METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND THEIR APPLICATIONS IN ORGANIC SYNTHESIS

By

JAYATIBHA CHAKRABARTI

A thesis submitted to the University of North London in
partial fulfilment of the requirements for the
degree of **Doctor of Philosophy**

MARCH 1995

CONTAINS
PULLOUTS

Dedicated to my parents

The right is to work only, but never to its fruits;
let not the fruit-of-action be thy motive, nor let thy
attachment be to inaction.

Shrimad Bhagavad Geeta

ABSTRACT

Systematic investigations of the reactions of 1,2-quinone monooximes (qoH) with alkali (lithium, sodium and potassium) and alkaline earth metal (magnesium and barium) hydroxides and acetates [$M(OH)_n$ or $M(OAc)_n$] have been carried out. In the case of 1,2-naphthaquinone 1-oxime (1-nqoH) and 1,2-naphthaquinone 2-oxime (2-nqoH), all the alkali metals form complexes of types M(qo).nS and M(qo)(qoH)(S) [S = H_2O or EtOH]. M(qo).nS arises when a reactant molar ratio [MOH:qoH] of 1:1 is used whereas M(qo)(qoH)(S) is formed when the ratio is 1:2 or 1:3. An analogous behaviour is also observed in the reactions of NaOH and KOH with 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (5-Et-4-MeqoH). The reaction of LiOH with 5-Et-4-MeqoH in the ratio of 1:1 gives Li(qo)(qoH)(H_2O) whereas using molar ratios of 1:2 and 1:$\geq$3 give Li(qo)$(qoH)_2$.1½H_2O. The alkaline earth metals form complexes of type $M(qo)_2.2H_2O$ with 1-nqoH and 5-Et-4-MeqoH. Complexes of type M(Mpo).nS and M(Mpo)(MpoH).S [M = Li, Na, K], $M(Mpo)_2.2H_2O$ and $M(1\text{-}Ppo)_2.2H_2O$ [M = Mg and Ba] result from the reactions of MOH, $Ba(OH)_2$ and $Mg(OAc)_2$ with 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (MpoH) and 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximes (1-PpoH).

Structural investigations of the qoH complexes noted above were carried out using spectroscopic, magnetochemical and X-ray crystallographic studies. All the complexes exhibit association as indicated by LSIMS. Their IR spectra indicate the quinone oximic character of the ligands and the involvement of the carbonyl group in the bonding of the ligand to the metal atom. X-ray studies of the lithium and sodium complexes of 5-Et-4-MeqoH show that the ligand chelates to the metal atom through the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group and suggest that its structure can be best described as an intermediate between the quinone oxime and imino oxime form. In the bis-chelates, the metal atom is penta coordinated whereas hexa coordination is shown by Li(qo)$(qoH)_2$.

IR studies of the complexes ML_2 [M = Mn, Ni, Cu and Zn; LH = 1-PpoH and MpoH] and their aquo and pyridine adducts indicate that the ligand exists essentially in the oximic form. The lack of reaction between these complexes and triphenylphosphine suggests that the oxygen atom of the NO group is involved in bonding to the metal atom. This feature is confirmed by the X-ray studies of $Zn(Mpo)_2(H_2O)_2$ and $Mn(1\text{-}Ppo)_2(py)_2$ which indicate the presence of six-membered chelate rings and octahedral coordination around the metal atom. Magnetic moment determinations of the aquo and pyridine adducts show that the compounds are magnetically dilute and hence monomeric in the solid state. The lowering of magnetic moment observed for anhydrous complexes is accounted for in terms of association. Support for association is also obtained from the LSIM spectra which show dimetallic and trimetallic species in their spectra.

The lithium, sodium and barium complexes of 1-nqoH react with dimethyl acetylenedicarboxylate (DMAD) at -75-50° to give the open chain adduct, O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime. Open chain adduct formation is also observed in the reactions of pyrazole-4,5-dione-4-oximes or their lithium complexes with DMAD at 0-40°C. At higher temperatures the reactions lead to Schiff Base type condensation products whose formation is accounted mechanistically in terms of the deoxygenation of the oxime group.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

qoH	1,2-quinone monooximes
1-nqoH	1-2-naphthaquinone 1-oxime
2-nqoH	1,2-naphthaquinone 2-oxime
nqoH	1,2-naphthaquinone monooximes
5-Et-4-MeqoH	5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime
Fig.	Figure
UV	ultra violet spectroscopy
IR	infrared spectroscopy
MM	magnetic measurements
C	conductivity measurements
NMR	nuclear magnetic resonance spectroscopy
ES	electronic spectra
CV	cyclic voltammetry
DPV	differential pulse voltammery
MP	melting point
OC	oxidation catalyst
MS	mass spectrometry
MSp	^{57}Fe Mossbauer spectra
SC	stability constant
TGA	thermal gravimetric analysis
Mr	relative molecular mass
ab	2-aminobenzoic acid
5-HxqoH	5-hexylamino-1,2-benzoquinone 2-oxime
py	pyridine
5-AcqoH	5-acetylamino-1,2-benzoquinone 2-oxime
bzt	benztriazole
6-EtdnrH	6-ethyl-2,4-dinitrosoresorcinol
pa	picolinic acid
5-MednrH	5-methyl-2,4-dinitrosoresorcinol
oxH	isoxazol-4,5-dione-4-oxime
2-MemnrH	2-methyl-4-nitrosoresorcinol

dipy	dipyridine
4-ClqoH	4-chloro-1,2-benzoquinone 2-oxime
dnrH$_2$	2,4-dinitrosoresorcinol
6-CldnrH	6-chloro-2,4-dinitrosoresorcinol
bpy	2,2$^{\prime}$-bipyridine
4-MeqoH	4-methyl-1,2-benzoquinone 2-oxime
phen	1,10-phenanthroline
5-BuqoH	5-butyrylamino-1,2-benzoquinone 2-oxime
pz	pyrazole
5-PeqoH	5-pentanoylamino-1,2-benzoquinone 2-oxime
im	imidazole
TOPO	trioctylphosphine oxide
EC	extraction constant
AFC	adduct formation constant
Ref.	references
7-S-1-nqoH	1,2-naphthaquinone 1-oxime 7-sulphonic acid
5-S-2-nqoH	1,2-naphthaquinone 2-oxime 5-sulphonic acid
8-S-2-nqoH	1,2-naphthaquinone 2-oxime 8-sulphonic acid
TT	transition temperatures
EtOH	ethanol
1-PpoH	3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime
3-PpoH	1-methyl-3-phenyl-1H-pyrazole-4,5-dione-4-oxime
MpoH	1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime
poH	3-methyl-1H-pyrazole-4,5-dione-4-oxime
DMAD	dimethyl acetylenedicarboxylate
Å	Angstrom
DMAD	dimethyl acetylenedicarboxylate
EGDE	ethylene glycol dimethyl ether
m.p.	melting point
h	hour(s)
ppm	parts per million
μ	magnetic moment
MHz	megahertz

t.l.c.	thin layer chromatography
COSY	correlated spectroscopy
DEPT	distortionless enhanced polarisation technique
FT	Fourier transform

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CHAPTER I

1,2-QUINONE MONOOXIMES AND RELATED LIGANDS-SYNTHESIS, STRUCTURE AND METAL COMPLEXES

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1.1 INTRODUCTION

1,2-Quinone monooximes (Fig. 1.1) and related ligands such as pyrazole-4,5-dione-4-oximes (Fig. 1.2) and isoxazole-4,5-dione 4-oximes (Fig. 1.3) are of considerable

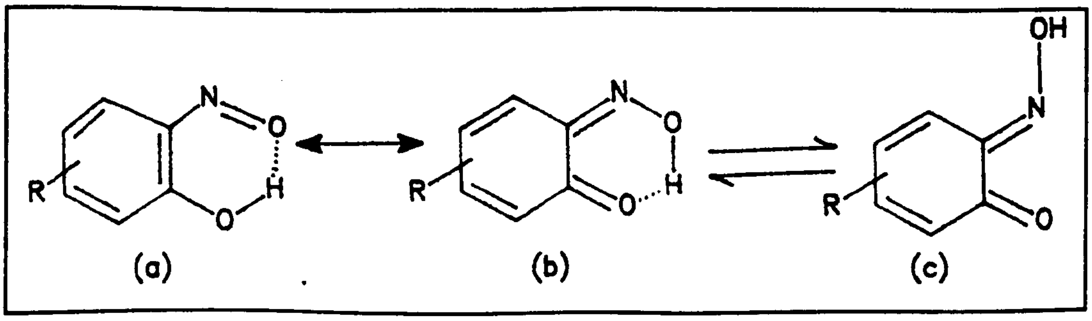


FIG. 1.1

interest because of their structural characteristics and metal complexation behaviour.[1]

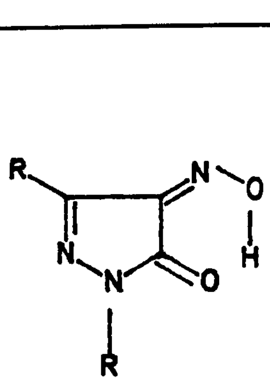


FIG. 1.2

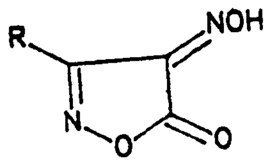


FIG. 1.3

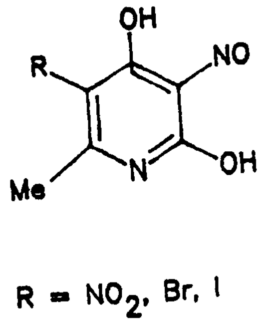
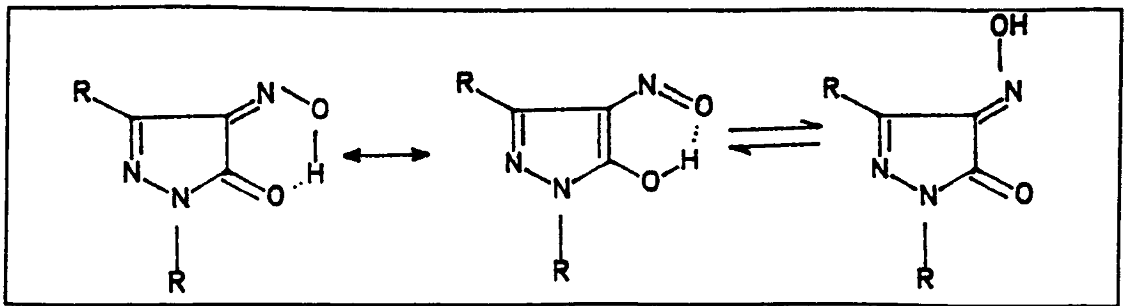


FIG. 1.4

The nitrosophenols (Fig. 1.1a) can exhibit tautomerism with the corresponding quinone monooximes (Fig. 1.1b and 1.1c).[2,3] Similar behaviour can also be exhibited by related ligands (eg. Scheme 1.1). These ligands (eg. Fig. 1.1-1.4) generally act as chelating agents and have been successfully used in metal extraction, metal separation and analysis. For example, 1,2-naphthaquinone 1-oxime can be used for separating rhodium from iridium.[4] Similarly 5-methoxy-1,2-benzoquinone 2-oxime has been successfully used as a reagent for the determination of iron and cobalt,[5] for the spot test detection of cobalt[6] and in the spectrophotometric determination of cobalt ions.[7] Its homologue 5-ethoxy-1,2-benzoquinone 2-oxime has been used in the photometric titration of iron(II) with EDTA.[8] The microdetermination of ruthenium using the Weisz Ring-Oven technique has been accomplished by using 1,2-naphthaquinone 2-oxime as the colour reagent.[9] The coloured complexes of



SCHEME 1.1

substituted 1,2-quinone monooximes with iron, cobalt and nickel have long been used in paints, inks and as dyes in rubber and fabrics and are noted for their excellent fastness.[10,11] Some nitrosopyridine type ligands (Fig 1.4) showed potential as solvent extracting reagents for certain group VIII metals.[12] 1,2-Quinone monooximes such as 5-hydroxy-1,2-benzoquinone 2-oxime and 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime have been considered as chelators for the treatment of iron overload and have been found to be effective in removing iron when administered intramuscularly.[13] Because of the structural characteristics, 1,2-quinone monooximes and their metal complexes have considerable value in synthesis as discussed in Section 1.5. Also, their complexes are used as catalysts; for example the manganese complexes of the monooximes of 1,2-naphthaquinone are effective catalysts for the epoxidation of alkenes.[14]

1.2 THE STRUCTURE OF 1,2-QUINONE MONOOXIMES

The structures of 1,2-quinone monooximes and to a lesser extent those of their related ligands have received considerable attention. These compounds have been studied using different spectroscopic methods and X-ray crystallography. Very extensive X-ray crystallographic studies of 1,2-quinone monooximes have shown that the compounds have essentially quinone monooximic character, adopting either the *syn* (Fig. 1.1b) or the *anti* (Fig. 1.1c) configuration.

Earlier solution studies based on U.V. and visible spectroscopy have shown absorptions attributable to both the nitrosophenolic and quinone monooximic forms.[3,15] The existence of tautomeric equilibria in solution between the oximic forms (Fig. 1.1b and 1.1c) and the nitrosophenolic form (Fig. 1.1a) have also been adequately confirmed by NMR spectroscopy.

A detailed study of the NMR spectra of 1,2-naphthaquinone 1-oxime and 1,2-naphthaquinone 2-oxime carried out in a variety of solvents indicated that in the former (Fig. 1.5), the aromatic protons at positions (3) and (4) show the AX splitting pattern ($J_{3,4}$ = 10 Hz).[16] The chemical shift of the aromatic proton at position (3) appeared in a very high field. These facts suggest that the oxime formulation (1.5b) represents the structure of 1,2-naphthaquinone 1-oxime in solution. This is also supported by its ^{14}N NMR spectrum which showed a ^{14}N chemical shift of 12±30 ppm downfield from NO_3^- suggesting that the latter should largely prevail in the equilibrium.[17,18] On the contrary, in 1,2-naphthaquinone 2-oxime (Fig. 1.6), the aromatic protons at positions (3) and (4) show a mixture of the AB ($J_{3,4}$ = 9.8Hz) and AX ($J_{3,4}$ = 10Hz) patterns depending on the solvent. This fact shows that detectable amounts of both nitroso (1.6a) and oxime (1.6b) are present.

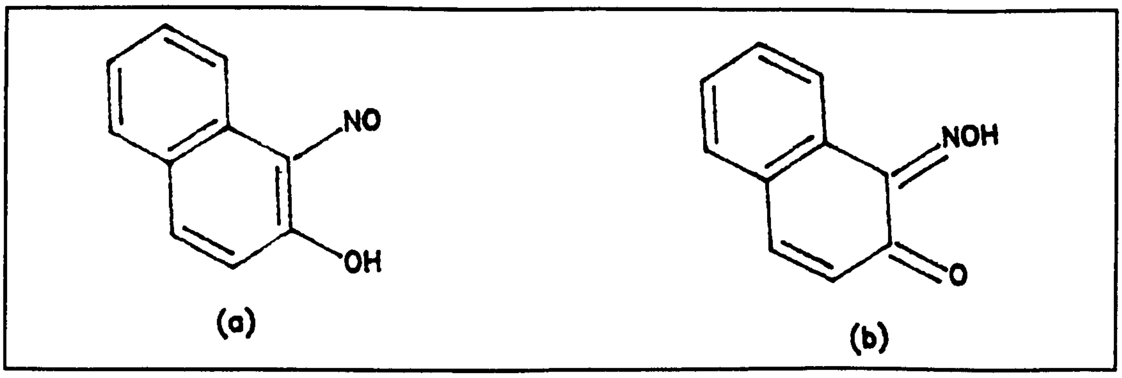


FIG. 1.5

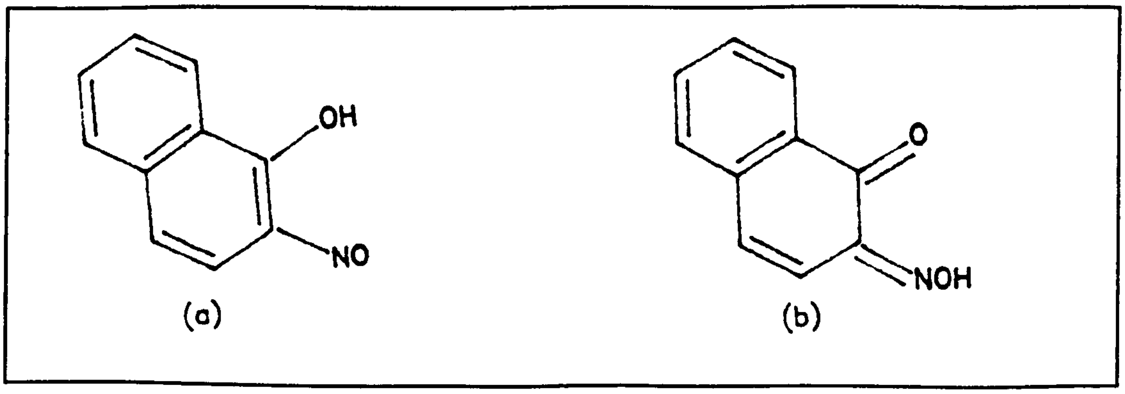


FIG.1.6

^1H and ^{13}C NMR studies of the 5-alkylamino-1,2-benzoquinone 2-oxime have recently been reported.[19] Significantly in the ^{13}C NMR spectra the presence of a signal between 175 and 210 ppm assignable to a quinonoid carbon supports the formulation of these compounds as quinone monooximes (Fig 1.7b).

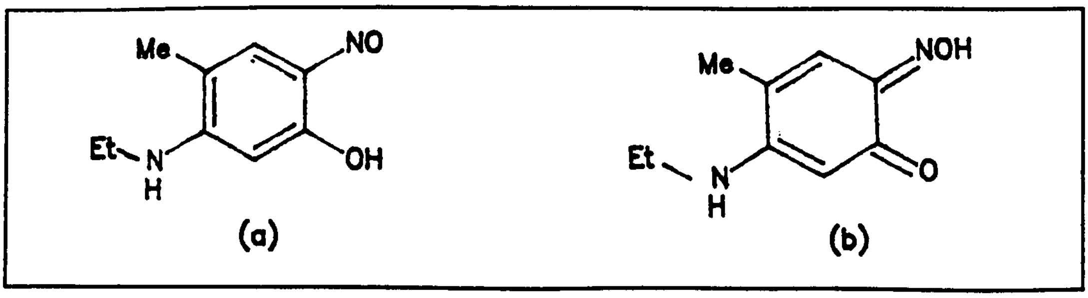


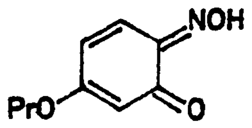
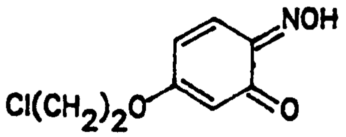
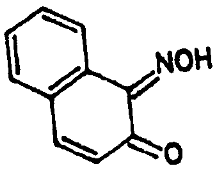
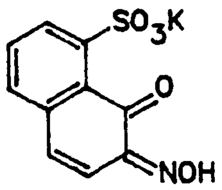
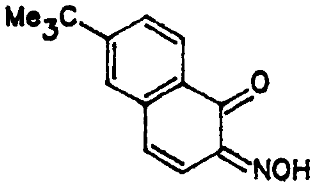
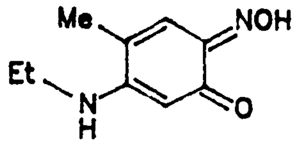
FIG. 1.7

The structures of 1,2-quinone monooximes in the vapour phase have also been investigated by mass spectrometry.[20] However, the results do not allow any unambiguous conclusions regarding the oximic or nitrosophenolic character of the compounds.

Infrared studies of several 1,2-quinone monooximes have been reported by various groups of workers.[21-23] Although there is very little agreement regarding the assignment of bands due to C=O, C=N and N=O absorptions, it has been generally concluded that these compounds exist in their oximic forms in the solid state.

Several 1,2-quinone monooximes have been characterised by single crystal X-ray studies. The oximic character of these compounds is indicated by the CO bond distance (1.21Å) which is closely equal to the C=O bond lengths found in benzoquinone[24] and naphthaquinone compounds,[25] and the long C_1-C_2 and short C_3-C_4 bond lengths (Table 1.1). The crystal structures of the 7-sulphonated derivative of 1,2-naphthaquinone 1-oxime[26] (Fig. 1.8) and the sulphonated derivatives of 1,2-naphthaquinone 2-oxime[27-29] show that in these compounds the OH of the NOH group is in an *anti* position relative to the CO group whereas in 1,2-naphthaquinone 1-oxime[30] (Fig. 1.9) the referred groups have a *syn* configuration. In the case of 5-methoxy-1,2-benzoquinone 2-oxime[31] and 5-(2′-chloroethoxy)-1,2-benzoquinone 2-oxime,[32] the oxime and the ring carbonyl groups are *anti* with respect to each other but in 5-propoxy-1,2-benzoquinone 2-oxime,[33] the oximic group is *syn* to the

TABLE 1.1 Selected Bond Lengths of Some Reported 1,2-Quinone Monooximes

Compound	*Bond length (Å)*				
	C-O	*C-N*	*C-C*[a]	*C-C*[b]	*Ref*
	1.27	1.32	1.35	1.45	33
	1.34	1.31	1.35	1.46	32
	1.25	1.31	1.36	1.46	30
	1.21	1.30	1.37	1.47	29
	1.24	1.30	1.37	1.47	34
	1.28	1.30	1.36	1.46	35

[a] Average length of the two short bonds [C_9-C_{10} and C_3-C_4 as in Figs. 1.8, 1.9];

[b] Average length of the four long bonds [C_1-C_2, C_2-C_3, C_4-C_{10} and C_9-C_1 as in Figs. 1.8, 1.9].

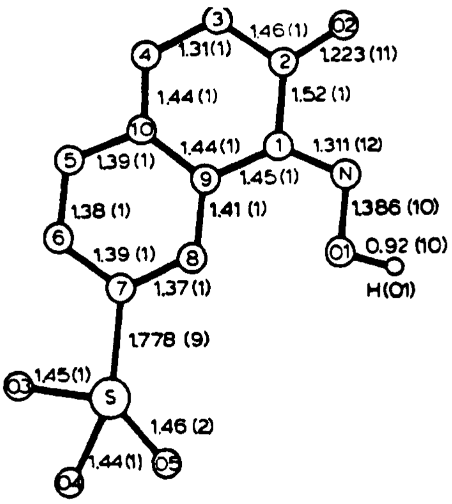


FIG. 1.8

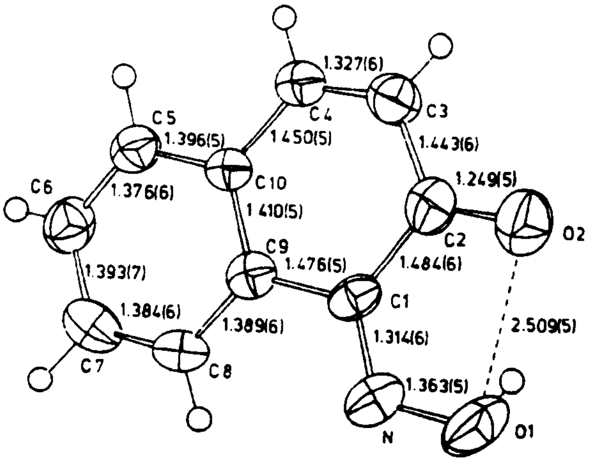


FIG. 1.9

carbonyl group. Differences in configuration are also observed in the 5-alkylamino-1,2-benzoquinone 2-oximes. For example, 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime[35] (Fig. 1.10) exhibits a *syn* configuration whereas its 5-hexylamino analogue has

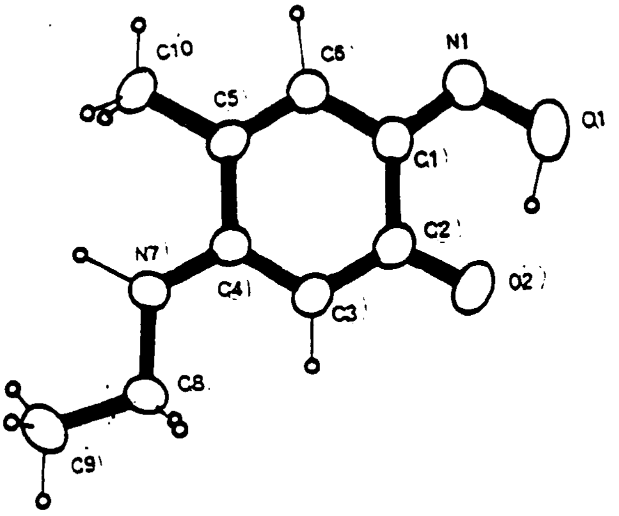


FIG. 1.10

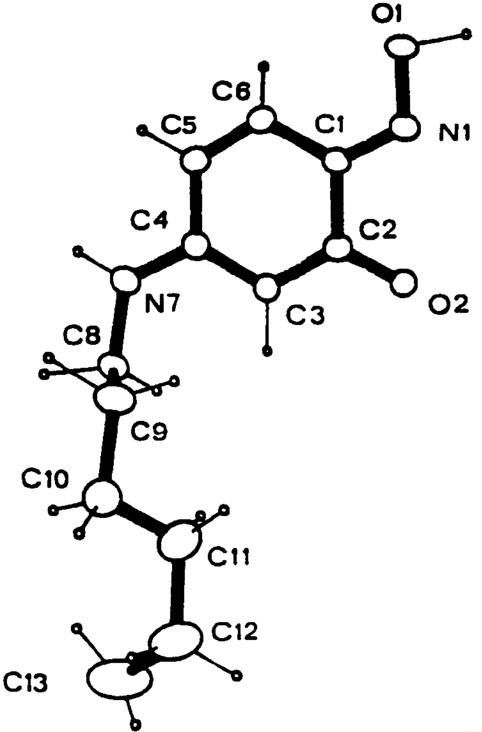


FIG. 1.11

an *anti* configuration (Fig. 1.11).[19] In general the compounds having *syn* oxime configuration exhibit intramolecular hydrogen bonding whereas the *anti* structure may involve intermolecular hydrogen bonding.

