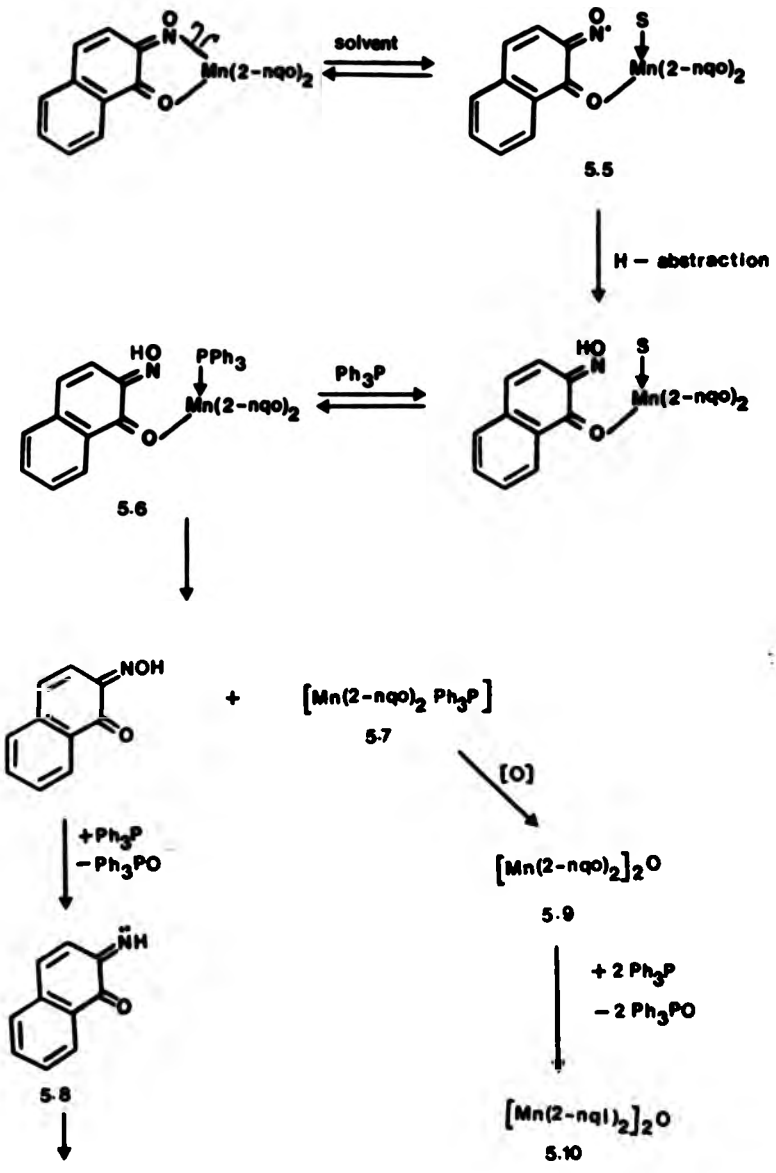
5.5.2 Reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine

The mechanism shown in Scheme 5.12 is based on kinetic results and isolation of 2-nqoH as one of the products of the reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine. Like the analogous reaction of $Cr(2\text{-nqo})_3$, the mechanism is dependent on the solvent interacting with $Mn(2\text{-nqo})_3$ to cause an internal redox reaction to give 5.5. The species 5.5 abstracts a hydrogen and then reacts with triphenylphosphine in a reversible step to give the adduct 5.6. Decomposition of 5.6 gives 5.7 and 2-nqoH. Deoxygenation of 2-nqoH by triphenylphosphine leads to the nitrene/quinoneimine 5.8. The nitrene/quinoneimine can then react with itself or with 2-nqoH to give the organic products obtained in this reaction. Oxidation of 5.7 by molecular oxygen leads to $[Mn(2\text{-nqo})_2]_2O$, 5.9, which then reacts further with triphenylphosphine to give $[Mn(2\text{-nqi})_2]_2O$, 5.10.

5.6 Reactivity of 1,2-naphthoquinone mono-oximes and their metal complexes

Assessment of past and present work with regard to the reactivity of 1,2-naphthoquinone mono-oximes and their metal complexes towards pyridine, primary amines and triphenylphosphine indicates that 1,2-naphthoquin-

Scheme 5.12 Reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine.



one 2-oxime and its metal complexes are always more reactive. This is particularly apparent in the reactions involving triphenylphosphine. Thus, $Fe(2\text{-nqo})_3$ reacts completely in thirty minutes whereas $Fe(1\text{-nqo})_3$ requires five hours. Similarly, $Cr(2\text{-nqo})_3$ is completely consumed by triphenylphosphine in fifty minutes but, in contrast, $Cr(1\text{-nqo})_3$ does not react with the phosphine.

Examination of models of 1-nqoH and 2-nqoH molecules indicated that the oxime group in 2-nqoH is sterically more accessible than the oxime group in 1-nqoH (Figures 5.14 & 5.15). In 1-nqoH, carbons adjacent (C9 and C2) to the oximic carbon (C1) are bonded to atoms other than hydrogen. In contrast, in 2-nqoH one of the carbons (C3) adjacent to the oximic carbon (C2) is bonded to a hydrogen atom.

In order to check the validity of the steric explanation proposed above, the reactions of $Cr(6\text{-Me-5-OHqo})_3$ and $Cr(3\text{-Me-5-OHqo})_3$ with triphenylphosphine were investigated. Like 1-nqoH, in 3-Me-5-OHqoH the C1 and C3 carbons are bonded to atoms other than hydrogen (Figure 5.16). In contrast, 6-Me-5-OHqoH is structurally similar to 2-nqoH because the C3 carbon is bonded to a hydrogen atom (Figure 5.17). Thus, $Cr(3\text{-Me-5-OHqo})_3$ should be less reactive towards triphenylphosphine than $Cr(6\text{-Me-5-OHqo})_3$. As expected, $Cr(3\text{-Me-5-OHqo})_3$ (1 mol eq.) did not react with triphenylphosphine (3 mol eq.) in acetone under

Figure 5.14 Structure of 1-nqoH.
(Hydrogen atoms are omitted.)

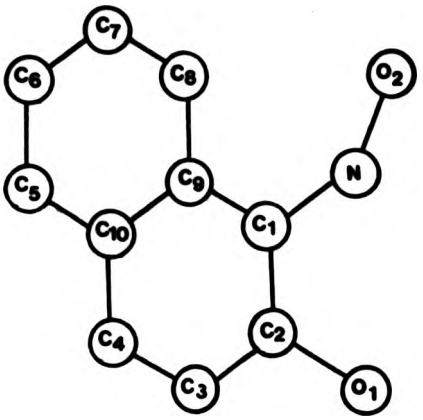


Figure 5.15 Structure of 2-nqoH.
(Hydrogen atoms are omitted.)

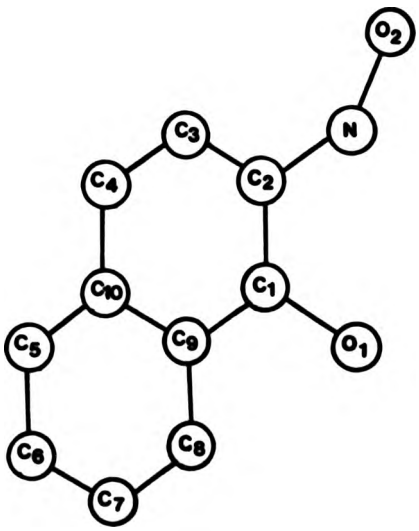


Figure 5.16 Structure of 3-Me-5-OHqoH

(Hydrogen atoms are omitted.)

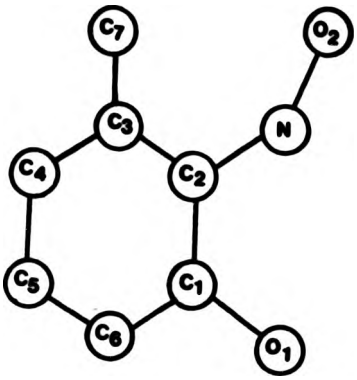
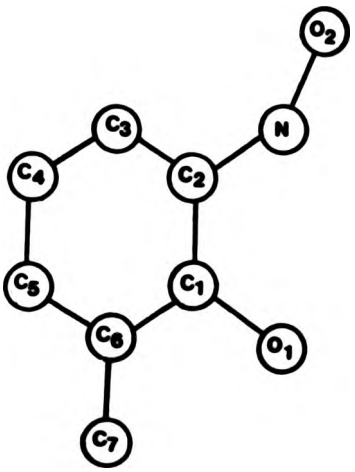


Figure 5.17 Structure of 6-Me-5-OHqoH

(Hydrogen atoms are omitted.)



ambient or reflux conditions. In contrast, $Cr(6\text{-}Me\text{-}5\text{-}OHqo)_3$ (1 mol eq.) reacted with triphenylphosphine (3 mol eq.) in acetone at room temperature.