In solution, quinone oxime / nitrosophenol isomerism is also exhibited by 1,4-quinone monooximes.[15] However, X-ray studies of 2-chloro- and 2-bromo-5-methyl-1,4-benzoquinone 4-oxime show that these compounds are essentially quinone monooximic in the solid state.[36] The NOH group is *syn* with respect to the halogen atom (Fig. 1.12).

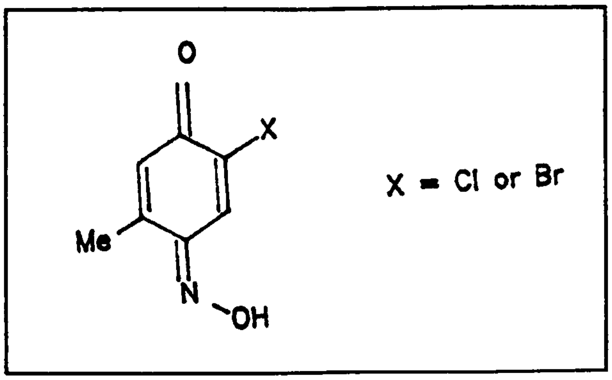
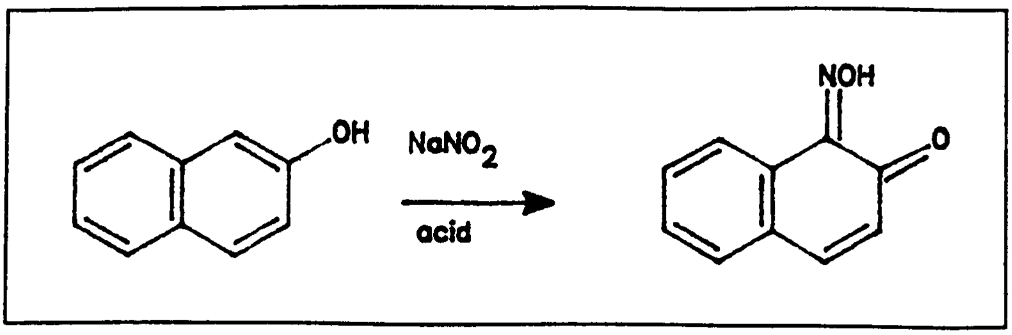


FIG. 1.12

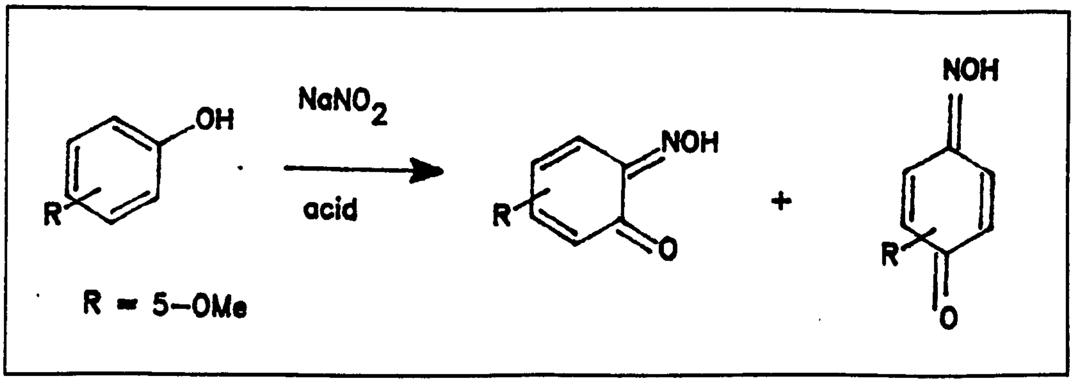
1.3 PREPARATION OF 1,2-QUINONE MONOOXIMES AND PYRAZOLE-4,5-DIONE-4-OXIMES

1.3.1 1,2-Quinone Monooximes

Several methods of synthesis of 1,2-quinone monooximes are reported[37] but some of the reports lack experimental and/or analytical data. The most commonly used method involves the nitrosation of a phenol using acetic acid and sodium nitrite.[38,39] This method has proved particularly successful for the preparation of 1,2-quinone monooximes derived from 3-alkoxyphenols, 3-acylaminophenols, 3-dimethylaminophenol and 1-naphthol (eg. Reaction 1.1). In most cases, the formation of 1,2-quinone monooximes is accompanied by the formation of the corresponding 4-isomer (Reaction 1.2).[40,41] The formation of 1,2-quinone monooximes derived from other phenols is difficult to achieve due to their instability towards acid.

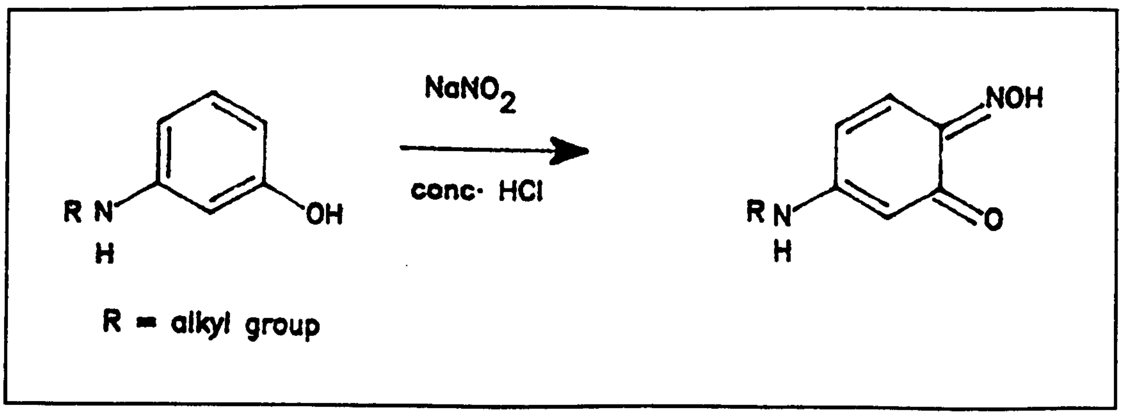


REACTION 1.1



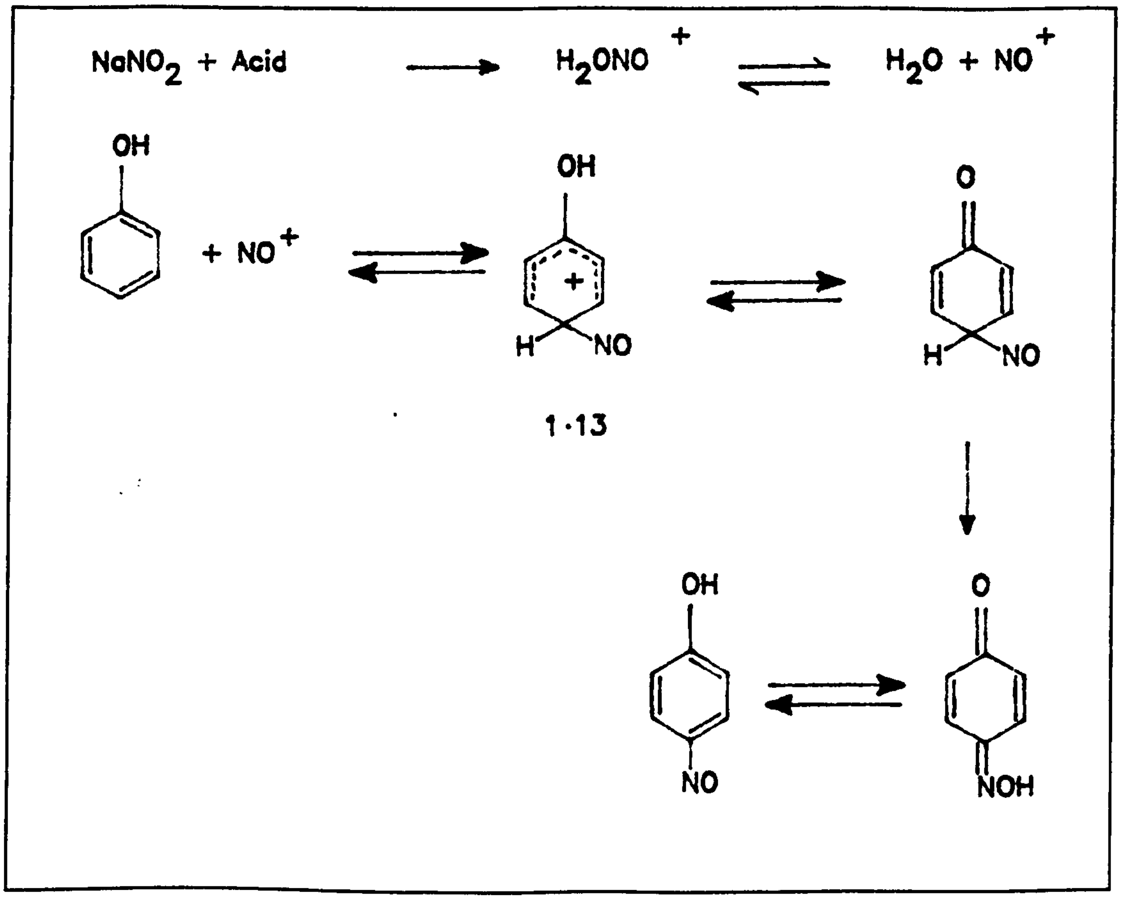
REACTION 1.2

Recently, the formation of 1,2-quinone monooximes derived from 3-alkylaminophenols and 3-aminophenol have been achieved by using concentrated hydrochloric acid instead of acetic acid[19] (Reaction 1.3). Importantly, the formation of N-nitroso derivatives do not occur because the strong acid used protonates the nitrogen atom of the amino group thereby protecting it from attack by the nitrosonium ion.



REACTION 1.3

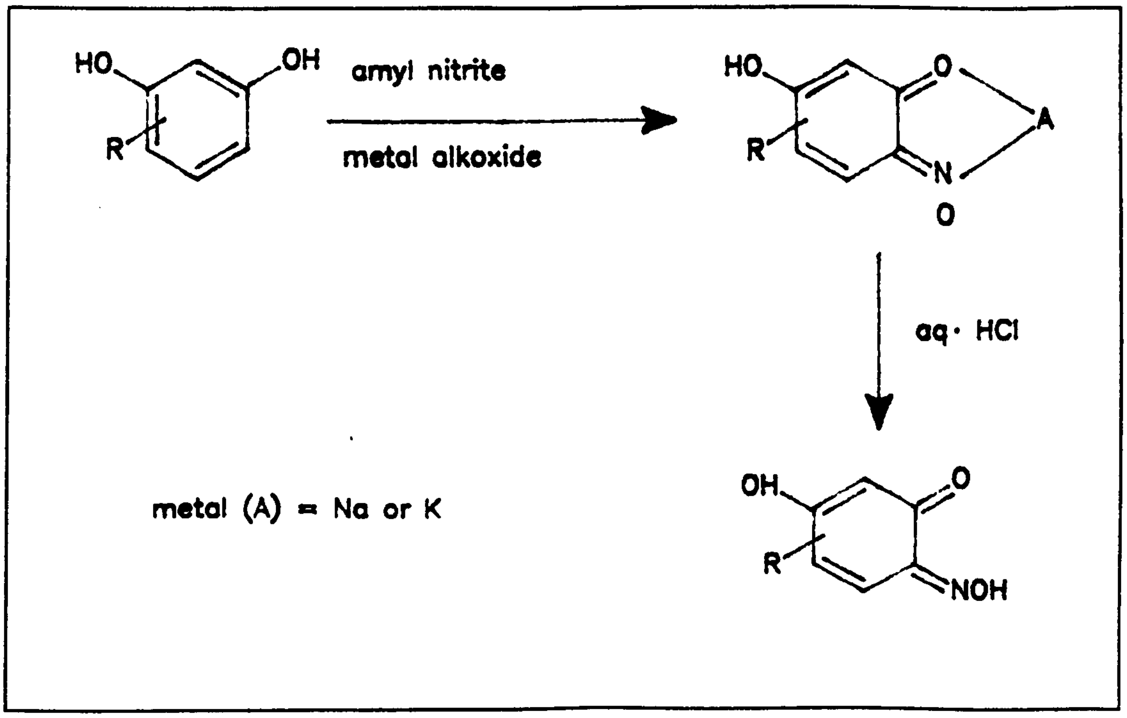
Mechanistically, the formation of 1,2-quinone monooximes by the nitrosation of phenols using the sodium nitrite/acid method may be explained by the standard mechanism for nitrosation of phenols. As indicated in Scheme 1.2, the reaction involves the nitrosonium ion which is produced *in situ* by the dehydration of nitrous



SCHEME 1.2

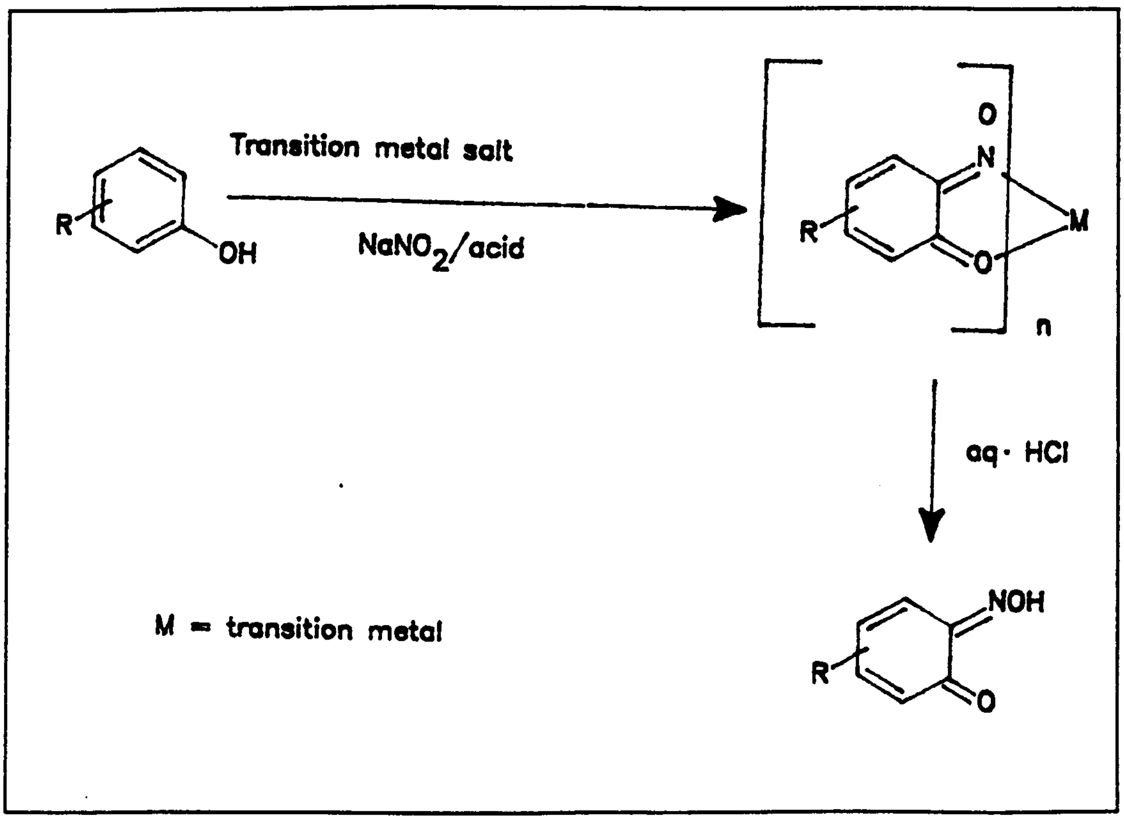
acid[42] and like other aromatic electrophilic substitution reactions, nitrosation proceeds *via* the Wheland intermediate (1.13).[43]

The synthesis of 1,2-quinone monooximes has also been accomplished by using amyl nitrite and an alkali metal alkoxide or hydroxide.[44] This method initially leads to the alkali metal complex of the oxime from which the free ligand can be obtained by acidification (Scheme 1.3). This approach has proved particularly useful for the formation of 1,2-quinone monooximes derived from 1,3-dihydroxybenzene and its homologues.



SCHEME 1.3

The synthesis of 1,2-quinone monooximes by the acidification of their transition metal complexes, which are readily obtainable, has also been reported.[38,45,46] However experimental details are only available for the preparation of compounds such as 5-hydroxy-1,2-benzoquinone 2-oxime and its 6-methyl analogues[45] (Scheme 1.4).



M = transition metal

SCHEME 1.4

Some 1,2-quinone monooximes have been obtained in high yield and purity from their copper and nickel complexes by using ion exchange resins.[47] This method has proved particularly useful in the case of 5-acylamino-1,2-benzoquinone 2-oximes which cannot be recovered from the acidification of their metal complexes or by the direct nitrosation of 3-acylaminophenol.

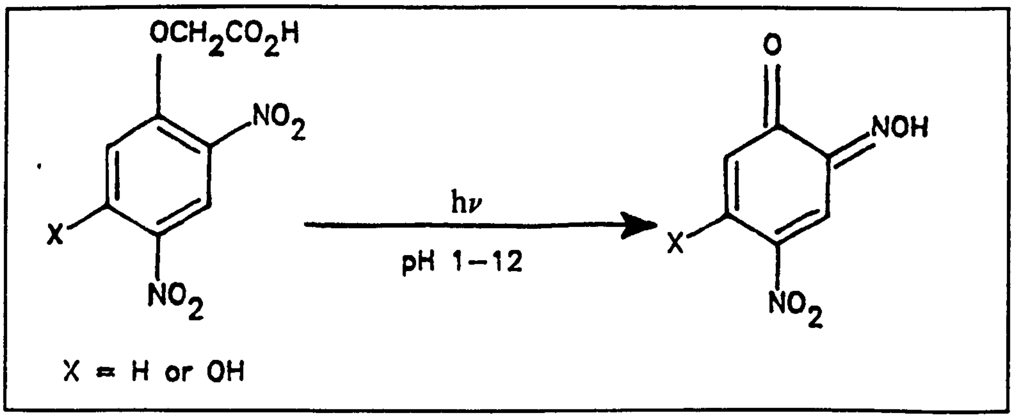
Recently, the monooximes of 1,2-naphthaquinone have been prepared by stirring methanolic solutions of the 1,10-phenanthroline or 2,2′-dipyridyl adducts of their copper complexes with silica.[47] (Reaction 1.4)

$$\mathrm{Cu(qo)_2X} \xrightarrow[\text{methanol}]{\text{silica}} \mathrm{Cu(qo)X + qoH}$$

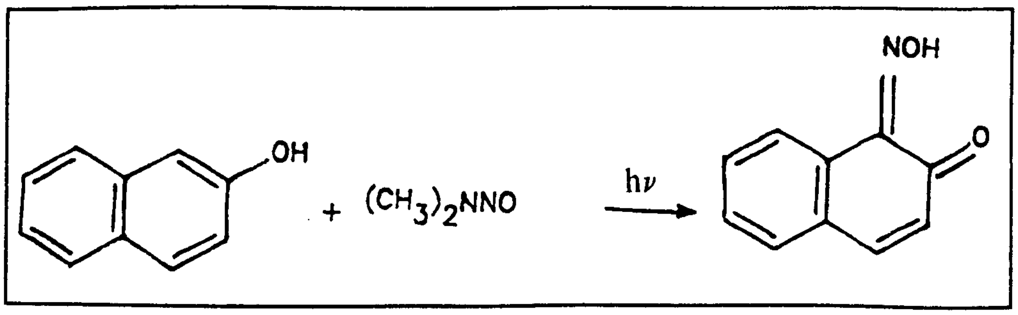
X = 1,10–phenanthroline or 2,2′–dipyridyl

REACTION 1.4

1,2-Quinone monooximes have also been successfully synthesised by photochemical methods. Two unique methods have been described. The first method involves the photolysis of 2-nitrosophenoxyacetic acids[48] (Reaction 1.5) The other, which has been exclusively used for the preparation of 1,2-naphthaquinone 1-oxime, involves the photolysis of a mixture of 2-naphthol and N-nitroso dimethylamine[49,50] (Reaction 1.6). Similar photolytic reaction involving 1-naphthol results in the formation of 1,4-naphthaquinone 4-oxime.

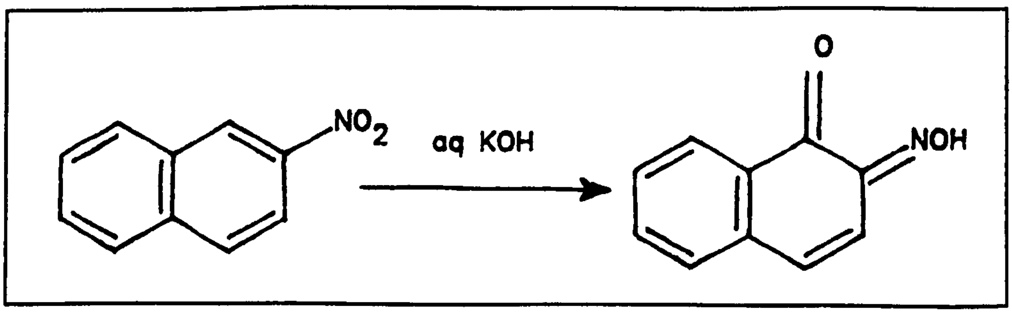


REACTION 1.5



REACTION 1.6

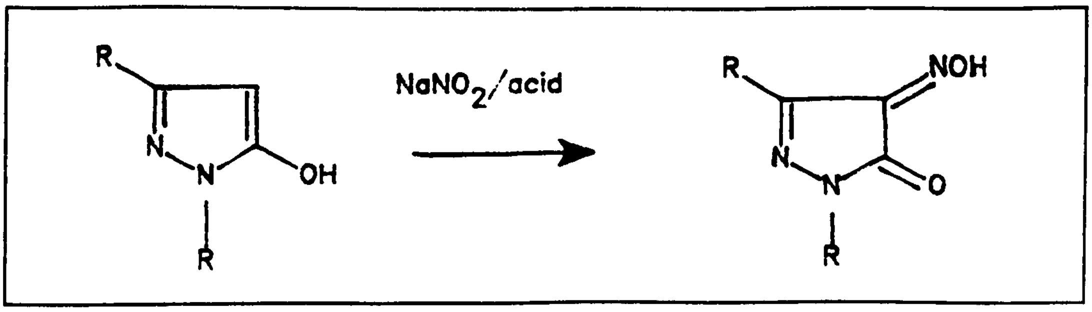
Some 1,2-quinone monooximes have been synthesised by a) heating hydroxylamine hydrochloride with the corresponding quinone[51] b) the action of sodium hydroxide on certain nitro aromatic compounds[52] (Reaction 1.7) and c) boiling nitrosoaniline in the presence of potassium bisulphate.[53] In general, these methods have limited applicability.



REACTION 1.7

1.3.2 Pyrazole-4,5-dione-4-oximes

As in the case of 1,2-quinone monooximes, the standard method for the preparation of pyrazole-4,5-dione-4-oximes is the sodium nitrite / acid method. This was first reported in 1887 and is known as Knorr's synthesis[54] (Reaction 1.8). Amyl nitrite[55,56] and dinitrogen trioxide[57] have also been used as the nitrosating agents but less extensively.



REACTION 1.8

1.4 METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND RELATED LIGANDS

1.4.1 Mode of Bonding and the Structure of the Ligand

1,2-Quinone monooximes and their related ligands, pyrazole-4,5-dione-4-oximes and isoxazole-4,5-dione-4-oximes, react readily with both transition and non-transition metal ions to give highly coloured, stable complexes. The formation of the complex involves the replacement of the acidic oximic proton by the metal ion. The types of complexes reported and the principal methods of their characterisation are illustrated in Tables 1.2 and 1.3. As evident from the Table 1.2, the complexation behaviour of 1,2-quinone monooximes have been studied with both main group and transition metals. However, in the case of pyrazole-4,5-dione-4-oximes, attention has been directed mainly to complexes of the first row transition metal (Table 1.3). With isoxazole-4,5-dione-4-oximes, only gold and platinum complexes have been investigated.

Most of the metal complexes derived from 1,2-quinone monooximes are chelates. They can be formulated with either a nitrosophenolic or quinone monooximic structure (Fig.1.14 and 1.15). Alternatively, they may be considered as a resonance hybrid of the two forms. The oxime (nitroso) group can coordinate to the metal atom through the nitrogen or oxygen atom forming a five or six-membered ring respectively. The quinone monooximic character and the formation of the five membered chelate rings was first suggested on the basis of both infrared[58,59] and mass spectral studies.[60] Extensive X-ray studies involving both transition[63,70,72,73,75,78] and

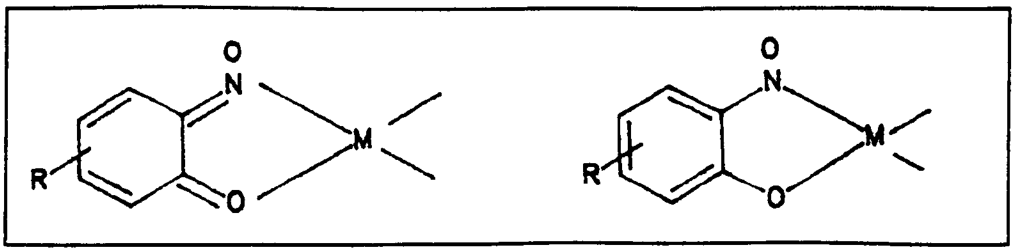


FIG. 1.14

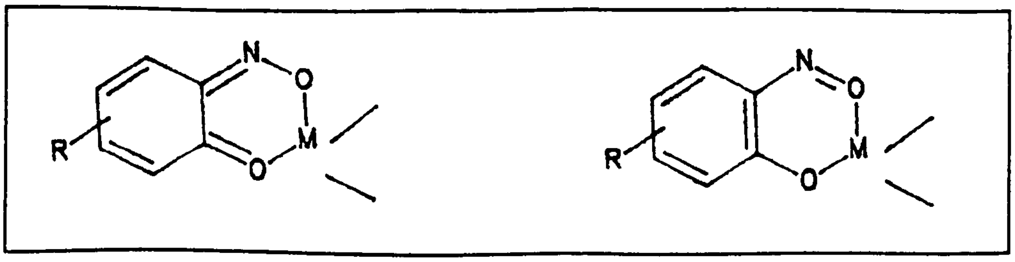


FIG. 1.15

TABLE 1.2 Metal Complexes of 1,2-Quinone Monooximes

Metal	*Ligand(s)*	*Complex*	*Data Reported*	*Refs*
Ag^{I}, T^{II}, Pd^{II}, Pb^{II}, Sc^{III}, Y^{III}, Cr^{III}, Bi^{III}	1-nqoH	$M(qo)_n$ n=1,2,3	UV, MM, IR, C	61
Mn^{II}, Mn^{III}	4-RqoH (R=Cl,Br,Me,^{t}Bu)	$[Mn(qo)_3]^Z$, z=0; 1-, cation=$[NEt_4]^+$	ES, MM, NMR, X-ray, CV, DPV,	62, 63
Mn^{III}, Co^{III}, Fe^{II}, Ni^{II}, Cu^{II}	5-AcqoH	$M(qo)_n.xH_2O$, $Na[Fe(5\text{-}qo)_3$, $Na[Co(qo)_2(NO_2)_2]$, $Ni(qo)_2X_n$ (X=py,n=2; X=dipy,n=1)	ES, IR, MM,	64
Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, VO^{IV}	1-nqoH, ab	M(qo)(ab), $M'(qo)(ab)(py)_2$ [M'=Co,Ni]	ES, ESR, IR, C, MP, MM,	65
Mn^{II}, Mn^{III}	1-nqoH, 2-nqoH	$Mn(qo)_n$	UV, IR, MM, OC	14, 23
Fe^{II}, Fe^{III}	1-nqoH, 2-nqoH, 5-MeOqoH, 5-MeqoH, Phen-9,10-qoH	$M(qo)_3$, $MCl(qo)_2$, $K[M(qo)_3]$	ES, IR, MS, MM, MSp, Mr, C, TGA	66, 21, 23
Co^{III}	1-nqoH, 2-nqoH	$M(qo)_3$, $M(qo)_2(NO_2)L$ $Na[Co(qo)_2(NO_2)_2]$, L=py or bz)	Mr, C, UV, IR	67, 21, 23
Co^{II}, Ni^{II}	1-nqoH, pa	$M(qo)_2(pa)$	UV, IR, MM, C, MP	68
Ni^{II}	X-dnrH_2 (X=H, 6-Et, 5-Me), 2-MemnrH	$Ni(qo).xH_2O$, $Ni(6\text{-}Etdnr)(py)_2$	EA, MA, TGA, MM,	45
Ni^{II}	5-MeOqoH, 4-ClqoH	$Ni(qo)_2.X_n$ (n=O; X=py,n=2; X=$PhNH_2$,n=1), $K[Ni(qo)_3]$	TGA, MM, ES, IR, MS, Mr, X-ray	69, 70
Ni^{II}	1-nqoH, 2-nqoH	$Ni(qo)_2(H_2O)_2$	UV, IR.	23
Cu^{II}	X-dnrH_2 (X=H, 6-Et, 6-Cl, 5-Me); 2-MemnrH	$Cu(qo).xH_2O$; $Cu(X\text{-}dnr)_2(py)$ (X=H, 6-Et, 6-Cl)	MM, TGA, MP,	71
Cu^{II}	1-nqoH, 2-nqoH	$Cu(qo)_2.H_2O$, $Cu(qo)_2(py)$, $Cu(1\text{-}nqo)_2.2Me_2CO$	UV, IR, MS, TGA, X-ray	21, 23, 72-74
Cu^{II}	4-MeqoH	$Cu(qo)_2(py)$ & $Cu(qo)_2$	TGA, MS, IR, MM, X-ray	74, 75
Cu^{II}	4-ClqoH	$Cu(qo)_2X$ (X=bpy, phen, im, pz)	IR, MP, MS, X-ray	74, 76
Zn^{II}, Cd^{II}	X-1-nqoH, X-2-nqoH; X=SO_3	$M(qo)_2$	UV, IR, SC,	23, 77
Hg^{II}	1-nqoH, 2-nqoH	$Hg(qo)_2$	EA, MA, UV, IR	23
Ru^{II}	1-nqoH, 2-nqoH	$Ru(qo)_2(py)$	TGA, IR, UV, MM, X-ray	78
Rh^{III}, Ir^{III}	1-nqoH, 2-nqoH	$M(qo)_3$, $[pyH][Ir(qo)(py)Cl_3]$	IR, MM, X-ray	79
Pd^{II}, Pt^{II}	5-XqoH (X=Ac, Bu, Hx, Et-4-Me)	$M(qo)_2$	ES, IR, TGA, MM, MS, NMR.	19
UO_2^{VI}	1-nqoH, 2-nqoH	$[M(2\text{-}nqo)(H_2O)_2]$. $2CHCl_3$, $[M(1\text{-}nqo)(H_2O)(OPPh_3)]$	X-ray	80
Sm^{III}, Eu^{III}, Dy^{III}	1-nqoH, TOPO	$M(qo)_3(TOPO)_n$ (n=1,2)	EC, AFC	81
Au^{I}, Pt^{II}	oxH	$PtH(ox)(PPh_3)_2$, $Au(ox)(PPh_3)$	EA, X-ray	82

non-transition metals[83] have confirmed the suggestions.

The quinone monooximic structure of the ligand in the 1,2-quinone monooximato complexes is indicated by the presence of two short C-C bonds which are 1,3 with respect to each [C_3-C_4 and C_9-C_{10}] and four long C-C bonds [C_1-C_2, C_2-C_3, C_4-C_{10}, C_9-C_1] (eg. Fig. 1.16 which shows the X-ray structure of [pyH][Ir(1-nqo)(py)Cl_3]).[79]

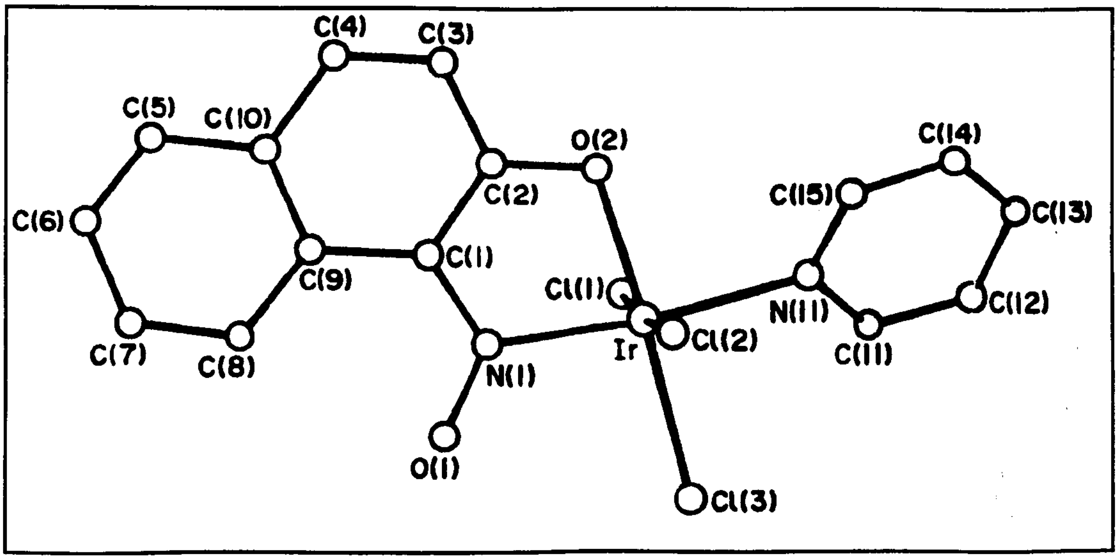


FIG. 1.16

In the uranyl complexes of 1,2-naphthaquinone monooximes, the mode of metal-ligand bonding is different. Single crystal X-ray structures of aquobis(1,2-naphthaquinone1-oximato-N)(triphenylphosphineoxide)dioxouranium(VI)(Fig.1.17) and diaquobis(1,2-naphthaquinone 2-oximato-N)dioxouranium(VI)-trichloromethane show that the oximato ligand is bonded to the metal through the nitrogen and oxygen atoms of the oxime group.[80] Although the bonding of the oximato group to the metal is proposed as chelation, it can also be explained as η^2 coordination involving the interaction of the metal orbitals with the π delocalised electron cloud of the C-N-O group.

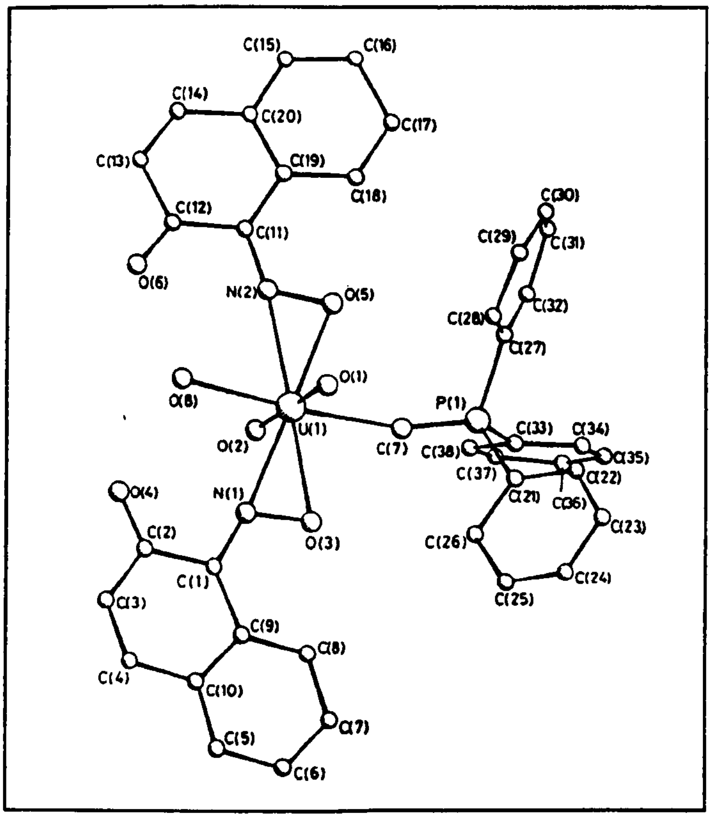


FIG. 1.17

An unusual type of bonding has been observed in the structure of potassium(4-chloro-1,2-benzoquinone 2-oximato)hemihydrate,[84] K(4-Clqo).½H_2O. Each 4-Clqo molecule shares its two oxygen donor atoms with different potassium ions, thus behaving as a bridging ligand but not a chelated ligand. The potassium ion is in a distorted octahedral coordination with each potassium ion being bonded to three ligands through the oximic oxygen and to the other two *via* the quinonoid oxygen atom. The sixth position is occupied by one molecule of water. The potassium ion is not coordinated to any of the nitrogen atoms (Fig. 1.18).

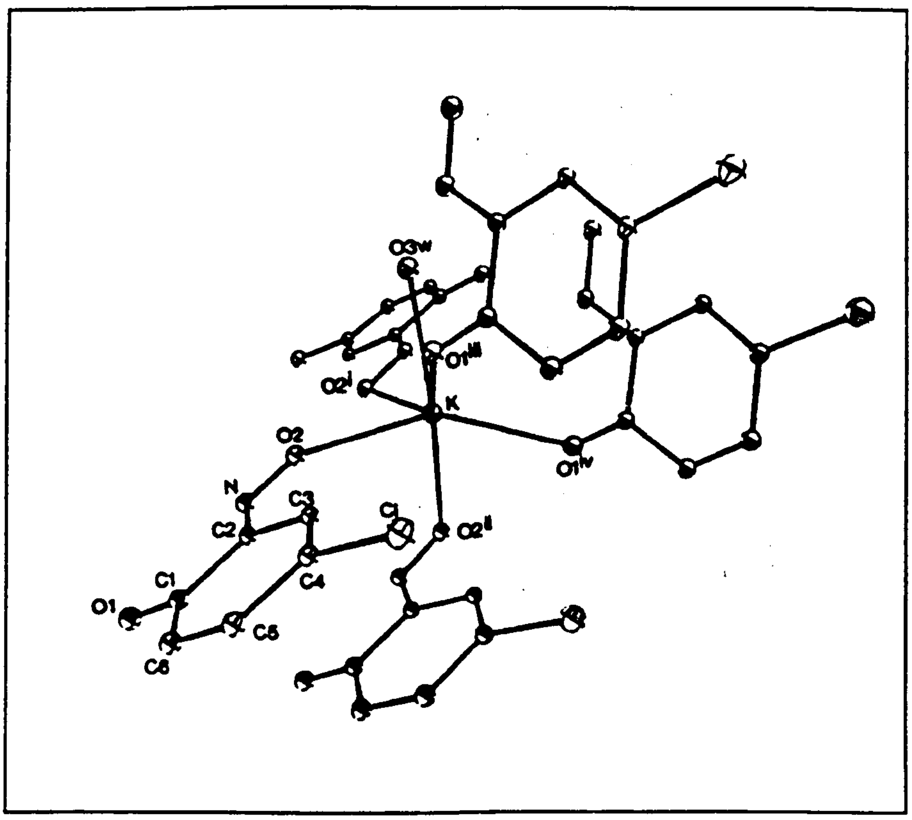


FIG. 1.18

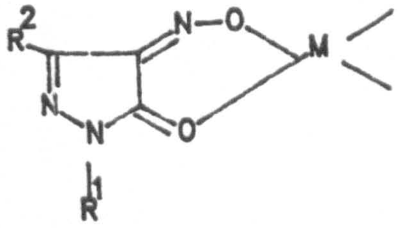
Some structural studies of pyrazole- and isoxazole-4,5-dione-4-oximes have also been reported. In the former, the oximic character of the ligand has been suggested on the basis of infrared studies.[85,88] However, in the Fe^{II} complex,[94] the chelate ring has been suggested to be six-membered on the basis of their reactions towards PPh_3. These suggestions have been adequately confirmed by the X-ray crystallographic studies of diaquobis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)zinc(II) and bis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)manganese(II)dipyridine (*cf.* Chapter IV).

In the platinum complexes of 3-phenylisoxazole-4,5-dione-4-oxime, the ligand acts in a monodentate manner as indicated by its X-ray crystallographic study (Fig. 1.19).[82] However, as only silver and platinum complexes of such ligands have been studied, it is not clear whether this interesting bonding behaviour is a consequence of the nature of the ligand or a general trend. Hence studies of such complexes merit attention.

TABLE 1.3 Complexes of Pyrazole-4,5-dione-4-oximes and their Lewis Base Adducts

R^2	R^1	$ML_2.nH_2O$		ML_2X_n X				$ML_2.nL'(L'=NH_3,py)$ n	
		M	n	Cl	Br	NO_3	ClO_4	NH_3	py
H	H	Cu	-	-	-	-	-	3,4	-
Me	H	Cu	2	2	-	2	-	-	2
Ph	H	Cu	2	-	-	-	-	1	-
H	Ph	Cu	2	-	-	-	-	2	2
Me	Ph	Cu	2	2	-	2	-	2	-
Me	4-$NO_2C_6H_4$	Cu	1	-	-	-	-	2	-
Me	4-ClC_6H_4	Cu	2	-	-	-	-	2,3	-
Ph	Ph	Cu	2	-	-	-	-	2	-
Ph	4-$NO_2C_6H_4$	Cu	2	-	-	-	-	2	-
H	H	Ni	2	-	-	-	-	-	2
Me	H	Ni	2,1	-	-	2	-	-	2
Ph	H	Ni	1	-	-	-	-	2	2
H	Ph	Ni	2	-	-	-	-	-	2
Me	Ph	Ni	2	2	2	2	2	-	-
Me	4-$NO_2C_6H_4$	Ni	0,2	-	-	-	-	4.5, 2	2
Me	4-ClC_6H_4	Ni	2	-	-	-	-	-	-
Me	2,4-$(NO_2)_2C_6H_4$	Ni	–	-	-	-	-	2,4	-
Ph	4-$NO_2C_6H_4$	Ni	0	-	-	-	-	2,3	-
Me	H	Fe	1	-	-	-	-	-	-
Ph	Me	Fe	1	-	-	-	-	-	2
Me	H	Mn	0,2	-	-	-	-	-	-
Ph	H	Mn	0	-	-	-	-	-	2
H	Ph	Mn	0,2	-	-	-	-	-	-
Me	Ph	Mn	0	-	-	-	-	-	-
Me	4-$NO_2C_6H_4$	Mn	2	-	-	-	-	-	-
Me	4-ClC_6H_4	Mn	2	-	-	-	-	-	-
Ph	Ph	Mn	0	-	-	-	-	-	-
Ph	4-$NO_2C_6H_4$	Mn	2	-	-	-	-	-	-
Me	H	Zn,Mg	2	2	-	2	-	-	-
Ph	H	Zn,Mg, Cd	2	-	-	-	-	-	-
H	Ph	Zn,Mg, Cd	2	-	-	-	-	-	-
Me	Ph	Zn	0	2	-	2	-	-	-
Me	4-$NO_2C_6H_4$	Zn,Cd	2	-	-	-	-	2	-
Me	4-ClC_6H_4	Zn,Cd, Mg	2	-	-	-	-	-	-
Ph	Ph	Zn,Mg, Cd	2	-	-	-	-	-	-
Ph	4-$NO_2C_6H_4$	Zn,Cd	-	-	-	-	-	1,2	-
Me	H	Cd	2	-	-	-	-	2	-
Me	Ph	Cd,Mg	2	-	-	-	-	-	-
Me	4-$NO_2C_6H_4$	Mg	2	-	-	-	-	-	-
H	H	Ag	1	-	-	-	-	-	-
H	H	Ag,Tl	0	-	-	-	-	-	-
Me	H	Ag	½	-	-	-	-	-	1
Ph	H	Ag,Tl	0	-	-	-	-	-	-
H	Ph	Ag	0,2	-	-	-	-	1	1
Me	Ph	Ag,Tl	0,1	-	-	-	-	-	-
Me	4-$NO_2C_6H_4$	Ag	1	-	-	-	-	-	-
Me	4-ClC_6H_4	Ag	0	-	-	-	-	1	1
Me	2,4-$(NO_2)_2C_6H_4$	Ag,Tl	0	-	-	-	-	-	-
Ph	Ph	Ag,Tl	0	-	-	-	-	-	-
Ph	4-$NO_2C_6H_4$	Tl	0	-	-	-	-	-	-
Me	H	Tl	0	-	-	-	-	-	-
H	Ph	Tl	0	-	-	-	-	-	-
Me	4-$NO_2C_6H_4$	Tl	0	-	-	-	-	-	-
Me	4-ClC_6H_4	Tl	0	-	-	-	-	-	-

Metal in complex	Ref.
Cu	85-87
Ni	85, 88
Fe	88, 89
Mn	88, 90
Zn	85, 88, 91
Mg, Cd	91
Ag	92
Tl	93



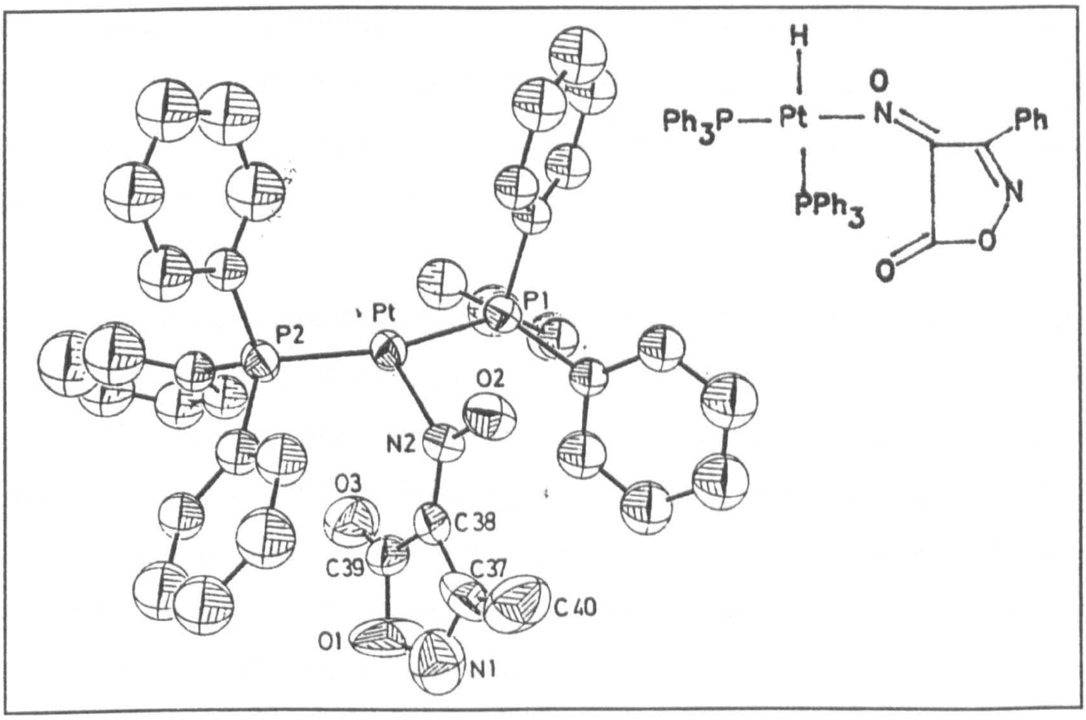


FIG. 1.19

1.4.2 Types of Complexes

The complexes derived from 1,2-quinone monooximes (qoH) can be classified into three classes:

a) ***neutral complexes of the type $M(qo)_n$***, which contain only anionic qo^- ligands.

b) ***neutral complexes of the type $M(qo)_n(qoH)_m$***, which contain both anionic and neutral ligands.

c) ***anionic complexes of the type $[M(qo)_n]^{(n-x)-}$*** , which contain more anionic ligands than the oxidation state of the metal (x).

The complexes of the related pyrazole- and isoxazole-4,5-dione-4-oxime ligands (LH) can be classified in two groups of type ML_n and $M(LH)_nX_y$ (X=Cl, Br, NO_3). Both these complexes are neutral. In the case of isoxazole-4,5-dione-4-oximes, only complexes of the type ML_n have been reported.