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CHAPTER SIX

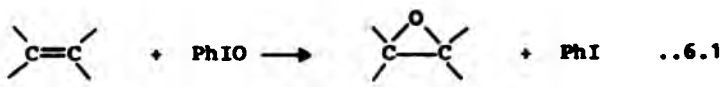
AEROBIC OXIDATION OF OLEFINS CATALYSED BY MANGANESE COMPLEXES DERIVED FROM 1,2-QUINONE MONO-OXIMES

The first successful application of non-porphyrin complexes as catalysts for the aerobic epoxidation of olefins is reported in this chapter. Using the complexes $Mn(nqo)_n$ as catalysts, aerobic oxidation of methyl oleate gave epoxymethyl oleate, as well as acidic and other products. The corresponding oxidation reactions of styrene, cyclohexene, or 1-octene led to the respective epoxide as the main product. The oxidation reactions have been mechanistically assessed and oxo-manganese(IV) intermediates proposed as the active catalysts.

6.1 Introduction

Interest in dioxygen complexes has intensified in

recent years because of their ability to catalyse the oxidation of olefins.[1-18] These oxidation reactions are commercially important processes and many catalyst systems, more or less biomimetic, have been developed. These are based on the use of transition metal complexes, such as Fe, Co, Rh, Mn, Cr, V, derived from porphyrins. Generally, these model systems give poor yields in terms of olefin conversion to oxidation products. Moreover, in most studies, the important problem of oxygen activation is bypassed and alternative oxygen sources such as iodosobenzene, hydroperoxides, hypochlorite are used. The systems involving these oxidants are expensive and have the drawback of stoichiometric coproduct formation (Reaction 6.1).[4]



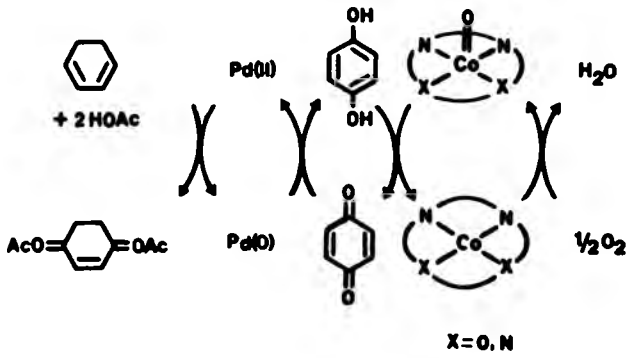
..6.1

Development of non-porphyrin metal complexes as catalysts for the oxidation of olefins has received limited attention, particularly with regard to aerobic oxidation. Thus, the phenyliodosyl (PhIO) epoxidation of olefins catalysed by non-porphyrin complexes of type OsL^1PPh_3Cl, MnL^1Cl, and MnL^2Cl has been reported (L^1H = 1,2-bis(pyridine-2-carboxamido)benzene and L^2H = 1,2-bis(pyridine-2-carboxamido)-4,5-dichlorobenzene).[15] The only paper to be published on aerobic oxidation catalysed by non-porphyrin complexes has reported the oxidation of olefins to aldehydes and

ketones by a 1:4 mixture of $Pd(MeCN)_2Cl(NO_2)$ and $CuCl_2$.[6] The palladium complex has also been used for the stoichiometric epoxidation of norbornene. During the course of this study, Barton et al. reported the aerobic oxidation of adamantane by the 'Gif system' which consists of dioxygen, a mixture of acetic acid in pyridine as solvent, iron powder, and sodium sulphide or hydrogen sulphide.[16]

Benzoquinones are well known oxidants in synthetic organic chemistry.[19] The 1,4-benzoquinone/hydroquinone redox couple has been used as part of a catalytic system involving the redox couples Pd(II)/Pd(0) and Co(TPP)(O)/Co(TPP) as catalysts.[17]

Scheme 6.1 A catalytic system involving 1,4-benzoquinone/hydroquinone redox couple

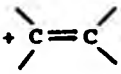
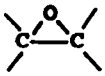


It has also been reported that systems based on the nitroso/nitro redox couple (Reactions 6.2 and 6.3) can catalyse the aerobic oxidation of alkenes to ketones and the stoichiometric oxidation of

norbornene to exo-epoxynorbornane.[17]

$$PdLCl(NO) + 1/2O_2 \longrightarrow PdLCl(NO) \qquad ..6.2$$

L = MeCN

$$PdLCl(NO_2) + \text{  } \longrightarrow PdLCl(NO) + \text{  } \qquad ..6.3$$

L = MeCN

The use of transition metal complexes derived from 1,2-quinone mono-oximes as catalysts for the oxidation of olefins is advantageous. As in addition to the ability of the metal to acitivate dioxygen, the 1,2-quinone mono-oximate ligands in such complexes have quinoid and oximic features which can expediate catalytic oxidation. Furthermore, 1,2-quinone mono-oximato complexes are cheaper and easier to prepare than metal complexes derived from porphyrins.

6.2 Oxidation of Olefins

A preliminary survey on the catalytic activity of the complexes $M(qo)_n$, $VO_2(qo)$, and $VO(qo)_2$ (qoH = 1-nqoH or 2-nqoH; n = 2, M = Mn, Fe, Ni, Cu; n =3, M = Cr, Mn, Fe, Co), using methyl oleate as substrate at 60 ^{o}C under an atmosphere of oxygen, was carried out. This demonstrated that only the manganese complexes give greater than ten percent conversion of methyl oleate to oxidation products. Furthermore, manganese is inexpensive and well known to be crucial for oxygen evolution in photosynthesis.[20] Thus, the complexes

$Mn(qo)_n$ were selected for study as aerobic oxidation catalysts.

6.2.1 Oxidation of methyl oleate (MO)

When methyl oleate (240 mol eq.) was stirred with Mn(1-nqo)2 (1 mol eq.), under an atmosphere of oxygen at 60 °C, complete conversion of the substrate to epoxymethyl oleate (epoxy-MO), as well as acidic and other products occurred (Table 6.1). Formation of acidic products indicates decomposition of epoxy-MO. It has previously been reported that hydrolysis of epoxyoleic acid leads to methyl-9,10-dihydroxystearic acid. Subsequent oxidative cleavage of the dihydroxy compound gives nonanal and azelaic half-aldehyde.[21] These aldehydes are readily oxidised to nonanoic acid and azelaic acid, respectively. The formation of acidic products in the oxidation of methyl oleate can be rationalised in a similar manner (Scheme 6.2).

The amount of acidic products formed was appreciably lower when the oxidation was carried out at 60 °C in air and at room temperature under an atmosphere of oxygen with a small quantity of pyridine (6 mmol). In contrast, the oxidation of MO at room temperature under an atmosphere of oxygen did not give a significant yield of epoxy-MO. This indicates that pyridine enhances epoxidation.

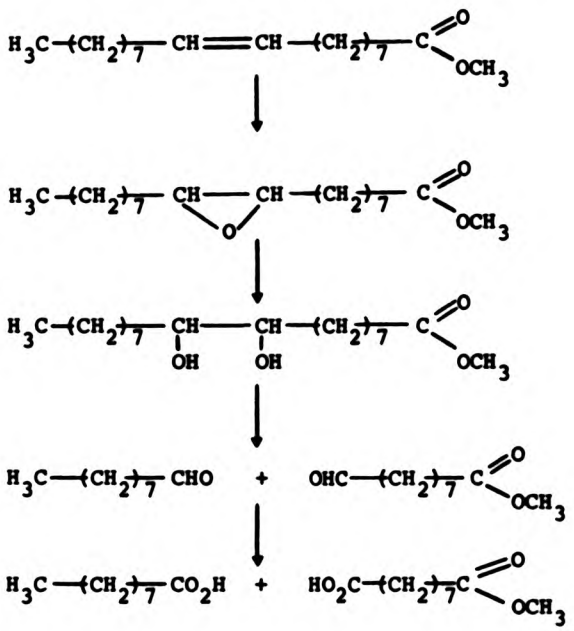
Comparable results were obtained when the above

Table 6.1 Aerobic oxidation of methyl oleate catalysed by manganese complexes derived from the mono-oximes of 1,2-naphthoquinone[a]

Catalyst	Conditions	mmol of epoxide	mmol of acid	mmol of unchanged MO	% Yield of epoxide[f]
$Mn(1\text{-nqo})_2$	b	14.2	36.5	0	24
$Mn(1\text{-nqo})_2$	c	1.3	1.5	46.5	2
$Mn(1\text{-nqo})_2$	d	7.2	9.1	25.1	12
$Mn(1\text{-nqo})_2$	e	7.2	1.8	49.1	12
$Mn(2\text{-nqo})_2$	b	10.7	30.4	10.3	18
$Mn(2\text{-nqo})_2$	c	0.5	1.5	48.7	1
$Mn(2\text{-nqo})_2$	d	5.8	7.6	28.5	10
$Mn(2\text{-nqo})_2$	e	6.5	1.4	50.1	11
$Mn(1\text{-nqo})_3$	b	13.5	14.7	20.5	23
$Mn(1\text{-nqo})_3$	c	1.5	2.2	47.0	3
$Mn(1\text{-nqo})_3$	d	6.5	3.7	29.8	11
$Mn(1\text{-nqo})_3$	e	7.5	2.1	48.6	13
$Mn(2\text{-nqo})_3$	b	14.1	16.4	18.9	24
$Mn(2\text{-nqo})_3$	c	1.7	1.9	46.4	3
$Mn(2\text{-nqo})_3$	d	6.9	4.5	28.6	12
$Mn(2\text{-nqo})_3$	e	7.1	3.6	47.9	12

[a] Initial concentration of MO = 60.0 mmol and catalyst = 0.25 mmol. [b] Oxygen atmosphere/60 ^{o}C/72 h. [c] Oxygen atmosphere/room temperature/216h. [d] Air/60 ^{o}C/72 h. [e] Oxygen atmosphere/room temperature/6 mmol of pyridine/144 h. [f] Yield based on MO.