The neutral complexes of the type $M(qo)_n$ and ML_n are by far the most common. These complexes are formed by both transition and main group metals. When n=2, the complexes are associated in the solid state but when n=3, they are monomeric and have octahedral structures. The complexes of type $M(qo)_2$ and ML_2 readily react with Lewis bases (LB) [LB = pyridine or aniline] to give adducts of the type $M(qo)_2(LB)_n$ and $ML_2(LB)_n$ respectively. The structures of some of these adducts have been studied by X-ray crystallography.[75,76,78,79]

Neutral complexes of type $M(qo)_n(qoH)_m$ have been reported mainly in the case of the alkali metals.[83] When n=1 and m=0, the structure has not been unambiguously established. However, when n=m=1, the complex usually exist in the penta-coordinated solvated form ie. M(qo)(qoH)(S). During this study, a novel hexa-coordinated lithium complex of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime, $Li(qo)(qoH)_2 1\frac{1}{2}H_2O$, has been prepared and characterised by X-ray crystallography (*cf.* Chapters II and III). In the case of pyrazole-4,5-dione-4-oximes, several complexes of type $[M(LH)_2X_2]$ [M = Cu, Co, Ni, Zn; X = Cl, Br, NO_3] have been reported.[85]

The first reported anionic complex of type $[M(qo)_n]^-$ is the naturally occurring Ferroverdin, $Na[Fe(qo)_3]$ (qoH = 4-vinylphenylester of 4-hydroxy-3-nitrosobenzoic acid).[95] Its structure which has been established crystallographically involves an iron atom surrounded by three quinone-oximic ligands in an approximately trigonal manner (Fig. 1.20). Other examples of this type of complexes are $K[Ni(4\text{-}Clqo)_3]$[70] and $Na[Fe(5\text{-}Acqo)_3]$.[64] Cobalt(III) also forms anionic complexes but in this case, the anion also contains nitro groups along with 1,2-quinone monooximato ligands eg., $Na[Co(qo)_2(NO_2)_2]$.[64,67] In the case of pyrazole- and isoxazole-4,5-dione-4-oximes, there are no examples of anionic complexes.

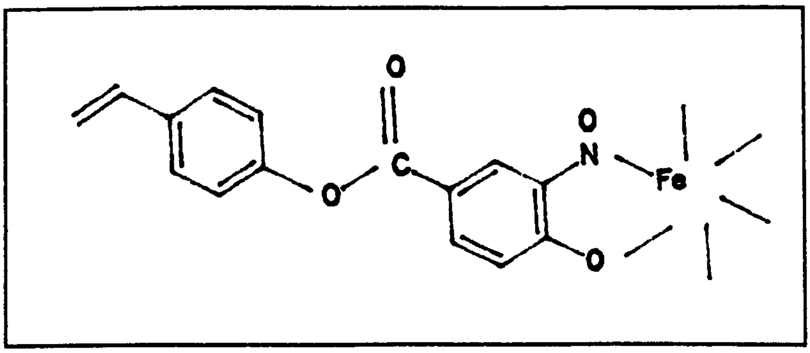


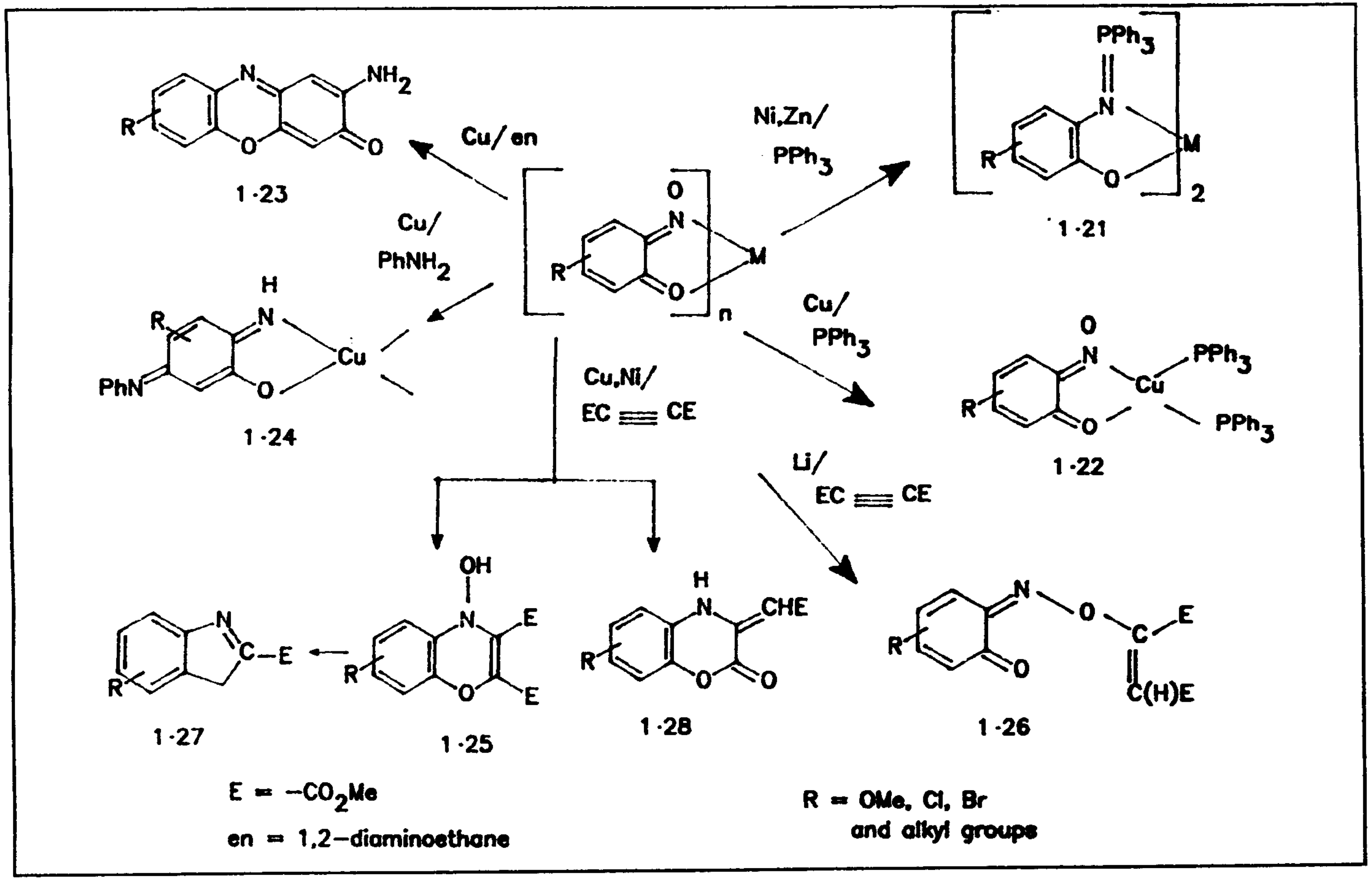
FIG. 1.20

1.5 REACTIONS OF THE COMPLEXES AND THEIR POTENTIAL IN SYNTHESIS

The multifunctional character of the metal complexes of 1,2-quinone monooximes has been utilised extensively for the synthesis of a variety of compounds, some of which are illustrated in Scheme 1.5.

Being highly reactive, the oxygen atom of the NO group is readily deoxygenated by tervalent phosphorus compounds like triphenylphosphine or by primary amines such as aniline or 1,2-diaminoethane to yield various organic and metal-containing products.[96-100] The reactions of triphenylphosphine with Ni^{II} and Zn^{II} complexes of 1,2-benzoquinone monooximes resulted in bis(2-triphenylphosphoranylideneamino-phenolato)nickel(II) or zinc(II) respectively (1.21) whereas their corresponding Cu^{II} complexes yielded quinone oximatobis(triphenylphosphine)copper(I) (1.22) which is in agreement with the well documented reduction of copper(II) bischelates by triphenylphosphine.[101,102] These reactions also afforded several organic products one of which, 2-amino-3H-phenoxazin-3-one (1.23), has also been isolated from the reaction of 1,2-diaminoethane with the corresponding metal complex. The reactions of copper complexes with aniline gave bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)bis(aniline)copper(II) (1.24) along with some azo and imino compounds.

The complexes of 1,2-quinone monooximes have heterodiene character and readily react with dimethyl acetylenedicarboxylate to give four different types of products



E = –CO$_2$Me

en = 1,2–diaminoethane

R = OMe, Cl, Br
and alkyl groups

SCHEME 1.5

a) The Diels Alder addition product (1.25)[103] b) The open chain Michael addition product (1.26)[104] c) A five-membered oxazole (1.27)[104,105] d) A six-membered benzoxazinone (1.28).[106] The open chain Michael addition product is only obtained from the alkali metal complexes whereas all the other three products are obtained from the reactions of the copper and nickel complexes.

As established during this study, dimethyl acetylenedicarboxylate also reacts with pyrazole-4,5-dione-4-oximes and their metal complexes to give novel types of products (*cf.* Chapter V). However, these complexes do not react with triphenylphosphine in accord with the different bonding mode of the pyrazole-oximato ligands to the metal atom (*cf.* Chapter VI and V).

1.6 REFERENCES

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CHAPTER II

PREPARATION AND STUDY OF ALKALI AND ALKALINE EARTH METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND PYRAZOLE-4,5-DIONE-4-OXIMES

CONTENTS

2.1 INTRODUCTION

The coordination chemistry of alkali metals and especially of Na^+ and K^+ is of great importance in biological systems. Because of this, the complexes of the alkali metals with various bidentate ligands like nitrophenols, β-diketones, β-ketonic esters, 2-hydroxy aromatic esters and aldehydes and 1,2-quinone monooximes received great attention since the early half of this century.[1,2] Throughout this period, there has been considerable discussion regarding the nature of bonding between the metal atom and the ligand i.e. whether ionic or covalent[3] (discussed in Section 3 of this chapter).

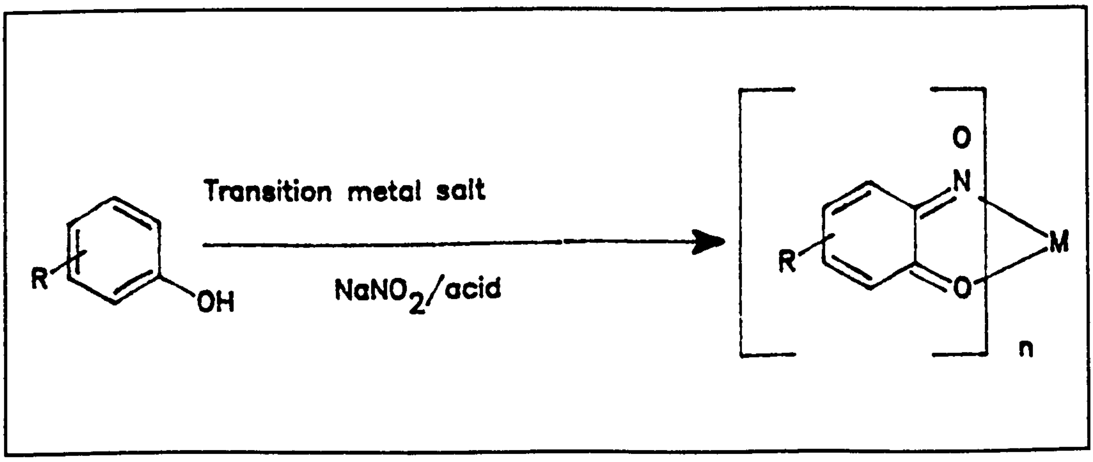
Several methods have been employed for the preparation of complexes derived from 1,2-quinone monooximes. These are usually referred to as the ***direct***, ***nitrosation***, ***metal carbonyl***, ***ligand exchange*** and ***amyl nitrite*** methods.

The ***direct method*** involves the interaction of a 1,2-quinone monooxime with a metal salt (Reaction 2.1). This method has limited applicability because only a few 1,2-quinone monooximes are readily available.

$$\boxed{\mathrm{MX_n + nqoH \xrightarrow[MeOH]{H_2O} M(qo)_n + nHX}}$$

REACTION 2.1

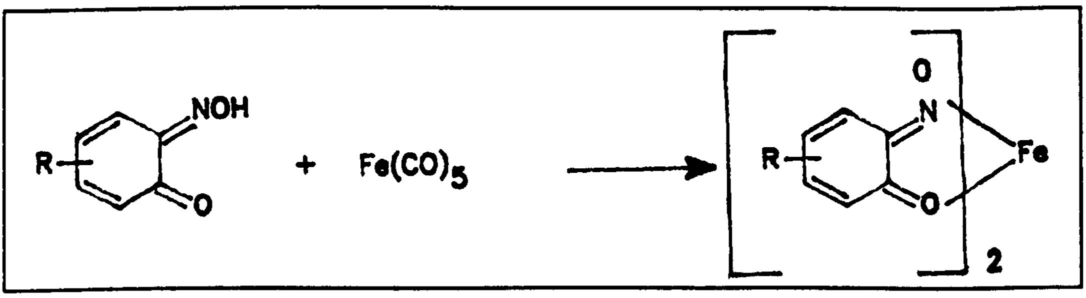
The ***nitrosation method*** involves the reaction of a phenol with sodium nitrite and acid in the presence of a transition metal salt.[4] The 1,2-quinone monooxime, which is generated *in situ*, complexes with the metal ion to give the corresponding metal complex (Reaction 2.2). This method was first reported by Cronheim[5] and later extended by other workers to prepare a wide range of neutral complexes of type



REACTION 2.2

$M(qo)_n$ [M = Ni^{II},[4] Cu^{II},[4] Fe^{III},[6] Co^{III},[7] Mn^{III} [8]] and anionic complexes of types $[Co(qo)_2(NO_2)_2]^-$ [7] and $[M(qo)_3]^-$ [9,10] [M = Ni or Cu].

The ***metal carbonyl method*** involves the interaction of 1,2-quinone monooxime with a metal carbonyl (eg., Reaction 2.3). So far only the reactions of iron(0) pentacarbonyl[6] and dicobalt(0) octacarbonyl[11,12] with the monooximes of 1,2-naphthaquinone and 5-methoxy-1,2-benzoquinone 2-oxime have been reported.



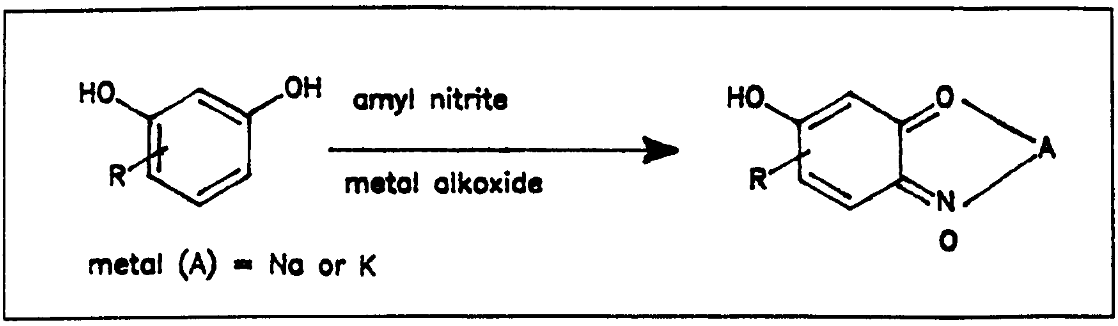
REACTION 2.3

The ***ligand exchange method*** involves the reaction of 1,2-quinone monooxime with another metal complex such as a β-diketonate and has been used for the preparation of manganese complexes of quinone monooximes (Reaction 2.4).[13]

$$\mathrm{Mn(acac)_2 + 1\text{-}nqoH \longrightarrow Mn(1\text{-}nqo)_n + nacacH}$$

REACTION 2.4

In the ***amyl nitrite method,*** the alkali metal complexes are obtained by the nitrosation of 3-hydroxyphenol and 3-alkylaminophenols or their homologues, with amyl nitrite and an alkali metal alkoxide.[14,15]



REACTION 2.5

For the synthesis of the metal complexes of pyrazole-4,5-dione-4-oximes, only the direct and the metal carbonyl methods have been employed.

2.2 PREVIOUS STUDIES OF THE ALKALI AND ALKALINE EARTH METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND PYRAZOLE-4,5-DIONE-4-OXIMES

Two of the methods outlined in the previous section, namely the direct and the amyl nitrite methods, have been widely used for the preparation of the alkali metal complexes of 1,2-quinone monooximes. The corresponding alkaline earth metal complexes have been prepared by the direct method only. However, the preparation of the alkali and alkaline earth metal complexes of pyrazole-4,5-dione-4-oximes received little attention. Only their magnesium complexes have been reported (Table 1.3). The alkali and alkaline earth metal complexes of 1,2-quinone monooximes reported so far as well as the methods employed for their characterisation are listed in Tables 2.1-2.3 which involve elemental analysis, conductivity and infrared studies. X-ray studies of few compounds have also been undertaken.

As indicated in the Tables, most of the complexes investigated involve alkali metals and are derived from the monooximes of 1.2-naphthaquinone, 5-hydroxy- and 5-acetylamino-1,2-benzoquinone 2-oximes and their derivatives.The X-ray studies indicate that the ligand in alkali metal complexes, as in their transition metal analogues, chelates to the metal via the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group and has a prominent quinone-oximic character

(Fig. 2.1).[16] However in the potassium complex of 4-chloro-1,2-benzoquinone 2-oxime, a different coordination mode of the ligand to the metal has been observed (Fig. 2.2). In this complex each oximato ligand shares its two oxygen donor atoms with different potassium ions thus behaving as a bridging rather than a chelating ligand.[17]

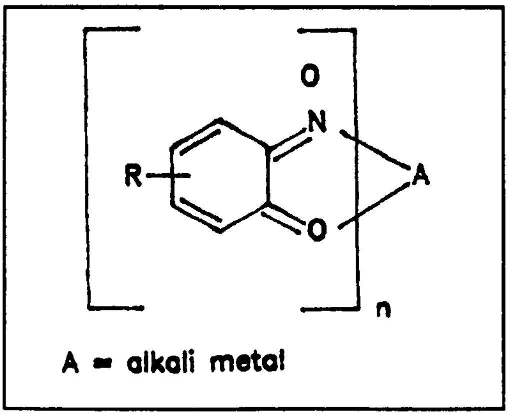


FIG. 2.1

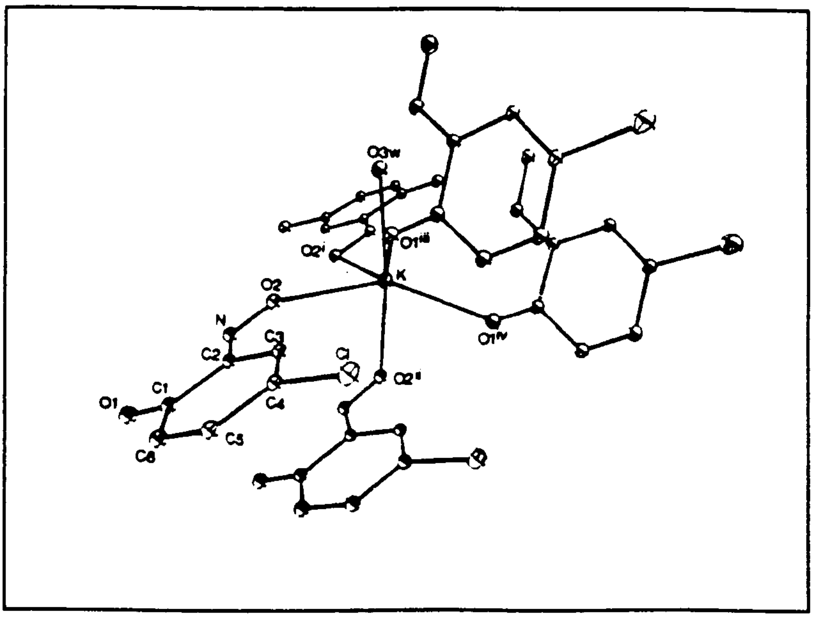


FIG. 2.2

TABLE 2.1 Reported Alkali Metal Complexes of 1,2-Quinone Monooximes

Metal(I)	*Ligand*	*Complex Formula*	*Reported Data*	*Refs*
Na, K, Rb, Cs	1-nqoH	M(qo)	EA, IR, C, NMR	18
Na, K, Rb, Cs	2-nqoH	M(qo)	EA, IR,	19
Li	1-nqoH/2-nqoH	M(qo).½EtOH	IR, C, TGA, NMR	16, 20
Li	1-nqoH	M(qo)(qoH)(EtOH)	IR, C, TGA, NMR, X-ray	16, 20
K, Rb, Cs,	1-nqoH	M(qo)(qoH)	EA, IR, C	18
Li, Na, K, Rb, Cs	2-nqoH	M(qo)(qoH)	EA, IR, TT,	19, 20
Cs	2-nqoH	$M(qo)(qoH)_2$	EA, IR	19
K	7-S-1-nqoH	$M(qo).H_2O$	Mr, X-ray	21
Na	5-S-2-nqoH	$M(qo).3/2H_2O$	IR	22
K	8-S-2-nqoH	$K(qo).2H_2O$	X-ray	23
K, Na	5-S-2-nqoH	$K[Na(qo)].3H_2O$	X-ray	24
K	4-ClqoH	$M(qo).½H_2O$	X-ray	17

TABLE 2.2 Mixed Ligand Complexes of Alkali Metals Containing Quinone Monooximic Ligands

Metal(I)	*Ligand1*	*Ligand2*	*Complex Formula*	*Reported Data*	*Refs.*
Li, Na, K	1-nqoH	bqmH	$[M(qo)]_2$.bqmH	EA, IR, C, TT	25
Li, Na	glyH	1-nqoH/2-nqoH	M(gly).qoH	EA, IR, TT	26, 27
K, Rb, Cs	glyH	1-nqoH/2-nqoH	$M(gly)(qoH)_2$	EA, IR, TT	26, 27
Na, K, Rb, Cs	salH	1-nqoH/2-nqoH	M(sal)(qoH)	EA, TT, IR	27, 28
Na, K, Rb, Cs	hnaH	1-nqoH/2-nqoH	M(hna)(qoH)	EA, TT, IR	27
Na, K, Rb, Cs	anH	2-nqoH	M(an)(qoH)	EA, TT, IR	27
Na, K, Rb, Cs	PhanH	2-nqoH	M(Phan)(qoH)	EA, TT, IR	27
Li, Na, K, Cs	alnH	2-nqoH	M(aln)(qoH)	EA, TT, IR	27
Li, Na, K, Cs	AcsalH	1-nqoH	M(Acsal)(qoH)	EA, TT, IR	27
Na, K	BzsalH	1-nqoH	M(Bzsal)(qoH)	EA, TT, IR	27
Na, K, Rb, Cs	NPhoH	1-nqoH	M(NPho)(qoH)	EA, TT, IR	28
K, Rb, Cs	1-nqoH	NAcpoH	M(qo)(NAcpoH)	EA, TT, IR	28
K, Rb	1-nqoH	hqoH	M(qo)(hqoH)	EA, TT, IR	28

bqmH = bis(8-hydroxy-5-quinolyl)methane
anH = anthranilic acid
AcsalH = acetyl salicylic acid
NAcpoH = isonitrosoacetophenone

glyH = glycine
PhanH = phenyl anthranilic acid
BzsalH = benzyl salicylic acid
hqoH = 8-hydroxyquinonline

salH = salicylic acid

hnaH = 2-hydroxy-3-naphthoic acid
alnH = β-alanine
NPhoH = o-nitrophenol

TABLE 2.3 Reported Alkali and Alkaline Earth Metal Complexes of 5-Hydroxy- and 5-acetylamino-1,2-benzoquinone 2-oximes[29]

Metal(I)	*Ligand*	*Complex*	*Reported Data*
Na	6-MehqoH_2/hqoH_2	M(qoH).H_2O	EA, IR, TGA, NMR
Na	6-MehqoH_2/3-MehqoH_2	M_2(qo)	EA, TGA
K	6-MehqoH_2	M(qoH).H_2O	EA, IR, TGA
Ca	6-MehqoH_2/hqoH_2	M$(qo)_2$	IR, IR, TGA
Na	3-MehqoH_2	M(qoH).2H_2O	IR, C, TGA, NMR
K	3-MehqoH_2/hqoH_2	M(qoH)	EA, IR, TGA
Na	hqoH_2	M_2(qo).½H_2O	EA, TGA
K	hqoH_2	M_2(qo)	EA, TGA
Na	AcqoH	M(qo)	EA, IR, TGA

6-MehqoH_2 = 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime
hqoh_2 = 5-hydroxy-1,2-benzoquinone 2-oxime
3-MehqoH_2 = 5-hydroxy-3-methyl-1,2-benzoquinone 2-oxime
AcqoH = N-acetyl-5-amino-1,2-benzoquinone 2-oxime

2.3 THE PREPARATION OF ALKALI AND ALKALINE EARTH METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND PYRAZOLE-4,5-DIONE-4-OXIMES

The earlier studies of the reactions of the monooximes of 1,2-naphthaquinone in aqueous ethanol with alkali metal hydroxide (MOH) led to the isolation of complexes of type M(qo).nS and M(qo)(qoH)(S) [S = solvent] when reactant molar ratios of 1:1 and 2:1 respectively are used (Fig. 2.3 and 2.4).[30,31] An X-ray study of [Li(1-nqo)(1-nqoH)(EtOH)] established that the lithium atom is in a distorted square pyramidal environment with EtOH molecule acting as the fifth ligand.[16]

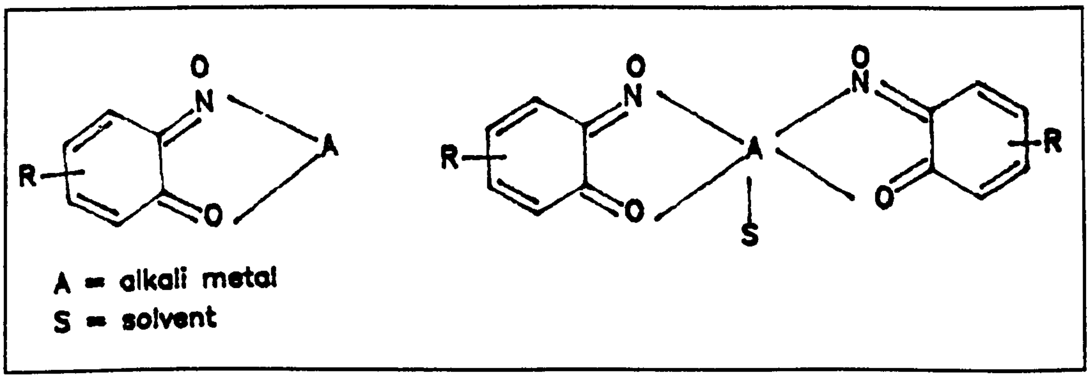


FIG. 2.3

FIG. 2.4

In this study, systematic investigations of the interaction of 1,2-naphthaquinone 1-oxime, 1,2-naphthaquinone 2-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime with lithium, sodium and potassium hydroxides in the molar ratios of 1:1, 2:1 and 3:1 were carried out. In all the cases, a solution of the oxime in aqueous ethanol was added to a solution of the alkali metal salt in the same solvent. The precipitate obtained from each reaction and/or the residue arising by evaporation of the corresponding filtrate were investigated. The results obtained which are summarised in Tables 2.4, 2.5 and 2.6 indicate that the complexation behaviour of the quinone monooximes towards MOH is much more complex and interesting than previously suggested.