Scheme 6.2 Epoxidation and cleavage of methyl oleate.



experiments were repeated using $Mn(2\text{-nqo})_2$ as the catalyst. However, the catalytic activity of $Mn(2\text{-nqo})_2$ was slightly lower than that of $Mn(1\text{-nqo})_2$.

The complexes $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$ also catalysed the aerobic oxidation of MO. Thus, when $Mn(1\text{-nqo})_3$ (1 mol eq.) and MO (240 mol eq.) were stirred at 60 ^{o}C under an atmosphere of oxygen, epoxy-MO and acidic products were obtained in comparable amounts. The amount of acidic products formed was relatively lower when the oxidation was carried out at 60 ^{o}C in air and at room temperature, under an atmosphere of oxygen, in the presence of pyridine (6 mmol). In the absence of pyridine, the corresponding reaction did not give a significant yield of epoxy-MO. Once again, this indicates the positive effect of pyridine upon the oxidation of MO.

6.2.2 Oxidation of styrene, cyclohexene, and 1-octene

Styrene, cyclohexene, and 1-octene were selected as suitable substrates because they represent a range of reactivities with regard to epoxidation. Also, these olefins have been used as substrates by other workers and, therefore, yields can be compared.

Optimum conditions for catalytic epoxidations were initially developed with cyclohexene. When cylcohexene

(400 mol eq.) and catalyst (1 mol eq.) were stirred at 60 ^{o}C under an atmosphere of oxygen, 1,2-epoxycyclohexane was obtained as the major product, in addition to a small amount of an unidentified product (Table 6.2). Yields of 1,2-epoxycyclohexane ranged between 40 - 65% and turnovers between 220 - 260. The highest yield and turnover was given by $Mn(1\text{-nqo})_2$. It has been reported that the MnL_1Cl- and MnL_2Cl-catalysed PhIO epoxidation of cyclohexene gives 1,2-epoxycyclohexane in yields of 39 - 58% and turnovers of 12 - 29.[15] Cr(salen)-catalysed PhIO epoxidation of cyclohexene affords the epoxide in yields of 2 - 22% based on the amount of PhIO converted to PhI.[9] Thus, yields and turnovers of 1,2-epoxycyclohexane obtained in this study are better than those previously reported for other systems.

When styrene (392 mol eq.) and catalyst (1 mol eq.) were stirred at 60 ^{o}C under an atmosphere of oxygen, styrene oxide was obtained in yields of 14 - 22% and turnovers of 47 - 73. Formation of coproducts was not observed. In contrast, the catalytic systems reported in the literature give phenylacetaldehyde and benzaldehyde as coproducts.[9] Yields of 58 - 78% have been reported for styrene oxide from the MnL_1Cl-, MnL_2Cl-, and Cr(salen)-catalysed PhIO epoxidations of styrene.[15,9] However, these are based on the amount of PhIO converted to PhI and not on styrene. The turnovers of styrene oxide obtained in this study

Table 6.2 Catalytic aerobic epoxidation of olefins by manganese complexes derived from the mono-oximes of 1,2-naphthoquinone[a]

Catalyst[b]	Olefin	Epoxide Yield, %[c]/Turnover[d]	Induction Time (h)
A	Cyclohexene	65/ 260[e]	19
B	Cyclohexene	46/ 184[e]	99
C	Cyclohexane	40/ 160[e]	89
D	Cylohexene	55/ 220[e]	33
A	Styrene	21/ 82	32
B	Styrene	14/ 55	110
C	Styrene	17/ 67	95
D	Styrene	22/ 86	39
A	1-Octene	30/53	48
B	1-Octene	24/43	120
C	1-Octene	19/34	110
D	1-Octene	27/48	65

[a] Reaction at 60 °C under an oxygen atmosphere. [b] A = $Mn(1\text{-nqo})_2$, B = $Mn(2\text{-nqo})_2$, C = $Mn(1\text{-nqo})_3$, D = $Mn(2\text{-nqo})_3$. [c] Yield based on olefin. [d] Turnover based on the amount of catalyst used. [e] In addition to an unidentified product in low yield.

(47 - 73) are better than those reported in the literature (49 - 64).[15]

When 1-octene (178 mol eq.) and catalyst (1 mol eq.) were stirred at 60 ^{o}C under an atmosphere of oxygen, 1-epoxyoctane was obtained in yields of 19 - 30% and turnovers of 30 - 47. Formation of coproducts was not observed. Yields and turnovers of 1-epoxyoctane obtained in this study are better than the values reported in the literature. For example, Cr(salen) type complexes give yields of 1-epoxyoctane in the range 2 - 12%.[9]

6.3 Mechanistic aspects of epoxidation

Reaction profiles of styrene, cyclohexene, and 1-octene epoxidations (Figures 6.1 - 6.3) show an initial induction period followed by a linear rise in epoxide yield and then a levelling-off of yield. Each catalyst gave a different induction period, $Mn(1\text{-nqo})_2$ < $Mn(2\text{-nqo})_3$ < $Mn(1\text{-nqo})_3$ < $Mn(2\text{-nqo})_2$, which was independent of catalyst concentration. This shows that the manganese complexes are not the active catalytic species.

There is agreement amongst workers in the field of catalytic olefin oxidation that high-valent oxo-metal intermediates are the active catalysts.[7-15,19,22] Thus, it has been reported that the rate determining step in olefin epoxidation, by the mono-oxygenase

Figure 6.1 Reaction profile for the epoxidation of cyclohexene with dioxygen, at 60 °C, catalysed by the complexes $Mn(nqo)_n$.

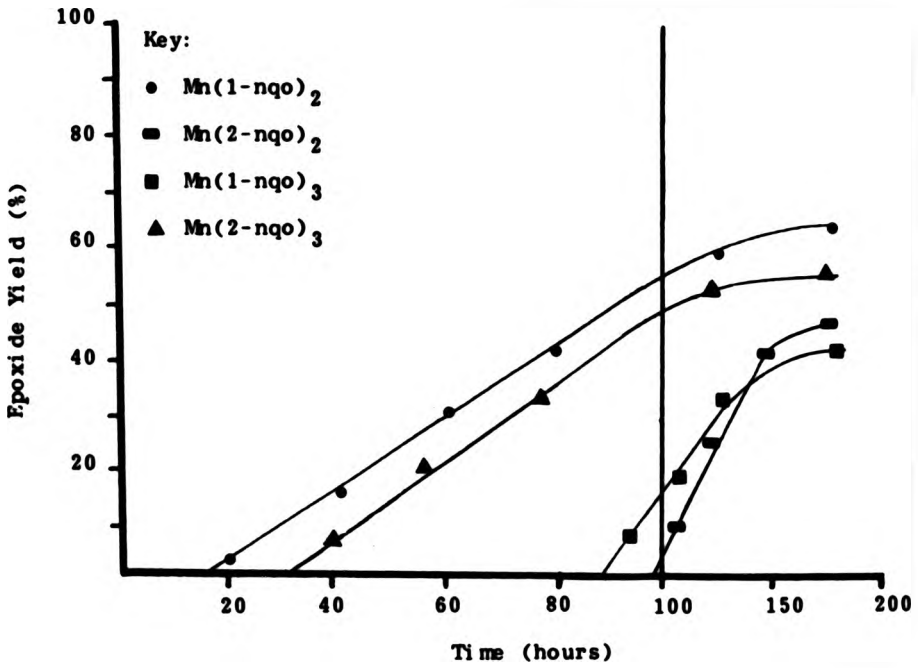


Figure 6.2 Reaction profile for the epoxidation of styrene with dioxygen, at 60 ^{o}C, catalysed by the complexes $Mn(nqo)_n$.

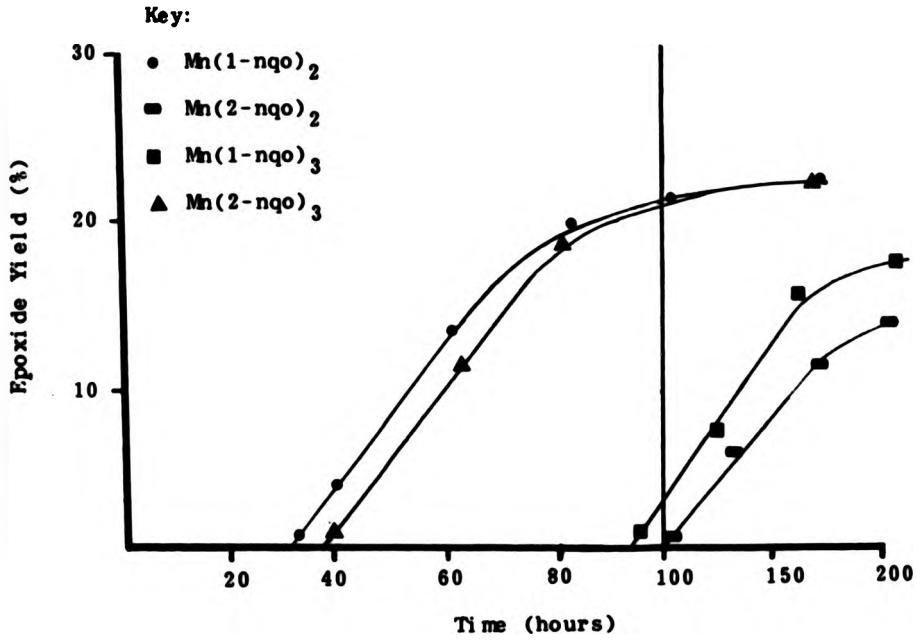
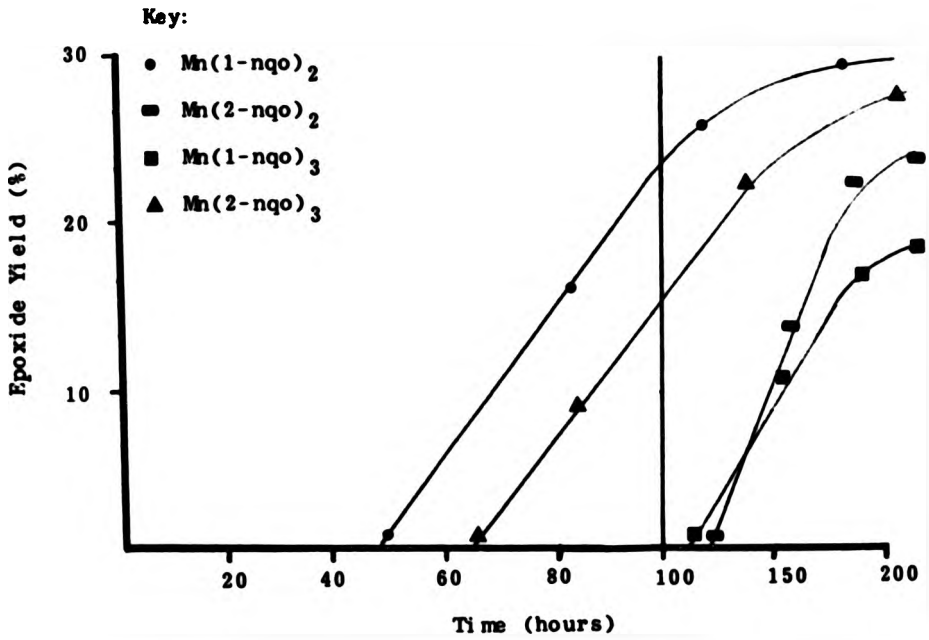


Figure 6.3 Reaction profile for the epoxidation of 1-octene with dioxygen, at 60 °C, catalysed by the complexes $Mn(nqo)_n$.

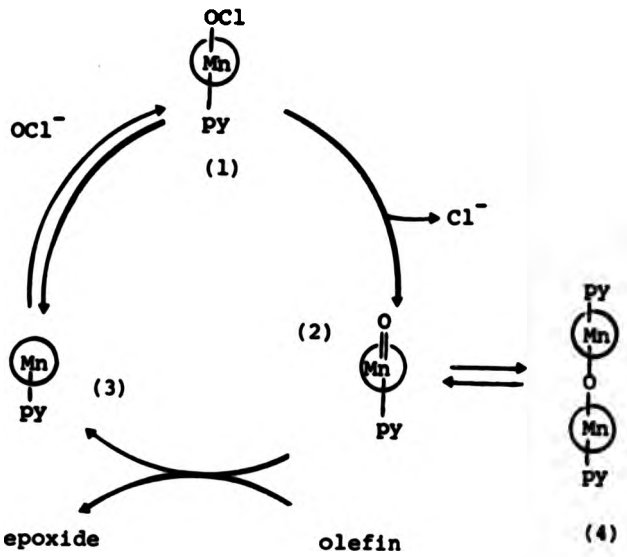


model (tetra-p-tolylporphinato)manganese(III) acetate/sodium hypochlorite, is the conversion of the manganese(III) hypochlorite complex (1) into a high-valent oxo-manganese(V) species (2) (Scheme 6.3).[10]

The complexes $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$, as well as the associated complexes $Mn(1\text{-nqo})_2$ and $Mn(2\text{-nqo})_2$, are coordinately saturated. The bis-chelates can form oxo-manganese intermediates of type $Mn(nqo)_2O$ or $Mn(2\text{-nqo})_2(O)_2$ only after their polymeric structure has been broken. Similarly, the tris-chelates can only form the catalytically active intermediates after one of the ligands is discharged or becomes mono-dentate by means of an internal redox reaction. Therefore, the induction periods can be partially rationalised as the time required for: (1) polymeric chains of the bis-chelates to break and, (2) for the tris-chelates to undergo internal redox reactions. (The occurrence of internal redox reactions is supported by the t.l.c. detection of 1-nqoH and 2-nqoH in the epoxidation reactions involving $Mn(1\text{-nqo})_3$ and $Mn(2\text{-nqo})_3$, respectively.) The coordinately unsaturated manganese centres arising after the induction period can form high-valent oxo-manganese intermediates. This is reflected in the linear rise in epoxide yields in the post-induction sections of the reaction profiles.

It has been reported that pyridine and substituted pyridines considerably enhance the rate of olefin

Scheme 6.3 Olefin epoxidation by the mono-oxygenase model (tetraphenylporphinato)manganese(III) acetate/ sodium hypochlorite.

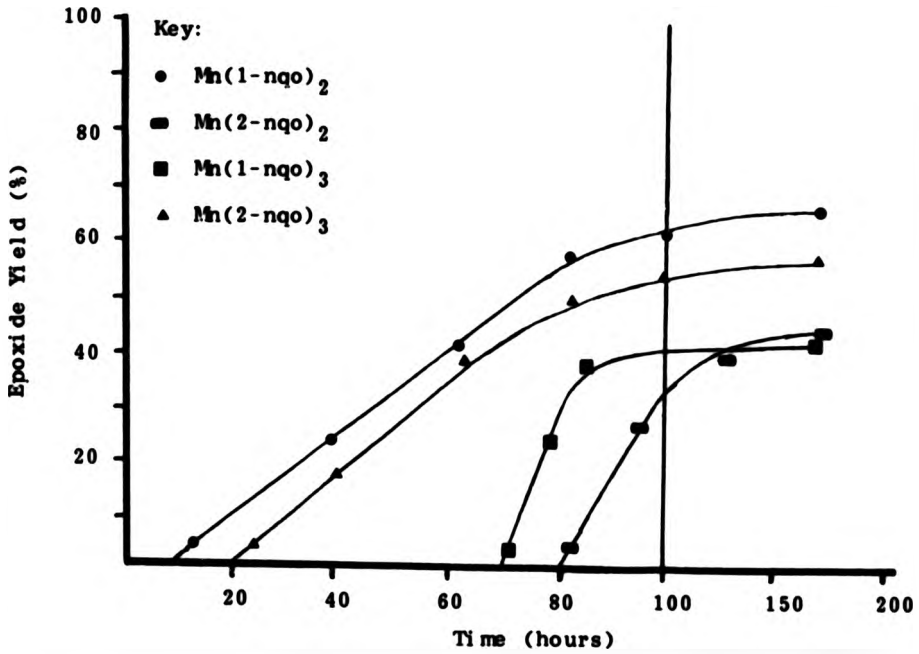


epoxidation as electron donation by coordinated pyridine expediates formation of the oxo-manganese(V) intermediate and oxygen transfer to the olefin (Scheme 6.3).[10] In addition, in the case of catalytic systems involving the $Mn(nqo)_n$ complexes, pyridine can reduce the induction period by: (1) assisting disintegration of the polymeric chains in $Mn(1\text{-}nqo)_2$ and $Mn(2\text{-}nqo)_2$ and, (2) inducing internal redox reactions in $Mn(1\text{-}nqo)_3$ and $Mn(2\text{-}nqo)_3$. As noted in section 6.2.2, pyridine enhances the oxidation of methyl oleate. The epoxidation of cyclohexene was, therefore, investigated in the presence of 6 mmol of pyridine. The reaction profile clearly showed decrease in induction periods for all the catalysts and increase in the rates of epoxidation (Figure 6.4).

The induction period of $Mn(2\text{-}nqo)_3$ was lower than that of $Mn(1\text{-}nqo)_3$ and this reflects the relative ease with which $Mn(2\text{-}nqo)_3$ undergoes internal redox reactions (see Chapter 4). The lower induction period of $Mn(1\text{-}nqo)_2$ in comparison to $Mn(2\text{-}nqo)_2$ can be attributed to a greater degree of association in $Mn(2\text{-}nqo)_2$.