TABLE 2.4 **Products formed by LiOH/qoH Reactions**

qoH	*Molar Ratio of LiOH:qoH*		
	1:1	*1:2*	*1:3*
1-nqoH	Li(qo)[*a]	Li(qo)(qoH)[*b]	Li(qo)(qoH)[b]
2-nqoH	Li(qo)[*a]	Li(qo)(qoH)[*b]	Li(qo)(qoH)[b]
5-Et-4-MeqoH	Li(qo)(qoH)[c]	Li(qo)(qoH)$_2$	Li(qo)(qoH)$_2$

[*] taken from reference 16

TABLE 2.5 **Products formed by NaOH/qoH Reactions**

qoH	*Molar Ratio of NaOH:qoH*		
	1:1	*1:2*	*1:3*
1-nqoH	Na(qo)[d]	Na(qo)(qoH)[b]	Na(qo)(qoH)[b]
2-nqoH	Na(qo)[d]	Na(qo)(qoH)[b]	-
5-Et-4-MeqoH	Na(qo)[d]	Na(qo)(qoH)[c]	Na(qo)(qoH)[c]

TABLE 2.6 **Products formed by KOH/qoH Reactions**

qoH	*Molar Ratio of KOH:qoH*		
	1:1	*1:2*	*1:3*
1-nqoH	K(qo)[a]	K(qo)(qoH)[b]	K(qo)(qoH)[b]
2-nqoH	K(qo)[a]	K(qo)(qoH)[b]	-
5-Et-4-MeqoH	K(qo)[d]	K(qo)(qoH)[c]	K(qo)(qoH)[c]

[a] the complex contains ½ mole of ethanol

[b] the complex contains one mole of ethanol

[c] the complex contains one mole of water

[d] the complex contains two moles of water

The findings indicate that the types of product formed depend not only on the molar ratio of the reactants used but also on the nature of the metal and ligand employed. Consequently, two distinct types of behaviour are evident.

1) In the case of the monooximes of 1,2-naphthaquinone, all the metal

ions form complexes of types M(qo) and M(qo)(qoH). Significantly complexes of the latter type are also formed when an excess of the ligand is used. An analogous behaviour is also observed in the reaction of sodium and potassium hydroxides towards 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime.

2) However, the behaviour of lithium towards 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime is sharply different. None of the reactions of lithium hydroxide with 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime afford complexes of the type M(qo). Interestingly, the reaction in the molar ratio of 1:1 results in the complex of type M(qo)(qoH). Increasing the ligand concentration to 1:2, 1:3 or 1:>3 (LiOH:qoH) result in a compound formulated as $[Li(qo)(qoH)_2]$ (Fig. 2.5).

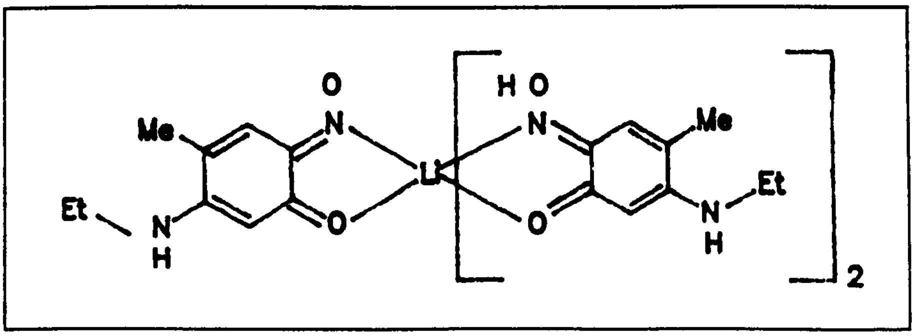


FIG. 2.5

These compounds under study are not coordination compounds of the type believed by Sidgwick.[32-34] It is now believed that their formation is not due to the coordinative properties of M^+ but due to the conjugative interaction of qo^- with qoH.[3] The interaction of M^+ with the ligand or ligand pair is largely electrostatic (ionic) in nature. The tendency of lithium to form complexes with more ligands than the stoichiometry of the reaction may be attributed to its smaller radius and higher charge density in comparison to the Na^+ and K^+ ions and the size of the ligand used.

The reactions of 1,2-naphthaquinone 1-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime with either magnesium acetate or barium hydroxide in 2:1 ratio afford complexes of type $M(qo)_2.2H_2O$. The same complexes also result when the ligand is used in excess.

In the case of the reactions of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime with alkali metal hydroxides, two types of complexes are formed ie., M(Mpo).nH_2O and M(Mpo)(MpoH).nH_2O [M = Li, Na, K]. The analogous reactions of magnesium acetate and barium hydroxide with MpoH and 1-PpoH give complexes of type $M(Mpo)_2.2H_2O$ and $M(1\text{-}Ppo)_2.2H_2O$ respectively. The formulation of the alkali metal complexes is indicated by the carbon:metal ratio established through elemental analysis. It should be noted, however, that the analytical results for nitrogen are poor (low) in all the cases. But the analytical results for the alkaline earth metal complexes are satisfactory in all the cases.

2.4 STRUCTURAL STUDIES OF THE METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES AND PYRAZOLE-4,5-DIONE-4-OXIMES

The structural characterisation of all the alkali and alkaline earth metal complexes prepared during this study i.e. M(qo), M(qo)(qoH) and $M(qo)(qoH)_2$ [M = Li, Na, K, qoH = 1-nqoH, 2-nqoH, 5-Et-4-MeqoH] and those obtained from pyrazole-4,5-dione-4-oximes have been undertaken using various techniques particularly infrared and NMR spectroscopy and mass spectrometry.

Infrared Studies: The IR spectra of all the complexes are well defined (e.g. Figure 2.1) and show prominent absorptions at 3100 - 3450 cm^{-1} assignable to νOH of the protonated ligand or solvent of crystallisation. The presence of strong carbonyl absorptions between 1616 - 1668 cm^{-1} in these spectra indicate the predominantly quinone oximic character of the ligand in these complexes. The νCO absorptions in 2-nqo^- and 5-Et-4-Meqo^- complexes appear lower than in the free ligand (Table 2.7) indicating the involvement of the carbonyl group in bonding to the metal. However, in 1-nqo^- complexes, the νCO absorptions appear slightly higher than in the free ligand. The involvement of the CO group in bonding in these complexes has been confirmed by the X-ray crystallographic studies of Li(1-nqo)(1-nqoH(EtOH)[16] and in this work by the analogous studies of lithium and sodium complexes of 5-Et-4-MeqoH (*cf.* Chapter III). In the case of 1,2-naphthaquinone 2-oximato complexes, the shift in νCO is *ca.* 30-50 cm^{-1} and is considerably greater than the corresponding shift *ca*. 2-10 cm^{-1} observed in the respective complexes of 1,2-naphthaquinone 1-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime. This observation can be rationalised in terms of the presence of strong intramolecular hydrogen bonding in 1,2-naphthaquinone 1-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime which have *syn* structures and the absence of such bonding in the *anti* structure of 1,2-naphthaquinone 2-oxime.

TABLE 2.7 νCO Absorptions in Alkali and Alkaline Earth Metal Complexes of 1,2-Quinone Monooximes

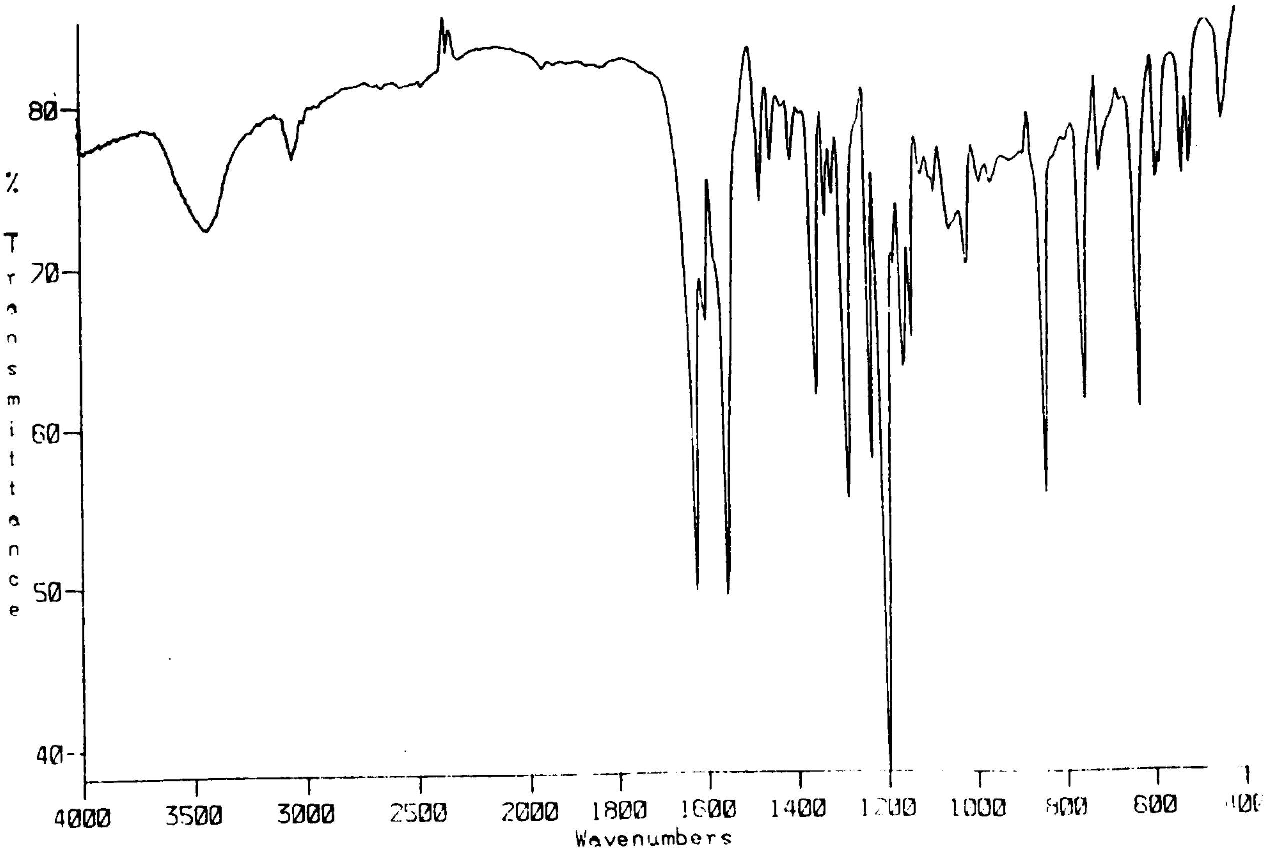
Complex	*Ligand configuration*	*Absorptions (cm^{-1})*	
		νCO	*$\Delta\nu$CO*
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)	syn	1624(s,sh)	11
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$	syn	1625(s,sh)	10
Na(1-nqo)	syn	1620(s,sh)	2
Na(1-nqo)(1-nqoH)	syn	1646(s,sh)	28
Na(2-nqo)	anti	1625(s,sh)	43
Na(2-nqo)(2-nqoH)	anti	1635(s,sh)	33
Na(5-Et-4-Meqo)	syn	1625(s,sh)	10
Na(5-Et-4-Me)(5-Et-4-MeqoH)	syn	1627(s,sh)	8
K(1-nqo)	syn	1622(s,sh)	4
K(1-nqo)(1-nqoH)	syn	1624(s,sh)	6
K(2-nqo)	anti	1616(s,sh)	52
K(2-nqo)(2-nqoH)	anti	1627(s,sh)	41
K(5-Et-4-Meqo)	syn	1630(s,sh)	5
K(5-Et-4-Meqo)(5-Et-4-MeqoH)	syn	1628(s,sh)	7
Mg(1-nqo)$_2$	syn	1624(s,sh)	6
Mg(5-Et-4-Meqo)$_2$	syn	1625(s,sh)	10
Ba(1-nqo)$_2$	syn	1620(s,sh)	2
Ba(5-Et-4-Meqo)$_2$	syn	1626(s,sh)	9

s = strong sh = sharp

νCO for 1-nqoH = 1618 cm^{-1} νCO for 2-nqoH = 1668 cm^{-1}

νCO for 5-Et-4-MeqoH = 1635 cm^{-1}

FIGURE 2.1 Infrared Spectrum of K(2-nqo)



The oximic character is also prominent in the alkali and alkaline earth metal complexes of pyrazole-4,5-dione-4-oximes. This is indicated by their IR spectra which show prominent carbonyl absorptions at 1624-1655 cm^{-1}. The pyrazole-4,5-dione-4-oximato complexes exhibit prominent shifts in νCO (*ca.* 36-67 cm^{-1}) towards lower wavenumber compared to the free ligand, thus indicating the involvement of the carbonyl oxygen in bonding to the metal. In view of this large shift in νCO on complexation and by comparing it with the trend observed in complexes of 1,2-quinone monooximes having *syn* and *anti* structures (Table 2.7), it is reasonable to assume that the free pyrazole-4,5-dione-4-oximes have an *anti* configuration.

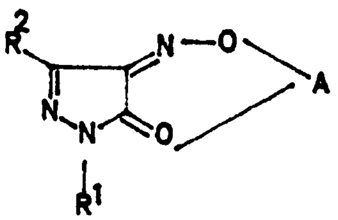


TABLE 2.8 νCO Absorptions of the Alkali and Alkaline Earth Metal Complexes of pyrazole-4,5-dione-4-oximes

Metal	*Ligand*		*Molar ratio of reactants*	*Infrared stretchings (cm^{-1})*	
	R^1	*R^2*		*νCO*	*ΔνCO*
Li(I)	Me	Me	1:1	1635	56
Li(I)	Me	Me	1:2	1634	57
Na(I)	Me	Me	1:1	1655	36
Na(I)	Me	Me	1:2	1655	36
K(I)	Me	Me	1:1	1647	44
K(I)	Me	Me	1:2	1648	43
Mg(II)	Me	Me	1:2	1649	42
Mg(II)	Ph	Me	1:2	1650	55
Ba(II)	Me	Me	1:2	1624	67
Ba(II)	Ph	Me	1:2	1650	55

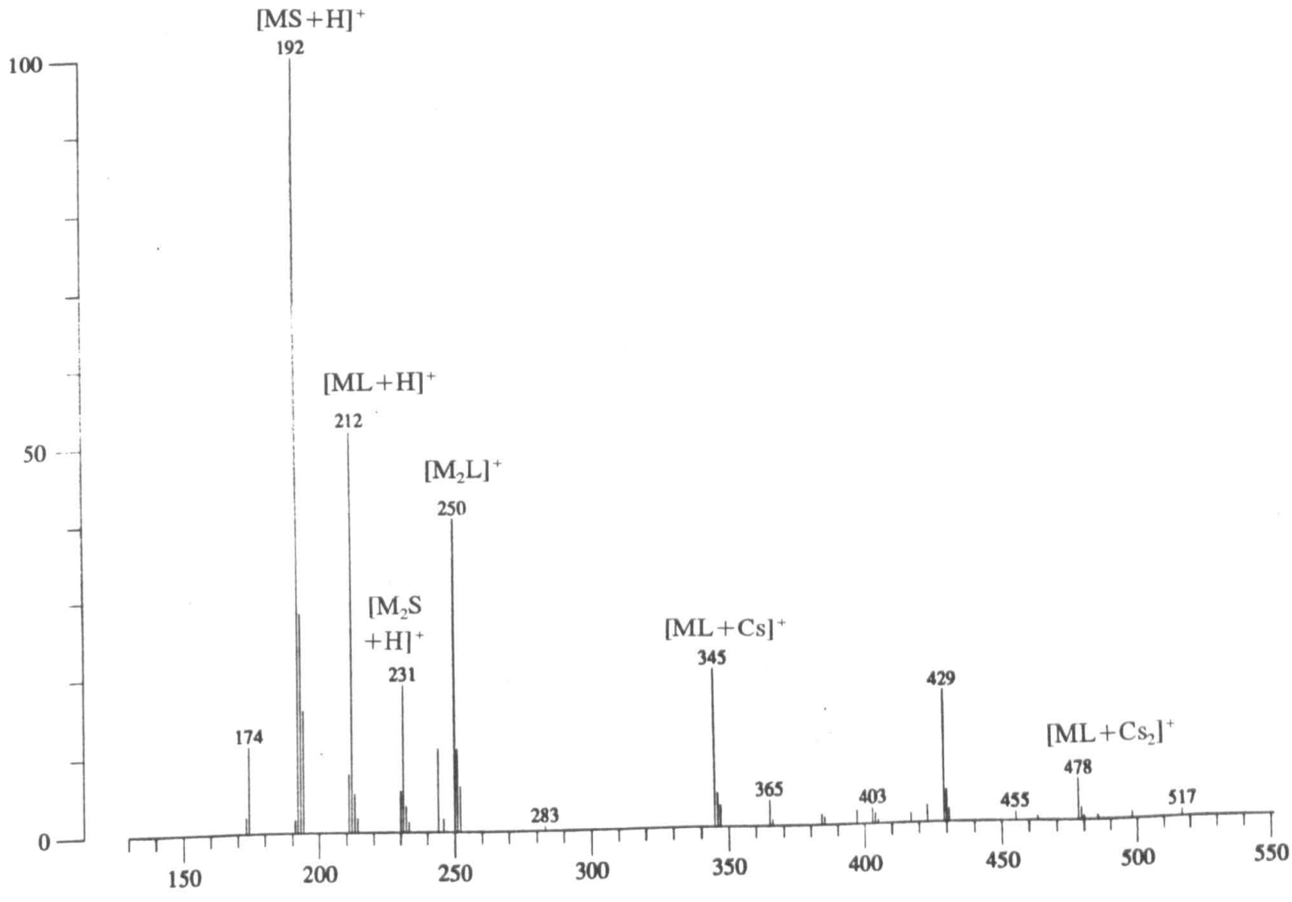
νCO for MpoH = 1691 cm^{-1} νCO for 1-PpoH = 1705 cm^{-1}

Mass Spectral Studies: The mass spectra of the alkali and alkaline eath metal complexes of 1,2-quinone monooximes and pyrazole-4,5-dione-4-oximes have been studied using both electron impact (EI) and Liquid Secondary Ion Mass Spectrometry (LSIMS) techniques.

In order to obtain EI spectra, high insertion temperatures have to be used because of the involatility of the complexes thereby leading to pyrolytic decomposition.[35] As a consequence, very complex spectra resulted which were not very informative. However, by using the LSIMS method, more informative spectra were obtained.

The LSIM spectra of the complexes indicated the presence of dimetallic and trimetallic species like $[M_2L_2]^+$, $[M_2L_3]^+$, $[M_3L_2]^+$, $[M_3L_3]^+$ (Table 2.9 and Figure. 2.2) suggesting that the complexes are associated in solution. The establishment of association in alkali and alkaline earth metal complexes by LSIMS technique is not only significant in terms of the structural information of these compounds but has a wider potential with regard to the detection of association in different types of alkali and alkaline earth metal complexes which, in contrast to the transition metals, cannot be established by magnetic measurements.

FIGURE 2.2 **Mass Spectrum of K(2-nqo)(2-nqoH)(EtOH)**



S = solvent

TABLE 2.9 m/z Values for Prominent Metal Containing Ions in the LSIMS Mass Spectra of the Alkali and Alkaline Earth Metal Complexes of 1,2-Quinone Monooximes

	Metal Containing Ions[a] *(% Abundances)*				
Complex	*$[ML]^+$*	*$[M_2L]^+$*	*$[ML_2]^+$*	*$[M_3L_2]^+$*	*$[M_2L_2]^+$*
Li(1-nqo).½EtOH	179(40)		-	-	-
Li(2-nqo).½EtOH	178(7)	187(2)	-	365(1)	358(1)
Li(1-nqo)(1-nqoH)(EtOH)	179(44)	186(30)	352(4)	365(2)	358(2)
Li(2-nqo)(2-nqoH)(EtOH)	180(100)	-	353(5)	-	-
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_20)	187 (73)	194 (5)	367 (6)	381 (2)	374 (5)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$	187 (25)	-	367 (7)	-	-
Na(1-nqo).2H_2O	196(15)	218(3)	-	413(9)	-
Na(2-nqo).2H_2O	196(71)	218(49)	-	413(15)	-
Na(5-Et-4-Meqo).2H_2O	203(100)	225(50)	383(3)	-	-
Na(1-nqo)(1-nqoH)(EtOH)	196(14)	218(2)	369(2)	413(2)	-
Na(2-nqo)(2-nqoH)(EtOH)	196(100)	218(74)	369(1)	413(3)	391(2)
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	203 (100)	225 (43)	383 (7)	427 (9)	405 (6)
K(1-nqo).½EtOH	212(29)	250(37)	-	-	-
K(2-nqo).½EtOH	212(52)	250(43)	384(2)	-	423(2)
K(5-Et-4-Meqo).2H_2O	219(100)	257(67)	399(3)	-	475(7)
K(1-nqo)(1-nqoH)(EtOH)	212(15)	250(8)	-	-	-
K(2-nqo)(2-nqoH)(EtOH)	212(38)	250(21)	-	-	-
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	219 (100)	257 (27)	383 (4)	-	-
Mg(1-nqo)$_2$.2H_2O	196(11)	220(6)	368(10)	416(1)	392(8)
Mg(5-Et-4-Meqo)$_2$.2H_2O					
Ba(1-nqo)$_2$.2H_2O	310(57)	445(1)	482(2)	-	-
Ba(5-Et-4-Meqo)$_2$.2H_2O	317(83)	454(1)	497(5)	-	634(1)

[a] In the LSIM spectra, these ions usually appear as cluster of ions composed of species such as ML_2, ML_2+nH and ML_2-nH

The mass spectra of these complexes also exhibited peaks involving Rb and Cs ions and matrix associated species such as $[MS]^+$, $[M_2S]^+$, $[MS_2]^+$, $[MS_2+Rb]^+$ and $[MS_2+Cs]^+$ (Table 2.10).