Reaction profiles also show that epoxide yields level-off after ca. 175 hours. This can be explained by (1) catalyst decomposition and, (2) formation of inactive or less active μ-oxo dimers of type $(nqo)_2MnOMn(nqo)_2$. Such dimers have been isolated in this study and other manganese(IV) dimers have

Figure 6.4 Reaction profile for the epoxidation of cyclohexene with dioxygen, at 60 °C, catalysed by the complexes $Mn(nqo)_n$ in the presence of pyridine.



previously been reported (Scheme 6.3).[10,19]

In order to reduce catalyst decomposition and dimer formation, $Mn(2\text{-nqo})_2$ was anchored onto a polymer backbone by refluxing $Mn(2\text{-nqo})_3$ and the polymer (P) in acetone (Reaction 6.4). Oxidation of cyclohexene by the polymer mounted catalyst gave a lower induction period (48 hours) and a higher yield of epoxide (75%) than previously obtained using $Mn(2\text{-nqo})_2$ (99 hours, 46 %).

$$Mn(2\text{-nqo})_3 + (P) \longrightarrow (P)\text{-}Mn(2\text{-nqo})_2 + [nqo^{\bullet}] \qquad ..6.4$$

Catalytic epoxidation of olefins is a commercially important process. The results obtained in this study are, therefore, very significant. They involve the first successful application of cheap and readily available non-porphyrin complexes as catalysts for the aerobic epoxidation of olefins.

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CHAPTER SEVEN

EXPERIMENTAL

7.1 General Techniques

The reagents and solvents used were generally of GPR grade. Solvents for column chromatography were freshly distilled. The adsorbent used in the chromatography columns was Merck Kieselgel 60 (70-230 mesh). T.l.c. was carried out using precoated Merck Kieslgel 60 F_{254} plates.

I.r. spectra were recorded on a Perkin-Elmer 781 spectrophotometer. U.v./vis. spectra were obtained using a Perkin-Elmer Lambda 5 spectrophotometer. An A.E.I. MS9 spectrometer was used for mass spectrometry. Relative molecular mass measurements were carried out with a Perkin-Elmer 115 osmometer. Room temperature magnetic moments were measured using a Gouy balance equipped with a

permanent magnet of field strength 3600 oersted. The variable temperature magnetic studies were carried out using a Newport Instruments Gouy balance at field strengths of 3500, 5500, 6400, and 7100 Öersted at intervals over the temperature range 93 - 295 ^{o}K. In both cases, the apparatus was calibrated with mercury tetrathiocyanatocobaltate(II). All the magnetic measurements were carried out in duplicate to check on packing errors. The magnetic susceptibility values were corrected for diamagnetism.[1]

Carbon, hydrogen, and nitrogen were determined by the microanalytical unit of the Polytechnic of North London. Metal analyses were obtained by atomic absorption spectrometry. Chromium was also determined by the ferrous sulphate method.[2] Wet-ashing was achieved by chaWing an accurately weighed quantity of sample (ca. 0.25 g) with a few drops of concentrated sulphuric acid and then boiling in a mixture of concentrated nitric acid (5 cm^3) and hydrogen peroxide (30%, 1.5 cm^3).

Note that most of the common organic products were identified by comparative t.l.c. and i.r. with authentic samples. This is denoted throughout this chapter by an asterisk after the name of the organic product.

7.2 Reactions

Nitrosation of phenols in the presence of chromium(III) chloride hexahydrate.

a) Nitrosation of 2-naphthol.-Sodium nitrite (44.85 g, 0.65 mol) in water (250 cm^3) was added dropwise to a solution of chromium(III) chloride hexahydrate (15.90 g, 0.06 mol), 2-naphthol (26.51 g, 0.18 mol), glacial acetic acid (45.10 g, 0.75 mol) and sodium acetate (27.13 g, 0.33 mol) in a 3:1 mixture of methanol and water (400 cm^3). After 7 days at room temperature the solid was filtered off, washed with water (5 x 200 cm^3), methanol (2 x 100 cm^3), and light petroleum (b.p. 30-40 ^oC) (3 x 100 cm^3). The crude product was chromatographed on a silica column. Elution was carried out with toluene followed by dichloromethane. Removal of the dichloromethane in vacuo afforded red tris(1,2-naphthoquinone 1-oximato)chromium(III) (21.8 g, 62%) (Found: C, 63.1; H, 3.1; Cr, 9.3; N, 7.1. $C_{30}H_{18}CrN_3O_6$ requires C, 63.4; H, 3.2; Cr, 9.2; N, 7.4%).

b) Nitrosation of 1-naphthol (26.30 g, 0.18 mol) in the presence of chromium(III) chloride hexahydrate (16.10 g, 0.06 mol) was carried out in a similar way to the nitrosation 2-naphthol to give wine-red tris(1,2-naphthoquinone 2-oximato)chromium(III) (24.26 g, 71%) (Found: C, 63.5; H, 3.6; Cr, 9.3; N, 6.6. $C_{30}H_{18}CrN_3O_6$ requires C, 63.4; H, 3.2; Cr, 9.2; N, 7.4%).

c) Nitrosation of 3-methyl-5-hydroxyphenol (22.35 g, 0.18

mol) in the presence of chromium(III) chloride hexahydrate (16.30 g, 0.06 mol) was carried out in a similar way to the nitrosation of 2-naphthol. The crude product was washed with water (50 cm^3), methanol (100 cm^3), and diethylether (3 x 100 cm^3), and chromatographed on a silica column. Elution was carried out with a 1:1 mixture of diethylether and methanol followed by water. The water extract was dried in vacuo and then over phosphorus pentoxide to give red-brown tris(3-methyl-5-hydroxy-1,2--benzoquinone 2-oximato)chromium(III) (14.65 g, 48%) (Found: C, 50.1; H, 3.2; Cr, 10.5; N, 8.6. $C_{21}H_{18}CrN_3O_9$ requires C, 49.6; H, 3.5; Cr, 10.2; N, 8.3%).

d) Nitrosation of 2-methyl-5-hydroxyphenol (22.5 g, 0.18 mol) in the presence of chromium(III) chloride hexahydrate (15.95 g, 0.06 mol) was carried out using the method described for 2-naphthol. The product was washed with water (50 cm^3), methanol (50 cm^3), diethylether (3 x 100 cm3), and chromatographed on a silica column. Elution was carried out with ether/methanol (1:1) followed by methanol. The methanol extract was dried in vacuo and then over phosphorus pentoxide to give tris(6-methyl-5-hydroxy--1,2-benzoquinone 2-oximato)chromium(III) (12.20 g, 40%) (Found: C, 50.6; H, 3.5; Cr, 10.4; N, 8.1. $C_{21}H_{18}CrN_3O_9$ requires C, 49.6; H, 3.5, Cr, 10.2; N, 8.3%).

e) Nitrosation of 4-methylphenol, 4-t-butylphenol, or 4-chlorophenol (0.18 mol) in the presence of chromium(III) chloride hexahydrate (15.90 g, 0.06 mol) was carried out using the method described for 2-naphthol. The black tar

obtained upon filtration was ill-defined by i.r. and multicomponent by t.l.c.

Reaction of sodium 1,2-naphthoquinone oximates with chromium(III) chloride hexahydrate.

Sodium 1,2-naphthoquinone 1-oximate (5.85 g, 0.03 mol) and chromium(III) chloride hexahydrate (2.67 g, 0.01 mol), were heated under reflux in ethanol (300 cm^3) for 3h. Filtration of the mixture gave a solid which was washed with water (3 x 100 cm^3), methanol (2 x 50 cm^3), light petroleum (b.p. 30-40 ^oC) (4 x 50 cm^3) and chromatographed on a silica column. Elution was carried out with toluene followed by dichloromethane. Removal of the solvent from the dichloromethane eluate gave tris(1,2-naphthoquinone 1-oximato)chromium(III) (2.56 g, 44%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Similarly, reaction of sodium 1,2-naphthoquinone 2-oximate (5.88 g, 0.03 mol) with chromium(III) chloride hexahydrate (2.65 g, 0.01 mol) afforded tris(1,2-naphthoquinone 2-oximato)chromium(III) (2.90 g, 49%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Reaction of 1,2-naphthoquinone mono-oximes with chromium-(III) chloride hexahydrate.

Chromium(III) chloride hexahydrate (2.67 g, 0.01 mol) and 1,2-naphthoquinone 1-oxime (5.20 g, 0.03 mol) were heated under reflux in ethanol (300 cm^3) for 3h. The reaction mixture was dried in vacuo and chromatographed on a silica column. Elution was carried out with toluene followed by dichloromethane. Removal of the solvent from the dichloromethane eluate gave tris(1,2-naphthoquinone 1-oximato)chromium(III) (1.25 g, 22%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Similarly the reaction of 1,2-naphthoquinone 2-oxime (5.74 g, 0.03 mol) with chromium(III) chloride hexahydrate (2.95 g, 0.01) afforded tris(1,2-naphthoquinone 2-oximato)chromium(III) (1.16 g, 18%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Reaction of 1,2-naphthoquinone mono-oximes with chromium(III) chloride hexahydrate in the presence of a sodium acetate/acetic acid buffer.

Chromium(III) chloride hexahydrate (5.10 g, 0.02 mol) was added to a solution of 1,2-naphthoquinone 1-oxime (10.31 g, 0.06 mol), acetic acid (30.10 g, 0.50 mol) and sodium acetate (20.05 g, 0.24 mol) in ethanol (400 cm^3). The reaction mixture was heated under reflux for 3h. The solid was filtered-off, washed with water (6 x 100 cm^3), methanol (3 x 25 cm^3), light petroleum (b.p. 30-40 ^oC) (4 x 50 cm^3) and chromatographed on a silica column. Elution was carried out with toluene followed by dichloromethane.

Removal of the solvent from the dichloromethane eluate gave tris(1,2-naphthoquinone 1-oximato)chromium(III) (5.10 g, 45%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Similarly, the reaction of 1,2-naphthoquinone 2-oxime (10.45 g, 0.06 mol) with chromium(III) chloride hexahydrate (5.30 g, 0.02 mol) yielded tris(1,2-naphthoquinone 2-oximato)chromium(III) (4.60 g, 40%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Reaction of hexacarbonylchromium(0) with 1,2-naphthoquinone 1-oxime.-1,2-Naphthoquinone 1-oxime (5.19 g, 0.03 mol) and hexacarbonylchromium(0) (2.20 g, 0.01 mol) were heated under reflux in toluene (100 cm^3) for 3.5h. Light petroleum (30 - 40 ^oC) (100 cm^3) was then added. Filtration gave a green solid (0.80 g) (Found: Cr, 5.10%) which was washed with light petroleum (b.p. 30 - 40 ^oC) (2 x 25 cm^3) and dried *in vacuo*. The residue remaining after removal of the solvents from the filtrate and washings was chromatographed on a silica column. Toluene eluted a mixture of organic products (1.55 g). Dichloromethane eluted tris(1,2-naphthoquinone 1-oximato)chromium(III) (1.42 g, 25%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Reaction of hexacarbonylchromium(0) with 1,2-naphthoquinone 2-oxime.-1,2-Naphthoquinone 2-oxime (5.20 g, 0.03 mol)

and hexacarbonylchromium(0) (2.24 g, 0.01 mol) in toluene (100 cm^3) were heated under reflux for 3.5h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica column. Toluene eluted 5-hydroxy-dibenzo[b,i]-phenazin-12(6H)-one (1.20 g, 23%)*. Toluene/ethyl acetate (8:2) eluted 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphtho-quinone 4-imine (<0.1 g)*, and unreacted 1,2-naphtho-quinone 2-oxime (0.99 g, 19% recovery)*. Dichloromethane eluted tris(1,2-naphthoquinone 2-oximato)chromium(III) (0.92 g, 16%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Decomposition of 1,2-naphthoquinone 2-oxime in toluene.- 1,2-Naphthoquinone 2-oxime (0.50 g, 2.90 mmol) was heated at reflux temperature in toluene (50 cm^3) for 4h. The reaction mixture was dried *in vacuo* and the residue was chromatographed on a silica column. Toluene eluted 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.09 g, 20%)*. Toluene/ethyl acetate (8:2) eluted 2-amino-N^4(1-hydroxy--2-naphthyl)-1,4-naphthoquinone 4-imine (0.10 g, 22%)* and unreacted 1,2-naphthoquinone 2-oxime (0.20 g, 40% recovery)*.

Decomposition of 1,2-naphthtoquinone 1-oxime in toluene.- 1,2-Naphthoquinone 1-oxime (0.52 g, 2.9 mmol) was heated under reflux in toluene (75 cm^3) for 4h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica column. Elution with toluene afforded 1,2-naphthoquinone 1-oxime (0.34 g, 68% recovery)*. A black material was left on top of the chromatography

Reaction of hexacarbonylchromium(0) with tris(1,2-naphthoquinone mono-oximato)chromium(III).

Reaction of tris(1,2-naphthoquinone 2-oximato)chromium(III) with hexacarbonylchromium(0).-Hexacarbonylchromium(0) (0.21 g, 0.95 mmol) and tris(1,2-naphthoquinone 2-oximato)-chromium(III) (1.08 g, 1.90 mmol) were heated at reflux temperature in toluene (100 cm^3) for 30h. The mixture was then concentrated in vacuo to 50 cm^3. Addition of n-hexane (25 cm^3) gave brown μ-oxotetrakis(1,2-naphthoquinone 2-oximato)dichromium(III) (1.10 g, 96%) (Found: C, 59.1; H, 3.1; Cr, 12.5; N, 6.6. $C_{40}H_{24}Cr_2N_4O_9$ requires C, 59.4; H, 3.0; Cr, 12.9; N, 6.9%) which was filtered, washed with diethylether (4 x 25 cm^3), and dried in vacuo.

Similarly, the reaction of hexacarbonylchromium(0) (0.23 g, 1.05 mmol) with tris(1,2-naphthoquinone 1-oximato)chromium(III) (1.19 g, 2.10 mmol) afforded brown μ-oxotetrakis(1,2-naphthoquinone 1-oximato)dichromium(III) (1.05 g, 92%) (Found: C, 59.0; H, 3.2; Cr, 12.4; N, 6.7. $C_{40}H_{24}Cr_2N_4O_9$ requires C, 59.4; H, 3.0; Cr, 12.9; N, 6.9%).

Nitrosation of phenols in the presence of manganese(II) chloride tetrahydrate.

a) Nitrosation of 2-naphthol.-Sodium nitrite (30.05 g, 0.43 mol) was dissolved in water (250 cm^3) and added dropwise to a solution of manganese(II) chloride

tetrahydrate (10.00 g, 0.05 mol), 2-naphthol (15.02 g, 0.10 mol), glacial acetic acid (30.20 g, 0.50 mol) and sodium acetate (20.10 g, 0.22 mol) in a 2:1 mixture of methanol and water (300 cm^3). After 6 days at room temperature, the solid was filtered off, washed with water (6 x 100 cm^3), methanol (2 x 50 cm^3), light petrol (b.p. 30-40 ^oC) (3 x 100 cm^3) and dried in vacuo to afford brown tris(1,2-naphthoquinone 1-oximato)manganese(III) (18.50 g, 91%) (Found: C, 58.6; H, 3.5; Mn, 8.9; N, 6.7. $C_{30}H_{18}MnN_3O_6$ requires C, 59.3; H, 3.6; Mn, 9.1; N, 6.9%).

b) Nitrosation of 1-naphthol (15.23 g, 0.10 mol) in the presence of manganese(II) chloride tetrahydrate (10.16 g, 0.05 mol) afforded brown-black tris(1,2-naphthoquinone 2-oximato)manganese(III) (11.70 g, 58%) (Found: C, 62.6; H, 3.3; Mn, 9.3; N, 7.4. $C_{30}H_{18}MnN_3O_6$ requires C, 63.1; H, 3.2; Mn, 9.6; N, 7.4%).

c) Nitrosation of 4-methylphenol, 4-t-butylphenol, or 4-chlorophenol (0.10 mol) in the presence of chromium(III) chloride hexahydrate (10.10 g, 0.05 mol) was carried out in a similar way the nitrosation of 2-naphthol. Filtration afforded a black tar which was ill-defined by i.r. and multicomponent by t.l.c. Atomic absorption spectrophotometry indicated that most of the manganese ion was present in the filtrate.

Reaction of sodium 1,2-naphthoquinone mono-oximates with manganese(II) chloride tetrahydrate.

Manganese(II) chloride tetrahydrate (3.96 g, 0.02 mol) and sodium 1,2-naphthoquinone 1-oximate (7.80 g, 0.04 mol) were heated under reflux in ethanol (350 cm^3) for 3h. Filtration gave brown bis(1,2-naphthoquinone 1-oximato)-manganese(II) (5.21 g, 65%) (Found: C, 59.1; H, 3.1; Mn, 13.5; N, 7.0. $C_{20}H_{12}MnN_2O_4$ requires C, 60.2; H, 3.0; Mn, 13.8; N, 7.0%) which was washed with water (4 x 100 cm^3), methanol (3 x 100 cm^3), diethylether (2 x 50 cm^3) and dried in vacuo.

Similarly, the reaction involving sodium 1,2-naphthoquinone 2-oximate (7.85 g, 0.04 mol) and manganese(II) chloride tetrahydrate (3.90 g, 0.02 mol) afforded brown bis(1,2-naphthoquinone 2-oximato)manganese-(II) (5.50 g, 69%) (Found: C, 59.5; H, 3.2; Mn, 13.7; N, 6.8. $C_{20}H_{12}MnN_2O_4$ requires C, 60.2; H, 3.0; Mn, 13.8; N, 7.0%).

Reaction of tris(acetylacetonato)manganese(III) with 1,2-naphthoquinone mono-oximes.

Reaction with 1,2-naphthoquinone 1-oxime.-Tris(acetyl-acetonato)manganese(III) (0.70 g, 2.0 mmol) and 1,2-naphthoquinone 1-oxime (1.04 g, 6.0 mmol) in benzene (200 cm^3) (care! carcinogenic) were heated under reflux, in a nitrogen atmosphere, for 36h. Filtration gave tris(1,2-naphthoquinone 1-oximato)manganese (III) (0.75 g, 66%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method) which was washed with benzene (3 x 10 cm^3) and dried in vacuo.

Similarly, the reaction of 1,2-naphthoquinone 2-oxime (1.07 g, 6.0 mmol) with tris(acetylacetonato)manganese-(III) (0.72 g, 2.0 mmol) afforded tris(1,2-naphthoquin-2-oximato)manganese(III) (0.68 g, 60%) (identical t.l.c. and i.r. with a sample synthesised by the nitrosation method).

Reaction of tris(1,2-naphthoquinone mono-oximato)manganese(III) with hydrochloric acid.