TABLE 2.10 m/z Values of Prominent Solvated and Alkali Metal Incorporated Ions in the LSIMS Mass Spectra of the Alkali and Alkaline Earth Metal Complexes of 1,2-Quinone Monooximes

	Ion Assignment (% Abundance)				
Complex	*$[MS]^+$*	*$[M_2S]^+$*	*$[MS_2]^+$*	*$[MS_2+Rb]^+$*	*$[MS_2+Cs]^+$*
Li(1-nqo).½EtOH	160(100)	-	313(18)	397(7)	446(0.7)
Li(2-nqo).½EtOH	161(3)	167(17)	-	-	-
Li(1-nqo)(1-nqoH)(EtOH)	160(100)	167(23)	313(23)	396(6)	446(3)
Li(2-nqo)(2-nqoH)(EtOH)	160(88)		313(14)	-	-
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	160 (16)	167 (3)	313 (3)	396 (3)	-
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$	160 (6)	-	313 (2)	-	-
Na(1-nqo).2H_2O	176(100)	-	329(21)	-	462(3)
Na(2-nqo).2H_2O	176(100)	-	329(15)	-	-
Na(5-Et-4-Meqo).2H_2O	176(58)		329(5)	-	-
Na(1-nqo)(1-nqoH)(EtOH)	176(100)	-	329(13)	-	-
Na(2-nqo)(2-nqoH)(EtOH)	176(48)	199(8)	329(2)	414(8)	462(2)
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	176 (18)	-	329 (2)	-	-
K(1-nqo).½EtOH	192(100)	231(23)	345(14)	-	478(4)
K(2-nqo).½EtOH	192(100)	231(19)	345(20)	429(17)	478(5)
K(5-Et-4-Meqo).2H_2O	192(100)	231(5)	345(13)	429(8)	478(3)
K(1-nqo)(1-nqoH)(EtOH)	192(100)	231(9)	345(5)	429(0.6)	-
K(2-nqo)(2-nqoH)(EtOH)	192(100)	231(10)	345(8)	429(6)	478(2)
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	192 (56)	231 (6)	345 (4)	429 (9)	478 (2)
Mg(1-nqo)$_2$.2H_2O	177(15)	201(14)	328(9)	-	430(5)
Ba(1-nqo)$_2$.2H_2O	290(18)	427(1)	-	525(2)	-
Ba(5-Et-4-Meqo)$_2$.2H_2O	290(18)	427(3)	-	527(2)	575(4)

The mass spectra of the alkali metal complexes of MpoH also showed dimetallic species like $[M_2L]^+$ which indicate the presence of dimers. However, ions like $[ML_2]^+$ are absent in all the spectra. These spectra are dominated by alkali metal incorporated and matrix associated species as shown in Table 2.11 and Figure 2.3.

FIGURE 2.3 Mass Spectrum of the Na(Mpo)

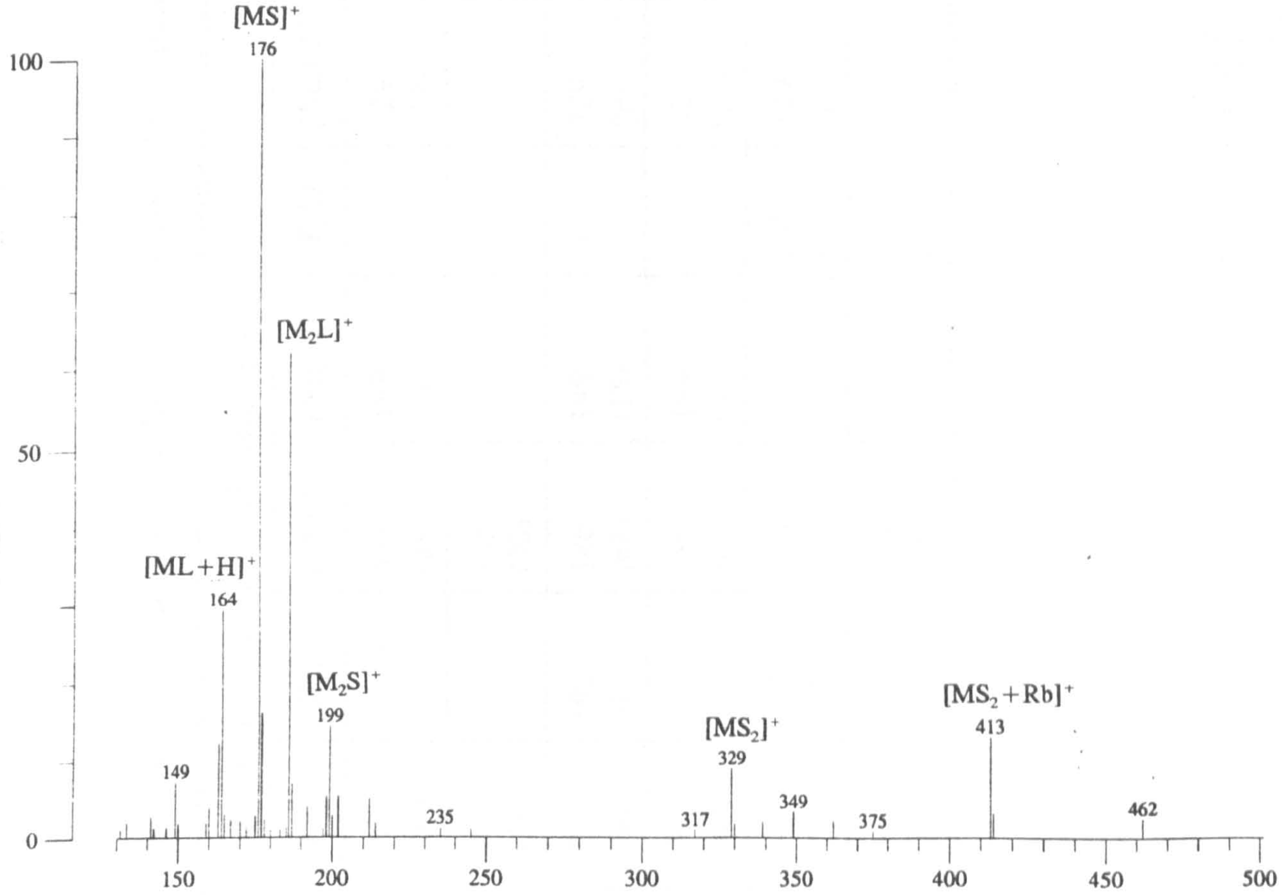
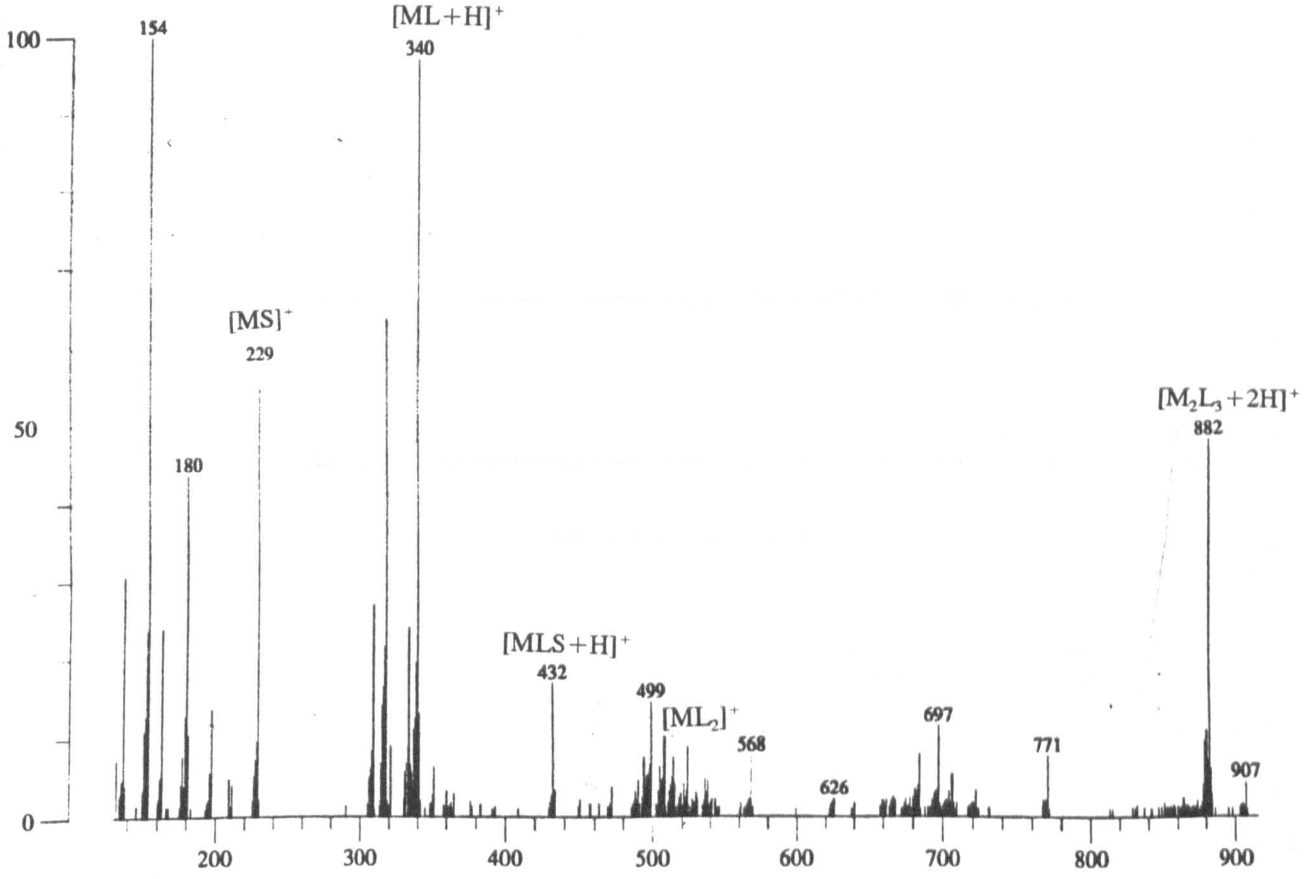


TABLE 2.11 m/z Values of Prominent Metal Containing Ions in the LSIM Spectra of the Alkali Metal Complexes of MpoH

Metal used	*Molar ratio of M/L*	*Metal Containing Ions (% Abundances)*								
		$[ML]^+$	*$[NaS]^+$*	*$[KS]^+$*	*$[M_2L]^+$*	*$[Na_2S]^+$*	*$[K_2S]^+$*	*$[NaS_2]^+$*	*$[KS_2+Rb]^+$*	*$[NaS_2+Rb]^+$*
Li	1:1	148 (18)	176 (100)	-	155 (29)	199 (7)	-	329 (13)		413 (11)
Li	1:2	148 (25)	176 (42)	-	155 (30)	-	-	-	-	413 (15)
Na	1:1	164 (29)	176 (100)	192 (4)	186 (62)	199 (15)	-	329 (9)		413 (13)
Na	1:2	164 (30)	176 (100)	-	186 (42)	199 (9)	-	329 (11)		413 (8)
K	1:1	179 (3)	176 (23)	192 (100)	218 (21)	-	231 (17)	329 (2)	429 (7)	-
K	1:2	179 (4)	176 (85)	192 (100)	218 (16)	199 (6)	231 (11)	329 (9)	429 (8)	413 (6)

FIGURE 2.4 Mass Spectrum of $Ba(1\text{-}Ppo)_2$

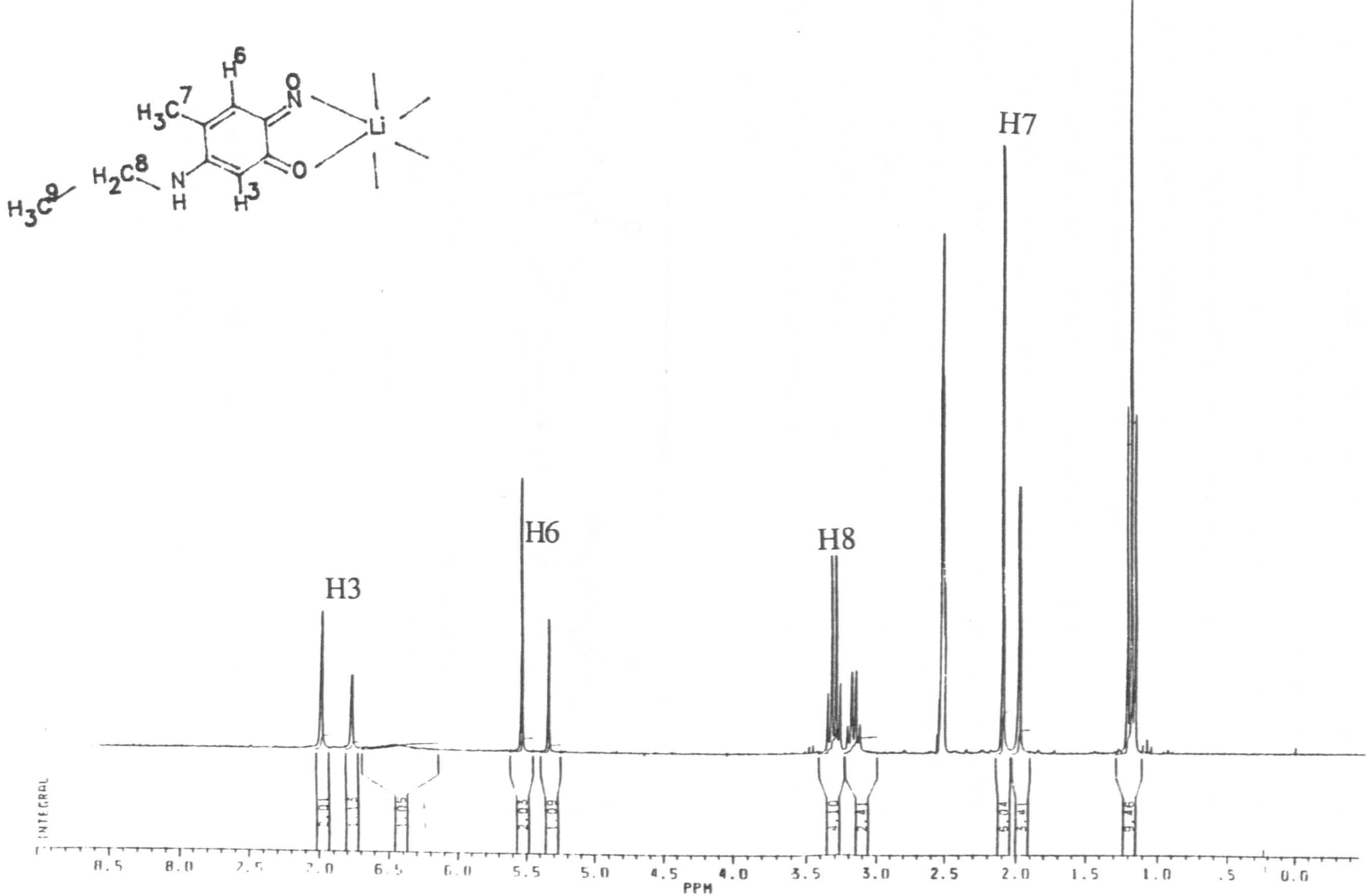


The magnesium and barium complexes of MpoH and 1-PpoH show the presence of dimeric species like $[M_2L_3]^+$ indicating the presence of dimers and several matrix associated species (typical of LSIMS spectra). This is illustrated in Figure 2.4 which shows the LSIM spectrum of $Ba(1\text{-}Ppo)_2$.

NMR Spectral Studies: The ^1H NMR spectra of the alkali and alkaline earth metal complexes of 1,2-naphthaquinone monooximes and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime were recorded in dimethylsulphoxide. All the spectra of the monooximes of 1,2-naphthaquinone exhibit multiplets at δ_H 6.5-9.0 due to the aromatic protons.

In the ^1H NMR spectra of the alkali and alkaline earth metal complexes of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime, the aromatic protons appear at δ_H 5.3-6.1 and δ_H 6.7-6.9 (eg. Figure 2.5). H(3) being flanked by two electron withdrawing groups appear at a more downfield position than H(6). Of the two sets

FIGURE 2.5 ^{1}H NMR Spectrum of Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$ in DMSO-d^6 at 250 MHz



of methyl protons, the one attached to the aromatic ring, H(7), appears at a downfield position of δ_H 2.0-2.1 and methyl protons of the ethylamino group, H(9), resonates at δ_H 1.2. The methylene protons of the ethylamino group, H(8), resonates at δ_H 3.2-3.3. The ^{1}H NMR spectrum of Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$ exhibited two signals for each proton environment which integrate in 1:2 ratio. This is consistent with two of the three ligands existing in the protonated form (5-Et-4-MeqoH) and the other adopting the non-protonated form (5-Et-4-Meqo), although the resonance for the oximic proton in the protonated form can not be clearly identified from the spectra. The NMR data reveals that even in solution the established coordination geometry around the Li atom remains unaltered. Interestingly, however, the resonance due to the amino proton is absent. This could be due to the fact that the nitrogen atom of the ethylamino group is sp^2-hybridised and the ligand in the complex may be an equilibrium mixture of the quinone oxime and imino oxime form as shown in Fig. 2.6.

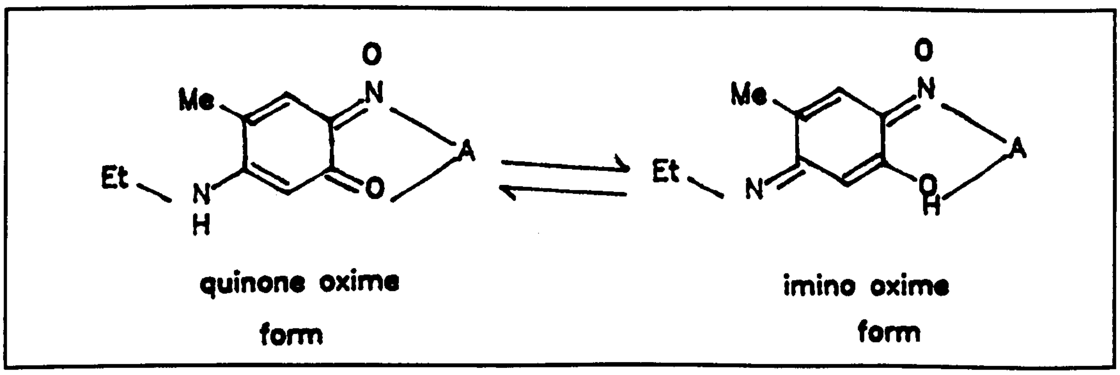
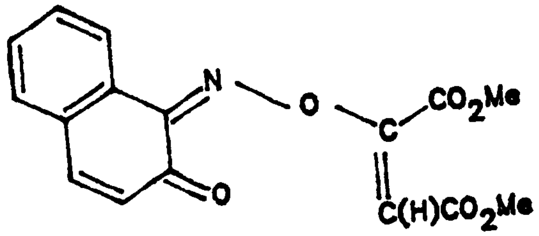


FIG. 2.6

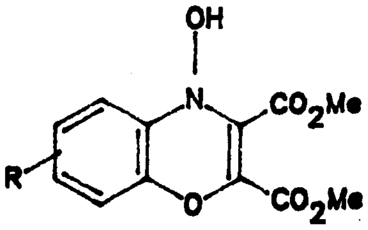
2.5 REACTIONS OF THE ALKALI AND ALKALINE EARTH METAL COMPLEXES OF 1,2-QUINONE MONOOXIMES WITH DIMETHYL ACETYLENEDICARBOXYLATE

Previous reports have indicated that the reactions of 1,2-naphthaquinone 1-oxime and its lithium complex with dimethyl acetylenedicarboxylate (DMAD) under relatively mild conditions resulted in the open chain 1,2-addition products, *cis-* and *trans-*[(O-1$'$,2$'$-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (2.7)^{20}. However, the transition metal complexes of 1,2-quinone monooximes yielded the cycloadducts (2.8-2.9).[36-38]

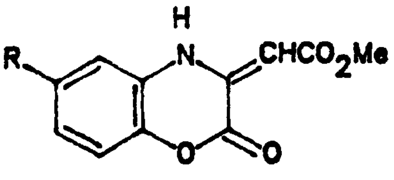
The present study has established that other alkali metal complexes of 1,2-naphthaquinone 1-oxime specifically sodium and potassium as well as the alkaline earth metal, barium also give the open chain 1,2-addition products, (2.7). The yield of the product arising from the system, DMAD/M(1-nqo)$_n$ [M = Na, K, Ba] is dependent on the temperature and the nature of the metal. Higher yields result when the reaction is carried out at a low temperature (Table 2.12) and when the metal is changed from alkali metals like sodium and potassium to barium. The mechanism of the formation of the product has been suggested in Scheme 2.1. The mechanism suggested involved Michael type addition of the oxime across the triple bond of dimethylacetylene dicarboxylate and water may serve as the source of proton.



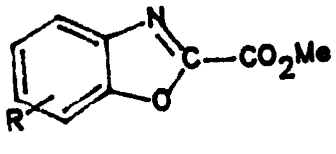
2.7. O[(1′,2′-dicarbomethoxyethenyl) 1,2-naphthaquinone 1-oxime



2.8. 1,4-oxazines



2.9. 1,4-oxazin-2-ones

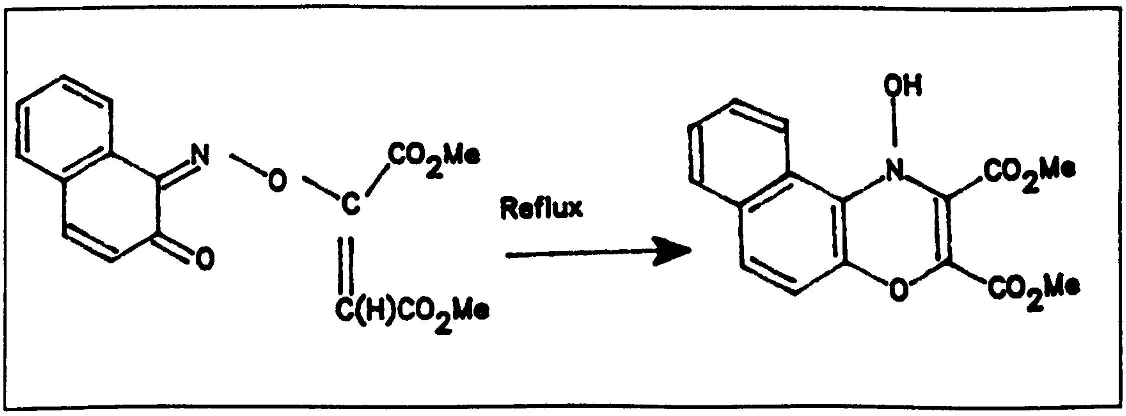


2.10. 1,3-oxazoles

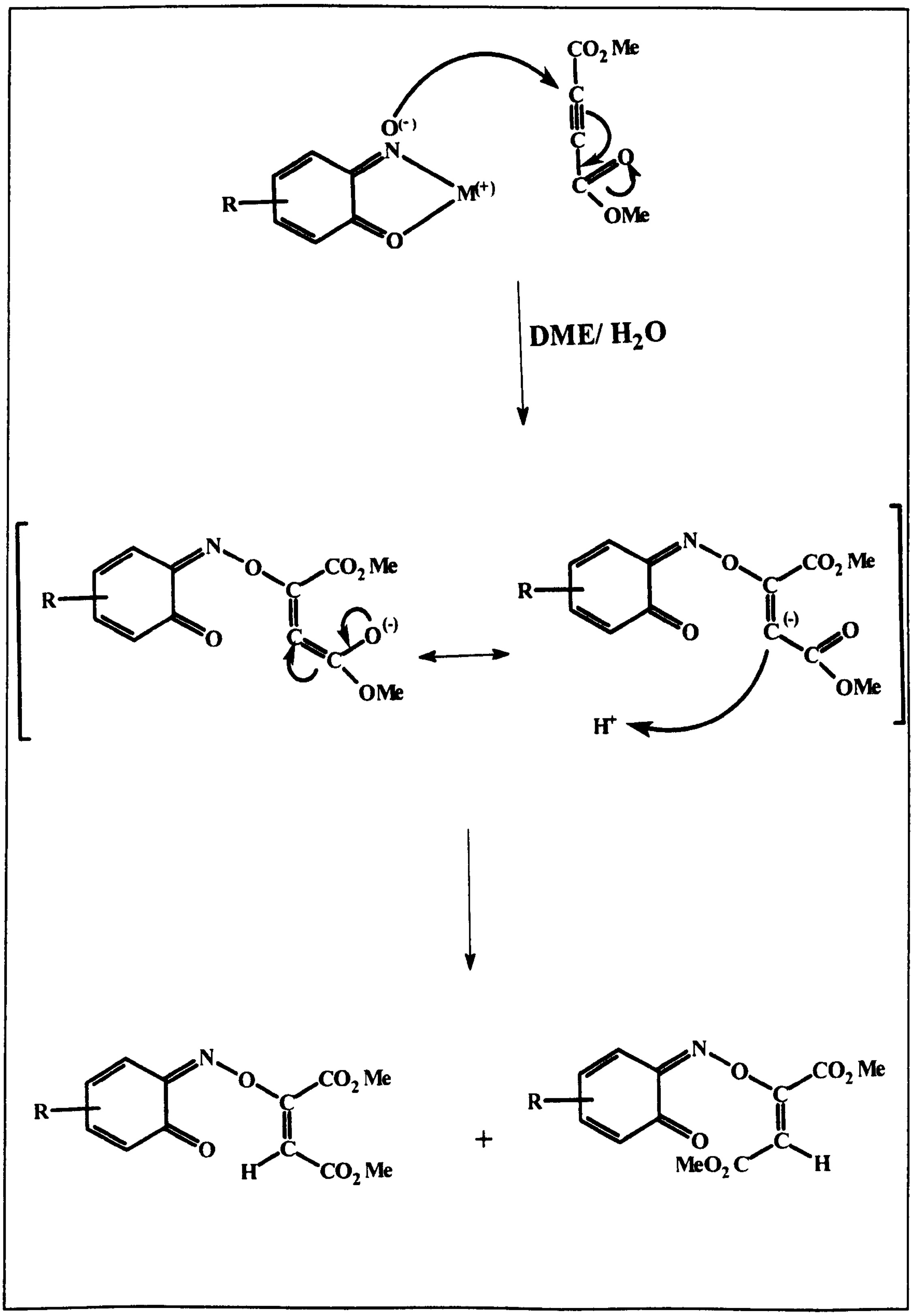
TABLE 2.12 The % yield of the Addition Products at different temperatures using different complexes

	% yield of O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime at			
Complexes	*-75°C*	*0°C*	*20°C*	*50°C*
Na(1-nqo)	58	56	53	5
K(1-nqo)	50	48	34	6
Ba(1-nqo)$_2$	-	84	55	-

Interestingly it has been found that the isomeric mixture (cis and trans) of O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime cyclises to 1,4-naphthoxazine when heated under reflux (Reaction 2.8). However, this isomerism reaction is found to be "*irreversible.*" The cyclic product, 1,4-naphthoxazine, do not isomerise to the open chain product under any thermal condition.



REACTION 2.8


CO2 Me
C
C
O
C
OMe
O(-)
N
M(+)
R
O
DME/ H2O
N
O
CO2 Me
C
C
O(-)
C
OMe
R
O
N
O
CO2 Me
C
C(-)
C
O
OMe
R
O
H+
N
O
CO2 Me
C
C
H
CO2 Me
R
O
+
N
O
CO2 Me
C
C
H
MeO2 C
R
O

SCHEME 2.1

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CHAPTER III

STRUCTURAL STUDIES OF ALKALI METAL COMPLEXES OF 5-ETHYLAMINO-4-METHYL-1,2-BENZOQUINONE 2-OXIME

CONTENTS

3.1 INTRODUCTION

As discussed in Chapter II, 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime reacted readily with sodium and potassium hydroxide in the molar ratio of 1:1 and 2:1 to form the mono- and bis-chelates (Fig. 3.1 and 3.2 respectively). However in the case of complexation with lithium, the mono-chelate form was not observed. Lithium formed the bis-chelate when the reaction was carried out in the molar ratio of 1:1

whereas a molar ratio of 2:1 and 3:1 both resulted in the formation of a novel tris-chelate [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H$_2$O] (Fig. 3.3). In contrast, the tris-chelate is not observed by the reaction of sodium and potassium hydroxide with 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime in the molar ratio of 1:3 or when an excess of the ligand was used.

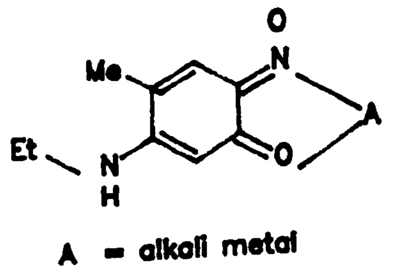


FIG. 3.1

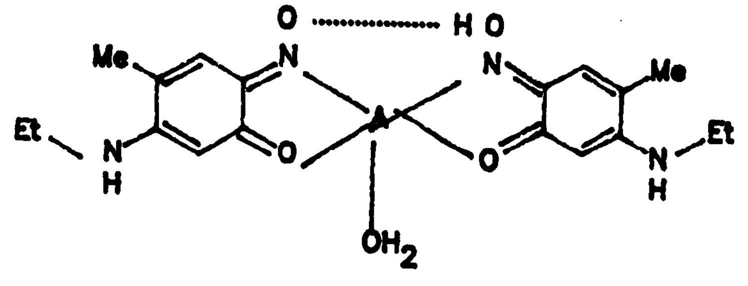


FIG. 3.2

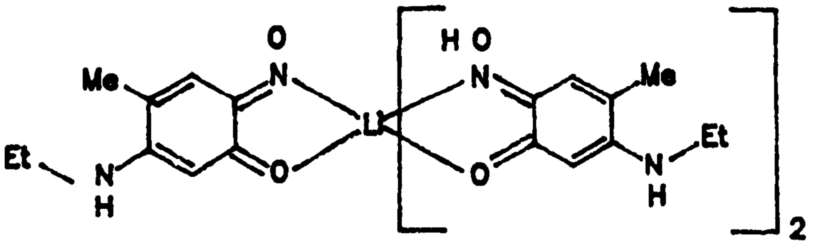


FIG. 3.3

3.2 PREPARATION OF CRYSTALS

Aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)lithium(I) [Li(5-Et-4-Mqo)(5-Et-4-MeqoH)(H$_2$O)] was obtained as red prismatic crystals from an aqueous ethanolic solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime and lithium hydroxide in the molar ratio of 1:1 on standing at 20°C.

Aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)sodium(I) [Na(5-Et-4-Mqo)(5-Et-4-MeqoH)(H_2O)] was obtained as red prismatic crystals from an aqueous ethanolic solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime and sodium hydroxide in the molar ratio of 2:1 at 20°C.

Bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)lithium(I).1½H_2O [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O] was prepared from the reaction of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime and lithium hydroxide in aqueous ethanolic solution in the molar ratio of 2:1 and 3:1. The red prismatic crystals of Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O were obtained from an aqueous ethanolic solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime and lithium hydroxide in the molar ratio of 2:1 at 20°C.

3.3 SINGLE CRYSTAL X-RAY STRUCTURAL DETERMINATION OF [Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)]

3.3.1 Data Collection and Processing[1]

The unit cell parameters and intensity data were collected under ambient conditions on an CAD4 Enraf-Nonius diffractometer using graphite monochromatised CuKα radiation (λ = 1.5418 Å). The intensity data for the structure were corrected for Lorentz-polarisation effects and for absorption.[2]

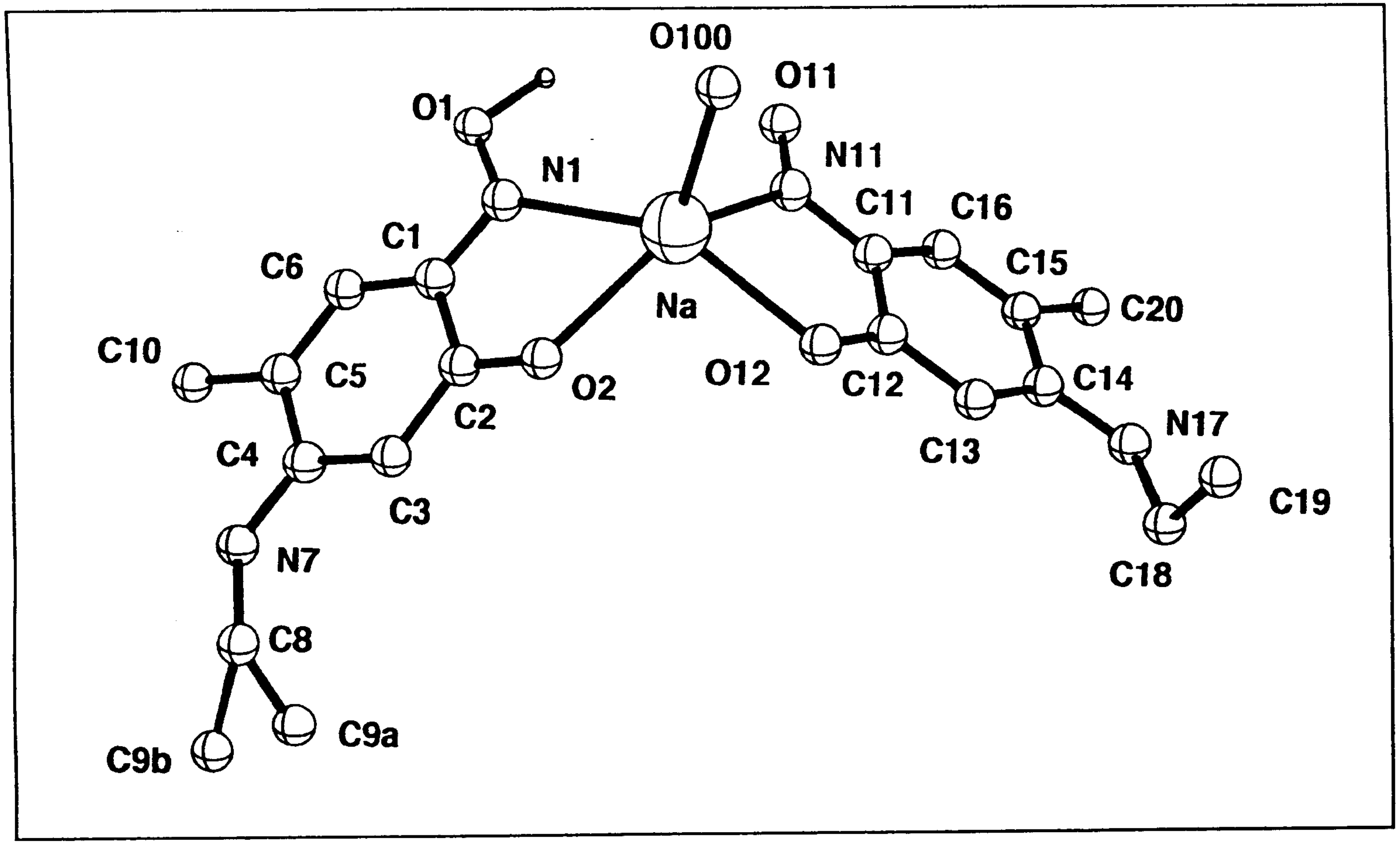
3.3.2 Structure Analysis and Refinement

The structure of this complex was solved by direct methods MULTAN 80[3] with the remaining non-hydrogen atoms located from subsequent Fourier difference syntheses. All the non-hydrogen atoms were anisotropically refined by full-matrix least-squares which converged at R and Rw values as 0.067 and 0.060 respectively with the weights of $1/\sigma^2(F_0)$ assigned to individual reflections. The C9 atom is disordered, it has been refined in two different positions. Pertinent experimental data are given in Table 3.1.

TABLE 3.1 Information about Data Collection and Structure Refinement

CRYSTAL DATA	
Formula	$C_{18}H_{27}N_4NaO_6$
Mr	418.43
System	monoclinic
Space group	$P2_1/c$ (no. 14)
a	8.141(2) Å
b	11.440(1) Å
c	22.877(3) Å
β	90.71(2)°
V	2130.4(7) Å^3
Z	4
D_{calc}	1.304 g cm^{-3}
Radiation	Cu Kα (λ=1.54184 Å) graphite monochromated
μ	9.598 cm^{-1}
T	293(2) K
Crystal size	0.50×0.25×0.20 mm
DATA COLLECTION	
Scan type	ω-2θ
Unique reflections	4028
Observed reflections [$I>3.0\sigma(I)$]	3008

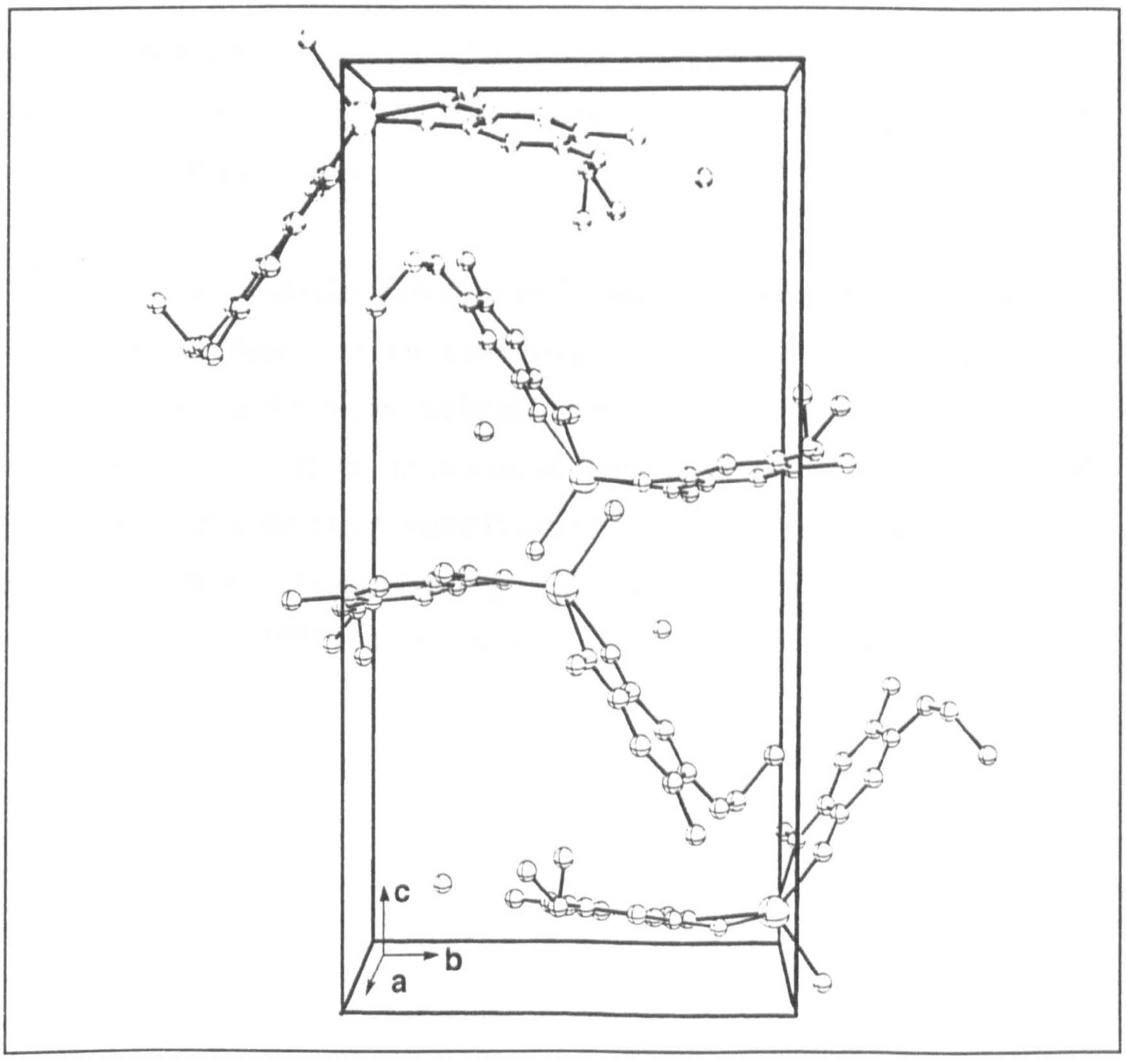
FIG. 3.4 A view of $[Na(5\text{-}Et\text{-}4\text{-}Meqo)(5\text{-}Et\text{-}4\text{-}MeqoH)(H_2O)]$ with atomic numbering scheme



3.3.3 Result and Discussion

The structure of aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)sodium(I) with the relevant atomic numbering is shown in Fig. 3.4. The extensive hydrogen bonding which is an important feature of this compound are shown in Figs. 3.6 and 3.7 respectively.

FIGURE. 3.5 Unit cell for the crystal of [Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)]



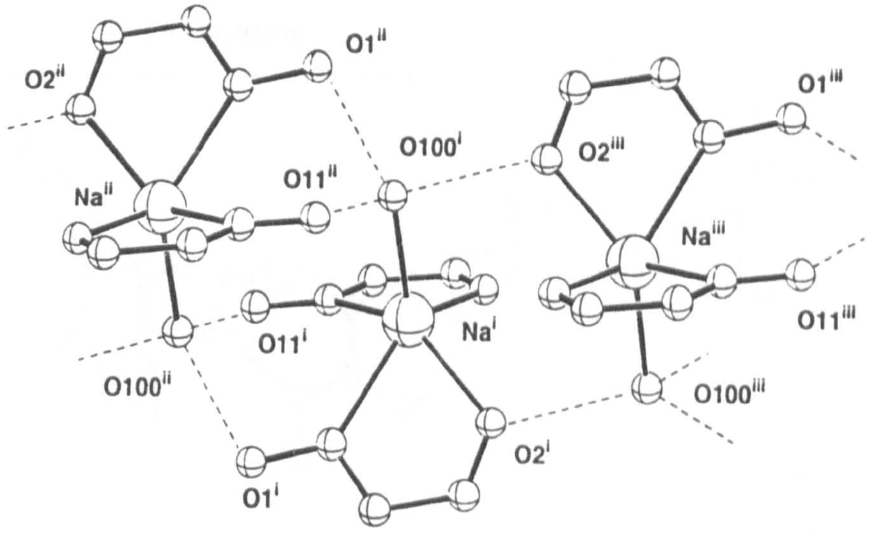
The structure of the complex indicates that the Na^+ ion is penta-coordinated and located approximately at the centre of a square pyramid (Fig. 3.5). Like the majority of the 1,2-quinone monooximato complexes, the two quinone monooximato ligands chelate the metal centre through the carbonyl oxygen and the oximato nitrogen atoms. The fifth coordination site is occupied by a water molecule. Only one of the ligands remain deprotonated. This implies a significant difference between the oxime moiety of the two ligands coordinated to the metal centre [N1-O1 = 1.383(4) Å, and N11-O11 = 1.299(4) Å; N1-C1 = 1.299(4) Å and N11-C11 = 1.348(5) Å].

The co-ordinative bonds with the carbonyl oxygen atoms [Na-O2 = 2.346(3)Å, Na-O12 = 2.275(3)Å] appear to be much stronger than those with the oxime nitrogen atoms [Na-N1 = 2.520(3)Å, Na-N11 = 2.544(3)Å].

The sodium atom is 63.8° above the plane of the molecule defined by the co-ordinate atoms N1, O2, N11 and O12. This results in the distorted square pyramidal geometry of the bis-chelate.

The most interesting and relevant feature in the packing of the crystal is the extensive hydrogen bonding. Apart from the water molecule which remains coordinated to the Na^+ ion, there is another water molecule present in the crystal. Both these water molecules are involved in the formation of hydrogen bonds. The water molecule (O100) coordinated to the metal centre is in a distorted tetrahedral environment since it participates in three hydrogen bonding (Fig. 3.6). The hydrogen bonding involves the water molecule (O100) with one carbonyl oxygen atom and two oximic oxygen atoms.

FIGURE 3.6 A view of the extensive hydrogen bonding



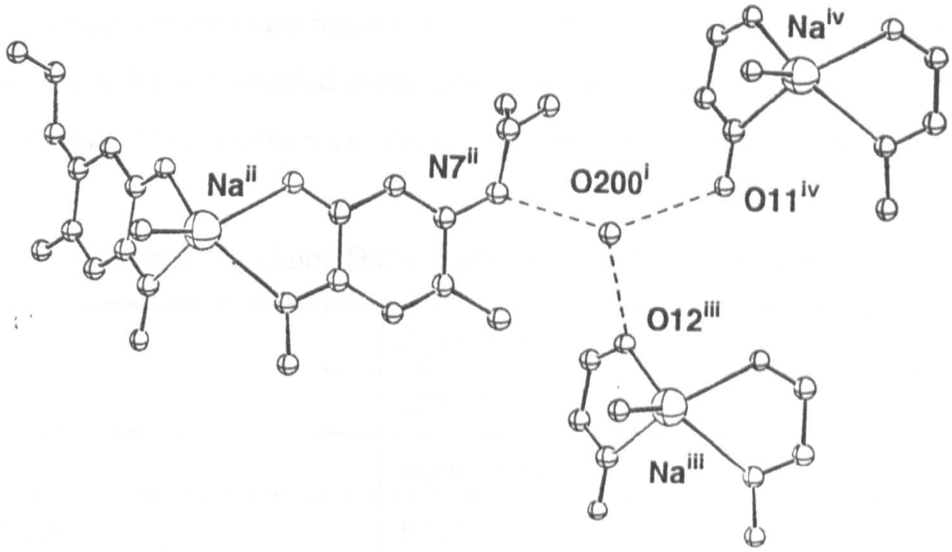
O100^{i}-H(O100B)^{i} = 1.137(2) Å
H(O100B)^{i}...O11^{ii} = 1.521(3) Å
O100^{i}-H(O100B)^{i}....O11^{ii} = 155.9(2)°
O100^{i}....O11^{ii} = 2.600(4) Å

O1^{ii}-H(O1)^{ii} = 1.174(2) Å
H(O1)^{ii}...O100^{i} = 1.500(2) Å
O1^{ii}-H(O1)^{ii}..O100^{i} = 165.5(2)°
O1^{ii}...O100^{i} = 2.653(3) Å

O100^{i}-H(O100A)^{i} = 1.107(2) Å
H(O100A)^{i}...O2^{iii} = 1.673(2) Å
O100^{i}-H(O100A)^{i}....O2^{iii} = 176.2(1)°
O100^{i}....O2^{iii} = 2.779(3) Å
(Symmetry codes (i) = x, y, z,; (ii) = 2-x, -y, 2-z; (iii) = 1-x, -y, 2-z)

The water of crystallisation present in the lattice (0200) is also involved in hydrogen bonding with three complex moieties as shown in Fig. 3.7. The water molecule (0200) forms hydrogen bonds with the oximic oxygen atom of one complex molecule, the carbonyl oxygen atom of another complex molecule and the amino nitrogen atom of the third complex molecule. Interestingly, such extensive hydrogen bonding is not a common feature in analogous complexes of lithium and potassium.