Reaction of tris(1,2-naphthoquinone 1-oximato)manganese-(III).-Tris(1,2-naphthoquinone 1-oximato)manganese(III) (1.14 g, 2.0 mmol) was stirred in 6M hydrochloric acid (50 cm^3) for 5h. The reaction mixture was extracted with dichloromethane using a continous extraction apparatus. Removal of the solvent from the extract gave 1,2-naphthoquinone 1-oxime (0.98 g, 94%)* as residue.

Similarly, acidification of tris(1,2-naphthoquinone 2-oximato)manganese(III) (1.20 g, 2.0 mmol) led to 1,2-naphthoquinone 2-oxime (0.95 g, 91%)*.

Reaction of $Cr(1\text{-nqo})_3$ with pyridine.-Tris(1,2-naphthoquinone 1-oximato)chromium(III) (2.27 g, 4 mmol) was heated under reflux in pyridine (30 cm^3) for 192h and the solvent was removed at 90 ^oC/10 mmHg. The residue was Soxhelt extracted with diethylether and dried <u>in vacuo</u> to give a dark brown solid (1.75 g) (Found: C, 60.8; H, 3.5; Cr, 10.6; N, 8.5%). The

extract was dried *in vacuo* and chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C)/toluene (6:4) eluted 1-nitro-2-naphthol (0.03 g, 4%)*. Toluene eluted 6-hydroxy-dibenzo[i,mn]acridine--8-one (0.20 g, 32%)*.

Similarly the reaction of tris(1,2-naphthoquinone 2-oximato)chromium(III) (4.05 g, 7 mmol) with pyridine (30 cm^3) afforded a dark green solid (3.35 g) (Found: C, 57.8; H, 3.5; Cr, 9.9; N, 7.9%). The extract was chromatographed on a silica column. Elution was carried out as above to give 2-nitro-1-naphthol (0.04 g, 3%)* and 5-hydroxy-dibenzo-[b,i]phenazin-12(6H)-one (0.50 g, 46%)*.

Reaction of $Mn(1\text{-nqo})_3$ with pyridine.-Tris(1,2-naphthoquinone 1-oximato)manganese(III) (1.15 g, 2 mmol) was stirred in pyridine (30 cm^3) at 20 °C for 168h. Pyridine was removed under a stream of nitrogen and the residue was extracted with light petroleum (b.p. 30-40 °C, 10 x 50 cm^3), acetone (10 x 50 cm^3) and dried *in vacuo* to give a manganese-containing product (0.12 g) which was ill-defined by i.r. (Found: Mn, 12.8%). The extracts were dried *in vacuo* to afford, respectively, 1,2-naphthoquinone 1-oxime (0.05 g)* and tris(1,2-naphthoquinone 1-oximato)manganese(III) (0.97 g, 85% recovery).

Reaction of $Mn(2\text{-nqo})_3$ with pyridine.-Tris(1,2-naphthoquinone 2-oximato)manganese(III) (1.15 g, 2 mmol) was

stirred in pyridine (30 cm^3) at 20 °C for 168h. Pyridine was removed under a stream of nitrogen. The residue was extracted with light petroleum (b.p. 30-40 °C, 10 x 50 cm^3), acetone (10 x 50 cm^3) and dried *in vacuo* to give brown *μ*-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese(III) (0.80 g, 98 %) (Found: C, 59.2; H, 3.1; Mn, 13.4; N, 7.0. $C_{40}H_{24}Mn_2N_4O_9$ requires C, 59.0; H, 2.9; Mn, 13.5; N, 6.9 %). The light petroleum extract was chromatographed on a silica column. Elution with light petroleum (b.p. 30-40 °C)/toluene (6:4) afforded 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.08 g, 26%)* and elution with methanol yielded 1,2-naphthoquinone 2-oxime (0.21 g, 62%)*. The acetone extract was dried to yield tris-(1,2-naphthoquinone 2-oximato)manganese(III) (<0.05 g)*.

Reactions of $Mn(2\text{-nqo})_3$ with other Lewis bases were carried out in an identical manner to the reaction involving pyridine. Yields and methods of characterisation are given in Table 7.1.

Reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine.-Tris-(1,2-naphthoquinone 2-oximato)chromium(III) (2.84 g, 5.0 mmol) was added to a solution of triphenylphosphine (3.93 g, 15.0 mmol) in acetone (200 cm^3). The resultant mixture was stirred at 20 °C for 240h. Dried under a stream of nitrogen and Soxhelt extracted with toluene. The residue was dried *in vacuo* to give '$Cr(2\text{-nqo})_2$' (1.87 g) (Found C, 60.7; H, 4.3;

Table 7.1 Reactions of tris(1,2-naphthoquinone 2-oximato)manganese(III) with Lewis bases (LB).

LB[a]	$Mn(2\text{-nqo})_3$ recovery g/%[b]	Products[c]		
		$[Mn(2\text{-nqo})_2]_2O$	2-nqoH	phenazinone
		g/% yield[d]		
1	0.92/80	0.14/89	0.05/73	Trace
2	0.77/67	0.21/78	0.08/70	Trace
3	0.47/41	0.40/83	0.14/68	0.05
4	0.29/25	0.45/74	0.17/65	0.09
5	0.23/20	0.52/79	0.19/68	0.07
6	0.00/0	0.80/98	0.21/62	0.08

[a] 1 = benzene, 2 = methyl cyanide, 3 = acetone, 4 = tetrahydrofuran, 5 = dimethyl sulphoxide, 6 = pyridine. [b] Based on the amount of $Mn(2\text{-nqo})_3$ used (1.15 g, 2 mmol). [c] Products characterized by comparative t.l.c. and i.r. with authentic samples. [d] Yields based on the amount of $Mn(2\text{-nqo})_3$ used-up.

Cr, 12.7; N, 7.2 %). The extract was dried and the residue was chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C)/toluene (9:1) eluted triphenylphosphine (2.45 g, 62% recovery)* and light petroleum (b.p. 30 - 40 °C)/toluene (2:8) eluted 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.48 g, 62%)*. Toluene/ethyl acetate (6:4) eluted 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.21 g, 27%)* and ethyl acetate/acetone (8:2) eluted triphenylphosphine oxide (1.29 g, 93%)*.

Reaction of $Cr(2\text{-nqo})_3$ with triphenylphosphine.-Tris-(1,2-naphthoquinone 2-oximato)chromium(III) (2.84 g, 5 mmol) was added to a solution of triphenylphosphine (3.93 g, 15 mmol) in acetone (200 cm^3). The reaction mixture was stirred at 20 °C for 1h, dried under a stream of nitrogen, and chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C)/toluene (9:1) eluted triphenylphosphine (2.50 g, 64% recovery)* and light petroleum (b.p. 30 - 40 °C)/toluene (2:8) eluted 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.25 g, 32%)*. Dichloromethane eluted bis(1,2-naphthoquinone 2-imine)tetrakis(1,2-naphthoquinone 2-oximato)dichromium(II) (1.85 g, 67%) (Found: C, 66.0; H, 3.6; Cr, 9.1; N, 7.4. $C_{60}H_{38}Cr_2N_6O_{10}$ requires C, 65.1; H, 3.4; Cr, 9.4; N, 7.6%). Dichloromethane/ethyl acetate (6:4) eluted 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.10 g, 13%)* and ethyl acetate/acetone (8:2) eluted triphenylphosphine oxide (1.28 g, 92%)*.

Reaction of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ with hydrochloric acid.-The complex (0.50 g, 0.45 mmol) was stirred in hydrochloric acid (6M, 50 cm^3) for 24h. The reaction mixture was extracted with diethylether (10 x 50 cm^3), dried *in vacuo*, and the residue was chromatographed on a silica column. Elution with light petroleum (b.p. 30 - 40 ^oC) and toluene gave 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.08 g, 57%)*. Toluene and ethyl acetate (6:4) eluted 2-amino-N^4-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.02 g, 14%)*. Ethyl acetate and methanol (8:2) eluted 1,2-naphthoquinone 2-oxime (0.10 g, 33%)*.

Reaction of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$ with pyridine.-The chromium complex (0.50 g, 0.45 mmol) was stirred in pyridine (20 cm^3) for thirty days and pyridine was removed under a stream of nitrogen. The residue was washed with toluene (10 x 50 cm^3) and dried *in vacuo* to give '$Cr(2\text{-nqo})_2$' (0.35 g). The washings were chromatographed on a silica column. Light petroleum (b.p. 30 - 40 ^oC)/toluene (2:8) eluted 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.12 g, 86%)*.

Reaction of $[Cr(2\text{-nqo})_2(2\text{-nqiH})]_2$, triphenylphosphine and 1,2-naphthoquinone 2-oxime.-The complex (0.55 g, 0.50 mmol), triphenylphosphine (0.52 g, 2 mmol) and 1,2-naphthoquinone 2-oxime (0.35 g, 2 mmol) were stirred in acetone (50 cm^3) for 24h. The solvent was removed under a stream of nitrogen and the residue was

washed with toluene (10 x 20 cm^3) and dried *in vacuo* to give '$Cr(2\text{-nqo})_2$' (0.25 g). The toluene extracts were chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C) eluted 5-hydroxy-dibenzo-[b,i]phenazin-12(6*H*)-one (0.37 g, 79%)*. Toluene and ethyl acetate (6:4) eluted 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.10 g, 21%)*. Ethyl acetate and toluene (8:2) eluted triphenylphosphine oxide (0.50 g, 90%)*.

Reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine.-Tris-(1,2-naphthoquinone 2-oximato)manganese(III) (2.28 g, 4 mmol) was added to a solution of triphenylphosphine (3.14 g, 12 mmol) in acetone (100 cm^3). The reaction mixture was stirred for 25 minutes and the solvent was removed *in vacuo*. The residue was extracted with diethylether (10 x 50 cm^3) and dried *in vacuo* to give *μ*-oxotetrakis(1,2-naphthoquinone 2-oximato)dimanganese(III) (1.58 g, 97 %) (Found: C, 59.2; H, 3.1; Mn, 13.4; N, 7.0. $C_{40}H_{24}Mn_2N_4O_9$ requires C, 59.0; H, 2.9; Mn, 13.5; N, 6.9%). The diethylether extracts were chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C)/toluene (9:1) eluted triphenylphosphine (1.98 g, 63%)*. Light petroleum (b.p. 30 - 40 °C)/toluene (2:8) eluted 5-hydroxy-dibenzo[b,i]-phenazin-12(6*H*)-one (0.35 g, 56%)* and toluene/ethyl acetate (6:4) eluted 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.15 g, 24%)*. Ethyl acetate eluted 1,2-naphthoquinone 2-oxime (0.11 g, 16%)* and ethyl acetate/methanol (8:2) eluted

triphenylphosphine oxide (1.03 g, 93%)*.

Reaction of $Mn(2\text{-nqo})_3$ with triphenylphosphine.-Tris-(1,2-naphthoquinone 2-oximato)manganese(III) (2.28 g, 4 mmol) was added to a solution of triphenylphosphine (3.14 g, 12 mmol), stirred at 20 °C in acetone (200 cm^3) for 168h. Filtration gave μ-oxotetrakis(1,2-naphthoquinone 2-iminato)dimanganese(III) (1.08 g, 75 %) (Found: C, 63.9; H, 3.5; Mn, 14.3; N, 7.2. $C_{40}H_{24}Mn_2N_4O_5$ requires C, 64.0; H, 3.2; Mn, 14.7; N, 7.5%) which was washed successively with acetone (6 x 50 cm^3), diethylether (4 x 25 cm^3) and dried *in vacuo*. The filtrate and washings were combined and chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C)/toluene (2:8) eluted 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.41 g, 66%)* and toluene/ethyl acetate (6:4) eluted 2-amino-N4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (0.10 g, 16%)*. Ethyl acetate eluted 1,2-naphthoquinone 2-oxime (0.05 g, 7%)*. Ethyl acetate/methanol (8:2) eluted triphenylphosphine oxide (3.05 g, 91%)*.

Reaction of $[Mn(2\text{-nqo})_2]_2O$ with triphenylphosphine.-Triphenylphosphine (1.05 g, 4 mmol) was dissolved in acetone (100 cm^3) and $[Mn(2\text{-nqo})_2]_2O$ (0.81 g, 1mmol) was added. The reaction mixture was stirred at 20 °C for 168h and filtered. The solid was washed successively with acetone (6 x 25 cm^3), diethylether (25 cm^3) and dried *in vacuo* to give μ-oxotetrakis(1,2-naphthoquinone 2-iminato)dimanganese-

(III) (0.49 g, 65 %) (identical t.l.c. and i.r. with a previously characterised sample).

Reaction of $[Mn(2\text{-nqo})_2]_2O$ with hydrochloric acid.-$[Mn(2\text{-nqo})_2]_2O$ (0.81 g, 1 mmol) was stirred at 20 °C in hydrochloric acid (6M, 100 cm^3) for 24h. The reaction mixture was dried *in vacuo* and extracted with methanol (10 x 50 cm^3). The extracts were dried over sodium sulphate, filtered and methanol was removed *in vacuo* to yield 1,2-naphthoquinone 2-oxime (0.65 g, 94 %)*.

Reaction of $Mn(1\text{-nqo})_3$ with triphenylphosphine.-Tris-(1,2-naphthoquinone 1-oximato)manganese(III) (2.28 g, 4 mmol) was added to a solution of triphenylphosphine (3.14 g, 12 mmol) in acetone (200 cm^3). The reaction mixture was stirred at 20 °C for 24h and dried *in vacuo*. The residue was extracted with diethylether (10 x 50 cm^3) and dried *in vacuo* to give green *μ*-oxotetrakis(1,2-naphthoquinone 1-oximato)dimanganese-(III) (1.45 g, 90 %) (Found: C, 59.0; H, 3.1; Mn, 13.2; N, 6.5. $C_{40}H_{24}Mn_2N_4O_9$ requires C,59.0; H, 2.9; Mn, 13.5; N, 6.9%). The extracts were chromatographed on a silica column. Light petroleum (b.p. 30 - 40 °C) and toluene (9:1) eluted triphenylphosphine (1.95 g, 93%)*. Ethyl acetate eluted 1,2-naphthoquinone 1-oxime (0.56 g, 81%)* and then an unidentified multicomponent mixture (0.10 g). Ethyl acetate/acetone (8:2) eluted triphenylphosphine oxide (0.98 g, 88%)*.

Reaction of $[Mn(1\text{-nqo})_2]_2O$ with hydrochloric acid.-$[Mn(1\text{-nqo})_2]_2O$ (0.80 g, 1 mmol) was stirred at 20 °C in hydrochloric acid (6M, 100 cm^3) for 24h. The reaction mixture was dried *in vacuo* and extracted with methanol (10 x 50 cm^3). The extracts were dried over sodium sulphate, filtered and the solvent removed *in vacuo* to give 1,2-naphthoquinone 1-oxime (0.60 g, 92%)*.

Reaction of $[Mn(2\text{-nqi})_2]_2O$ with hydrochloric acid.-$[Mn(2\text{-nqi})_2]_2O$ (0.75 mmol, 1 mmol) was stirred at 20 °C in hydrochloric acid (6M, 30 cm^3) for 24h and filtered. The solid was washed with water and dried *in vacuo* over silica-gel to give mauve 1,2-naphthoquinone 2-imine (0.60 g, 96%) m.p. 224-226 °C (decomp.) (Found: C, 79.5; H, 4.2; N, 8.8. $C_{10}H_7NO$ requires C, 76.9; H, 3.8; N, 9.0%).

Thermolysis of 1,2-naphthoquinone 2-imine.-The imine (0.16 g, 0.5 mmol) was heated under reflux in ethanol (50 cm^3) for 48h. The solvent was removed *in vacuo* to give 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one (0.15 g, 96%) m.p. 281-282 °C (decomp.) (lit.[3] 280-283 °C)*.

Acetylation of 1,2-naphthoquinone 2-imine.-Acetic anhydride (5 cm^3) and the imine (0.20 g, 1.3 mmol) were stirred in pyridine (10 cm^3) for 72h. Water (30 cm^3) was stirred in and the mixture was filtered. The solid was washed with water (2 x 10 cm^3) and crystallised from a mixture of toluene (16 cm^3) and

light petroleum (b.p. 100 - 120 °C) (6 cm^3) as red crystals of 5,12-diacetoxydibenzo[b,i]phenazine (0.22 g, 92%)*.[3]

Catalytic oxidations of methyl oleate.-Methyl oleate (15.96 g, 60 mmol) and catalyst (0.25 mmol) were stirred under conditions specified in Table 6.1 (Chapter 6). The reaction mixture was analysed by measuring acid, oxirane, and iodine values using volumetric methods.[4]

Catalytic epoxidations of olefins.-Olefin and catalyst were stirred at 60 °C in an oxygen atmosphere, in quantities specified in Table 7.2. Toluene (1 mmol) was used as internal standard. From time to time samples (1 cm^3) were taken and analysed for epoxide by g.l.c. (Carbowax 20M on Chromosorb W-HP).

Table 7.2 Catalytic epoxidations of olefins

Catalyst[a] g/mmol	Olefin g/mmol	Epoxide g/mmol
1	Styrene	Styrene oxide
0.10/0.25	10.0/98	2.43/21
2	Styrene	Styrene oxide
0.10/0.25	10.0/98	1.62/14
3	Styrene	Styrene oxide
0.14/0.25	10.0/98	1.97/17
4	Styrene	Styrene oxide
0.14/0.25	10.0/98	2.54/22
1	Cyclohexene	1,2-epoxycyclohexane
0.30/0.75	24.6/300	19.1/195 (19.3/197)[b]
2	Cyclohexene	1,2-epoxycyclohexane
0.30/0.75	24.6/300	13.5/138 (13.8/141)[b]
3	Cyclohexene	1,2-epoxycyclohexane
0.43/0.75	24.6/300	11.8/120 (12.3/125)[b]
4	Cyclohexene	1,2-epoxycyclohexane
0.43/0.75	24.6/300	16.2/165 (16.3/166)[b]

$Mn(2\text{-nqo})_2$--P	Cyclohexene	1,2-epoxycyclohexane
1.05	24.6/300	22.1/225
1	1-Octene	1-epoxyoctane
0.20/0.50	10.0/89	3.4/26.7
2	1-Octene	1-epoxyoctane
0.20/0.50	10.0/89	2.7/21.4
3	1-Octene	1-epoxyoctane
0.29/0.50	10.0/89	2.2/16.9
4	1-Octene	1-epoxyoctane
0.29/0.50	10.0/89	3.1/24.0

7.3 References

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