FIGURE 3.7 A view of the hydrogen bonding involving the water of crystallisation



N7^{ii}-H(N7)^{ii} = 0.909(3) Å
H(N7)^{ii}...O200^{i} = 1.966(3) Å
N7^{ii}-H(N7)^{ii}...O200^{i} = 168.8(2)°
N7^{ii}...O200^{i} = 2.863(4) Å

O200^{i}-H(O200A)^{i} = 1.21(3) Å
H(O200A)^{i}...O12^{iii} = 1.705(3) Å
O200^{i}-H(O200A)^{i}...O12^{iii} = 169.8(2)°
O200^{i}...O12^{iii} = 2.716(4) Å

O200^{i}-H(O200B)^{i} = 0.845(3) Å
H(O200B)^{i}...O11^{iv} = 2.069(3) Å
O200^{i}-H(O200B)^{i}...O11^{iv} = 162.8(3)°
O200^{i}...O11^{iv} = 2.888(4) Å

(Symmetry codes: (i) = x, y, z; (ii) = 1-x, -½+y, 3/2-z; (iii) = 1-x, ½+y, 3/2-z; (iv) = 2-x, ½+y, 3/2-z)

3.4 SINGLE CRYSTAL X-RAY STRUCTURAL DETERMINATION OF [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)]

3.4.1 Data Collection and Processing

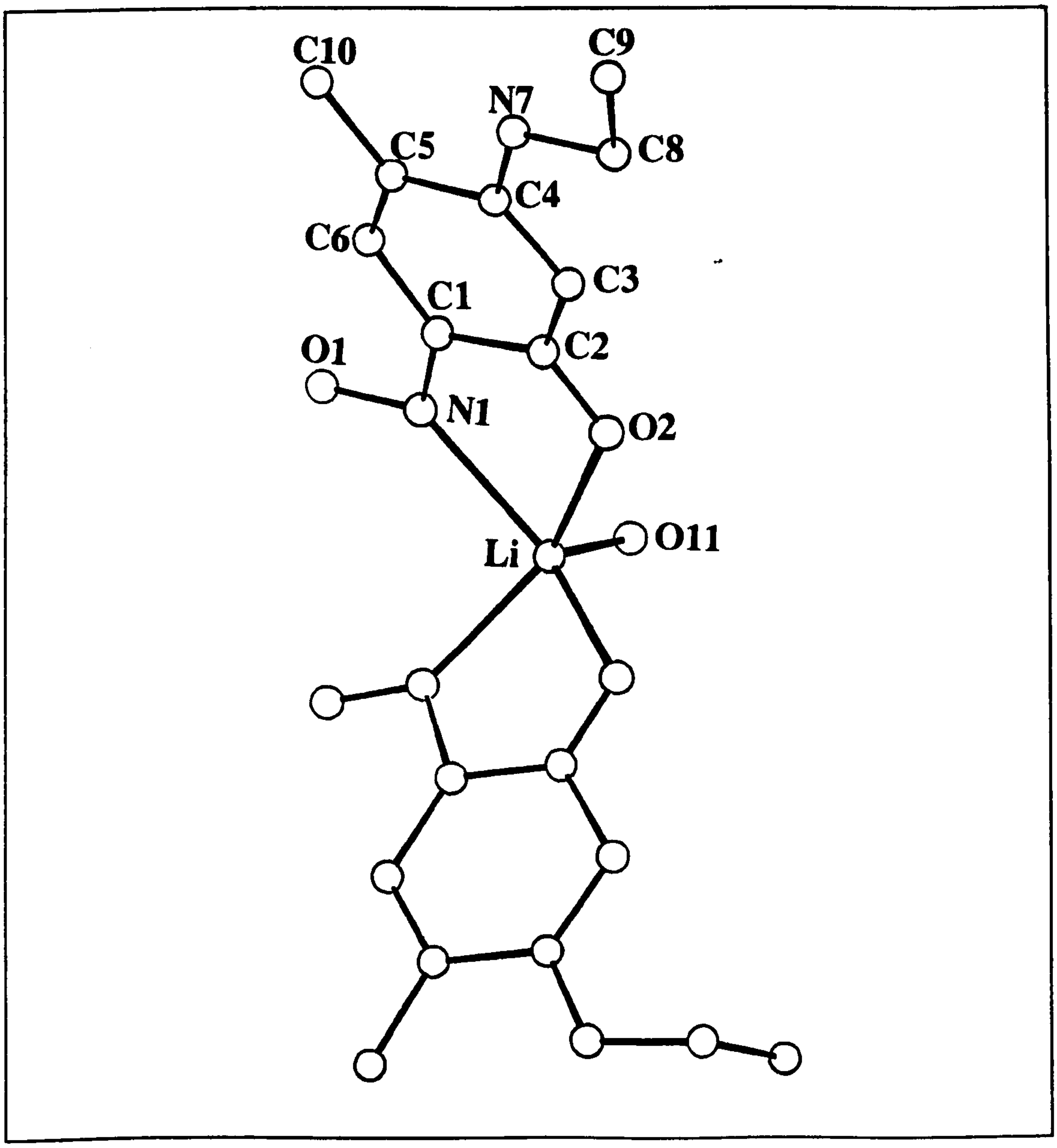
Unit cell parameters and intensity data were obtained on a Phillips PW1100 diffractometer at room temperature using a graphite-monochromated Mo-Kα radiation (λ = 0.71069Å). The method of data collection and processing were similar to those described previously [scan type ω-2θ, 2θ_{max} 50°].[4] The intensities were corrected for Lorentz-polarisation effects but not for absorption. The structure was solved by means of direct methods[5] and Fourier difference syntheses[6] [1044 unique refections with $I > 3.0\sigma(I)$ were used in refinement]. A Fourier-difference synthesis in which the structure factors were calculated with only those refections with $(\sin\theta)/\lambda < 0.3$ e Å^{-3} revealed the positions of the hydrogen atoms of the (5-Et-4-MeqoH) ligand. These atoms were included in structure-factor calculations with

TABLE 3.2 Information about Data Collection and Structure Refinement

Formula	$C_{18}H_{27}LiN_4O_6$
Mr	402.37
System	monoclinic
Space group	$P2_1/C$
a	8.107(2) Å
b	11.835(2) Å
c	22.330(3) Å
α	90°
β	90.602°
γ	90°
V	2060.91 Å^3
Z	4
D_{calc}	1.33 g cm^{-3}
Radiation	Mo-Kα (λ = 0.71069 Å) graphite-monochromated
μ	0.09 mm^{-1}
T	298 K
Crystal size	0.18×0.20×0.24 mm
Scan type	ω-2θ
Unique reflections	1044
Observed reflections [$I > 3.0\sigma(I)$]	995
Refined parameters	117

fixed thermal parameters of 0.08 Å^2, but were not refined. Final cycles of full-matrix refinement converged at R and R$'$ values of 0.1082 and 0.1099 respectively, with weights of w = $1/\sigma^2$(Fo) assigned to individual reflections [final Fourier-difference map showed a maximum height of 0.18 e Å^{-3}]. The details of the crystal parameters, data collection parameters and structure refinement are summarised in Table 3.2.

3.8 A view of [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)] with atomic numbering scheme



3.4.2 *Result and Discussion*

The structure of [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)] with its relevant atomic numbering is shown in Figure 3.8. Like its sodium analogue, the metal is in a penta coordinated state being bonded to two ligand molecules through the nitrogen atom of the oxime group and oxygen atom of the carbonyl group. The fifth position is occupied by a water molecule

3.5 SINGLE CRYSTAL X-RAY STRUCTURAL DETERMINATION OF [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O]

3.5.1 *Data Collection and Processing*

Unit cell parameters and intensity data were obtained on a Phillips PW1100 diffractometer at room temperature using a graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The method of data collection and processing were similar to those described previously [scan type ω-2θ, $2\theta_{max}$ 50°].[4] The intensities were corrected for Lorentz-polarisation effects but not for absorption. The structure was solved by means of direct methods[5] and Fourier-difference syntheses[6] [1128 unique reflections with $I \geq 3\sigma(I)$ were used in refinement]. A Fourier-difference synthesis in which the structure factors were calculated with only those refections with $(\sin\theta)/\lambda < 0.3$ e Å^{-3} revealed the positions of the hydrogen atoms of the (5-Et -4-MeqoH) ligand. These atoms were included in structure-factor calculations with fixed thermal parameters of 0.08 Å^2, but were not refined. During the final stages of refinement. all the non-hydrogen atoms were assigned anisotropic thermal parameters [the atoms, Li, Ow1 and Ow2, located on sites of symmetry were refined anisotropically using appropriate symmetry constraints[7]]. Final cycles of full-matrix refinement converged at R and R$'$ values of 0.0604 and 0.0612 respectively, with weights of $w = 1/\sigma^2(Fo)$ assigned to individual reflections [final Fourier-difference map showed a maximum height of 0.18 e Å-3]. The details of the crystal parameters, data collection parameters and structure refinement are summarised in Table 3.3.

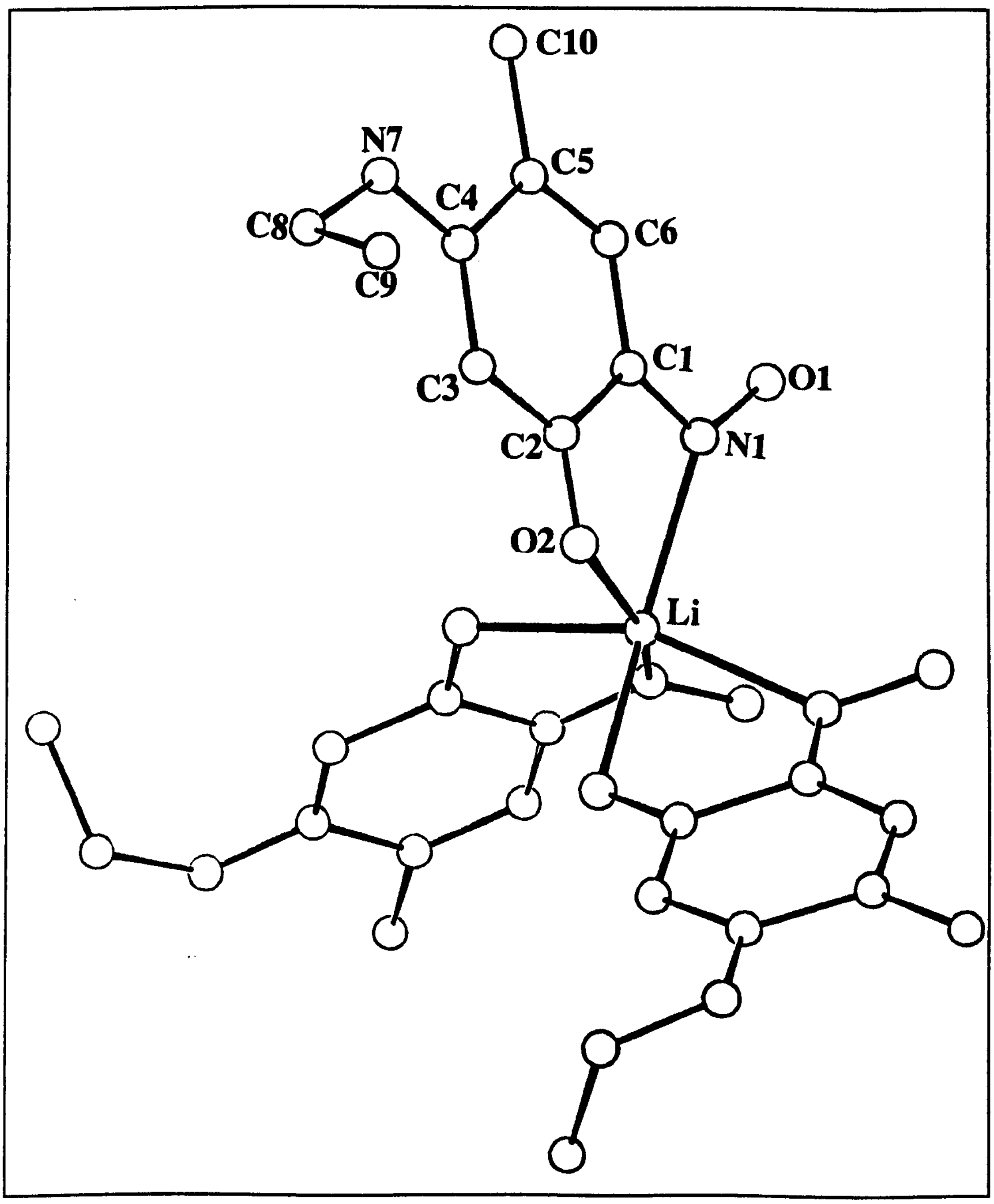
TABLE 3.3 Information about Data Collection and Structure Refinement

Formula	$C_{27}H_{31}LiN_6O_6.1\frac{1}{2}H_2O$
Mr	569.54
System	trigonal
Space group	$R\bar{3}$ (n. 148)
a	17.532(3) Å
b	17.532(3) Å
c	16.078(3) Å
α	90°
β	90°
γ	120°
V	4279.82 $Å^3$
Z	6
D_{calc}	1.326 g cm^{-3}
Radiation	Mo-Kα (λ = 0.71069 Å) graphite-monochromated
μ	0.09 mm^{-1}
T	298 K
Crystal size	0.18×0.20×0.24 mm
Scan type	ω-2θ
Unique reflections	4028
Observed reflections [$I > 3.0\sigma(I)$]	1377
Refined parameters	162

3.5.2 Result and Discussion

The molecular structure of the hexa-coordinated lithium complex [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O] is displayed in Fig. 3.9 with the atomic numbering. In this complex, both the deprotonated 5-Et-4-Meqo$^-$ and the protonated 5-Et-4-MeqoH ligands are quinone monooximic in character and are chelated to the lithium atom via the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group.

3.9 A view of [Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$] with atomic numbering scheme



The lithium atom is located on a site of three-fold symmetry in the space group R$\bar{3}$, with the coordinates 0, 0, z. Therefore, in the asymmetric unit the atom positions of only one ligand is identified; the other two ligands defining the overall coordination geometry are generated by symmetry.The oxygen atoms of the two water molecules are found to be distributed on the sites of symmetry, 3 and 3- respectively.

3.6 A COMPARATIVE STUDY OF THE STRUCTURES OF THE METAL COMPLEXES AND THE FREE LIGAND

The synthesis and structural studies of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime, its hydrochloride salt and potassium complex have been previously reported.[8] X-ray studies have showed that 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime has a cis configuration with the quinonoid carbonyl and the oximic OH groups being *syn* with respect to each other (Fig. 3.10).The molecule exhibits an intramolecular hydrogen-bonding between the quinonoid carbonyl and the oximic hydrogen atoms. The bond lengths are given in Table 3.4.

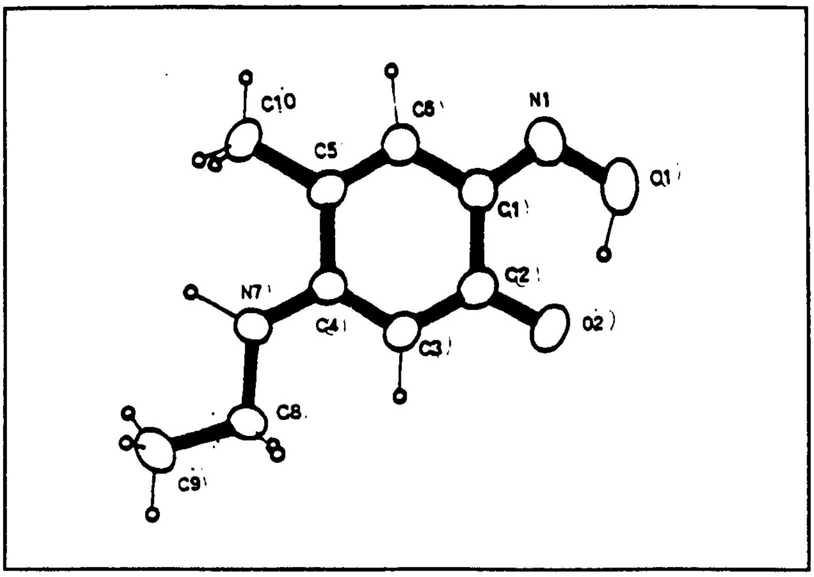


FIG. 3.10

In contrast to 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime, the oximic OH group of the hydrochloride salt is found to be *anti* (trans) to the quinonoid carbonyl group. The molecular packing arrangement of the crystal (Fig. 3.11) show extensive bonding in which the three acidic protons of each molecule are hydrogen-bonded. Two of the three acidic protons bond to two different chloride anions and the third with a water molecule. The bond lengths are given in Table 3.4.

The lithium, sodium and potassium complexes of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime of type M(qo)(qoH)(S) show a common bonding pattern. The five-membered chelate ring formed by the coordination of the ligand to the metal ion is similar to situation found in transition metal complexes[9,10] and the lithium complex of 1,2-naphthaquinone 2-oxime.[11] This is, however, in contrast to the potassium complex of 4-chloro-1,2-benzoquinone 2-oxime[12] in which the ligand behaves in a bridging mode.

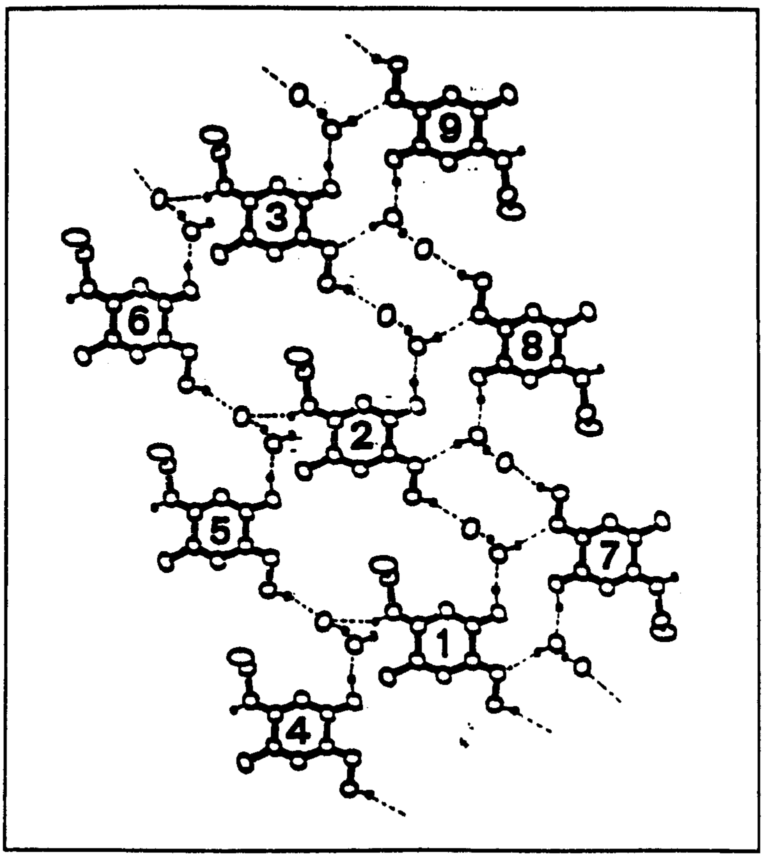


FIG. 3.11

Comparisons of the bond length of the carbonyl group (C2-O2) in 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime hydrochloride monohydrate to those reported for compounds of confirmed quinone monooxime character[13-17] and to the free ligand show that C2-O2 [1.326(3)] in 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime hydrochloride monohydrate is longer than the average CO bond lengths of this type. This increased bond length is consistent with more single bond character and

TABLE 3.4 Selected bond lengths of the complexes and the free ligand

Compound	***Bond distances (Å)***							
	C2-O2	***C2-C3***	***C3-C4***	***C4-N7***	***C1-N1***	***N1-O1***	***O2-M***	***N1-M***
5-Et-4-MeqoH	1.281(3)	1.381(3)	1.394(3)	1.337(3)	1.304(3)	1.367(3)	-	-
5-Et-4-MeqoH.HCl.	1.326(3)	1.356(4)	1.425(4)	1.310(4)	1.302(4)	1.363(4)	-	-
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.287(15) 1.301(15)	1.414(16) 1.472(18)	1.407(16) 1.420(18)	1.363(15) 1.366(16)	1.319(14) 1.439(17)	1.411(12) 1.272(14)	2.075(21) 1.990(21)	2.402(23) 2.218(23)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$. 1½H_2O	1.262(7)	1.401(7)	1.373(8)	1.333(6)	1.305(6)	1.353(5)	2.091(8)	2.218(7)
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.263(4) 1.275(4)	1.406(5) 1.420(5)	1.384(5) 1.387(5)	1.326(5) 1.344(5)	1.299(4) 1.345(5)	1.383(4) 1.299(4)	2.346(3) 2.275(3)	2.520(3) 2.544(3)
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.256(8) 1.255(8)	1.405(9) 1.420(8)	1.357(9) 1.382(9)	1.351(8) 1.357(8)	1.308(8) 1.340(8)	1.381(8) 1.342(8)	2.848(5) 3.082(5)	2.901(6) 3.022(6)
Li(1-nqo)(1-nqoH)(EtOH)	1.237(16) 1.256(16)	1.470(18) 1.456(19)	1.335(20) 1.311(21)	-	1.332(16) 1.277(17)	1.305(13) 1.340(15)	2.046(22) 2.033(22)	2.198(23) 2.150(22)
K(4-Clqo).½H_2O	-	-	-	-	1.348(5)	1.283(4)	2.728(4)	-

confirms the CO group as bearing one of the acidic hydrogen atoms. Also the C2-O2 bond lengths in the metal complexes are shorter than in the free ligand and its hydrochloride salt probably due to its involvement in complexation to the metal atom.

Like the lithium complex of 1,2-naphthoquinone 1-oxime, the oximic NO groups in all the complexes are mutually *cis* to each other. In the structures of the bis-chelates of lithium and sodium, a possible position for the oximic hydrogen atom has been experimentally determined.

In the bis-chelates, the two quinone monooximato ligands in the metal complexes have different N1-O1 and C1-N1 bond distances (as evident from Table 3.4). This difference could arise from the fact that in the bis-chelates one of the NO groups remain protonated. The protonated oximato ligand may have longer N-O and shorter C-N bond length than the unprotonated ligand.

In all these compounds, the quinone monooximic character of the ligands is indicated by the presence of two short C-C bonds [C(3)-C(4) and C(5)-C(6)] and four long C-C bonds [C(1)-C(2); C(2)-C(3); C(4)-C(5); C(6)-C(1)] (Table 3.5 gives the bond distances in the aromatic ring). A comparative study between the complexes and the free ligand shows that the mean of the two short C-C bonds within the aromatic ring is shorter than the corresponding mean in the free ligand. In contrast the mean of the four long C-C bond lengths is longer than than the mean of the free ligand.

In the complexes and the free ligand the C(2)-C(3) bond length (as given in Table 3.4) is considerably shorter than expected for a single C-C bond thereby suggesting the presence of 5-centred conjugation involving the atoms N(7), C(4), C(3), C(2) and the oxygen atom O(2) of the carbonyl group. This is further supported by the presence of a relatively long C(2)-O(2) bond length which is longer than observed in related Li(1-nqo)(1-nqoH)(EtOH)[11] and transition metal containing structures.[9,10] Also the bond length between N(7) of the ethylamino substituent and C(4) of the aromatic ring (Table 3.4) is considerably shorter than expected for a typical $C_{sp}{}^{2}$-

NHR bonding situation and thus shows that the latter has greater double bond character.

Significantly, the value of the angle [C(4)-N(7)-C(8)] is within the range of 122.0-127.5° therby indicating the sp^2 hybridisation of the nitrogen atom of the ethylamino substituent. The value of the angle in all the compounds are greater than 120° (typical value for sp^2 hybridised nitrogen atom) probably due to the repulsion by the lone pair of electrons on the nitrogen atom. These observations can be rationalised in terms of a complex equilibrium involving imino oxime form (Fig. 3.12). Hence these types of compounds can be described as an intermediate between the quinone oxime and imino oxime form.

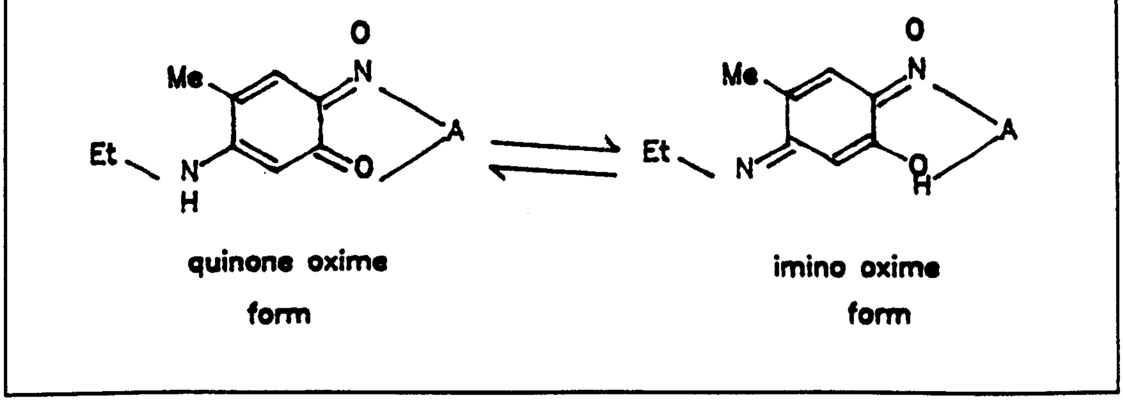


FIG. 3.12

The complexation of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime with lithium, sodium and potassium ions has a considerable effect on the structure of the ligand. In the free ligand and its hydrochloride salt, the two double bonds in the aromatic ring are 1,4 with respect to each other whereas in the complexes the double bonds are 1,3 with respect to each other thereby indicating that the quinone oxime character of the ligand can be more pronounced in the complexes than in the uncomplexed state. On the other hand, imino oxime form of the ligand can be more predominant in its free state.

TABLE 3.5 C-C Bond Lengths of the Aromatic Ring in the Metal Complexes and the free ligand

Compound	*Bond distances (Å)*					
	C1-C2	*C2-C3*	*C3-C4*	*C4-C5*	*C5-C6*	*C6-C1*
5-Et-4-MeqoH	1.476(3)	1.381(3)	1.394(3)	1.467(3)	1.335(3)	1.444(3)
5-Et-4-MeqoH.HCl.	1.458(5)	1.356(4)	1.425(4)	1.461(5)	1.339(4)	1.450(3)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.436(18) 1.448(19)	1.505(16) 1.447(17)	1.414(16) 1.412(18)	1.407(16) 1.420(18)	1.336(17) 1.387(19)	1.497(16) 1.481(17)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$. 1½H_2O	1.498(7)	1.401(7)	1.373(8)	1.495(7)	1.325(7)	1.433(8)
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.491(5) 1.485(5)	1.406(5) 1.420(5)	1.384(5) 1.387(5)	1.478(5) 1.460(5)	1.342(5) 1.349(6)	1.450(5) 1.435(5)
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)	1.480(1) 1.470(1)	1.405(9) 1.420(8)	1.357(9) 1.382(9)	1.480(1) 1.455(9)	1.341(9) 1.348(9)	1.438(9) 1.430(1)

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CHAPTER IV

STRUCTURAL INVESTIGATIONS OF Mn^{II}, Ni^{II}, Cu^{II} AND Zn^{II} COMPLEXES OF PYRAZOLE-4,5-DIONE-4-OXIMES

CONTENTS

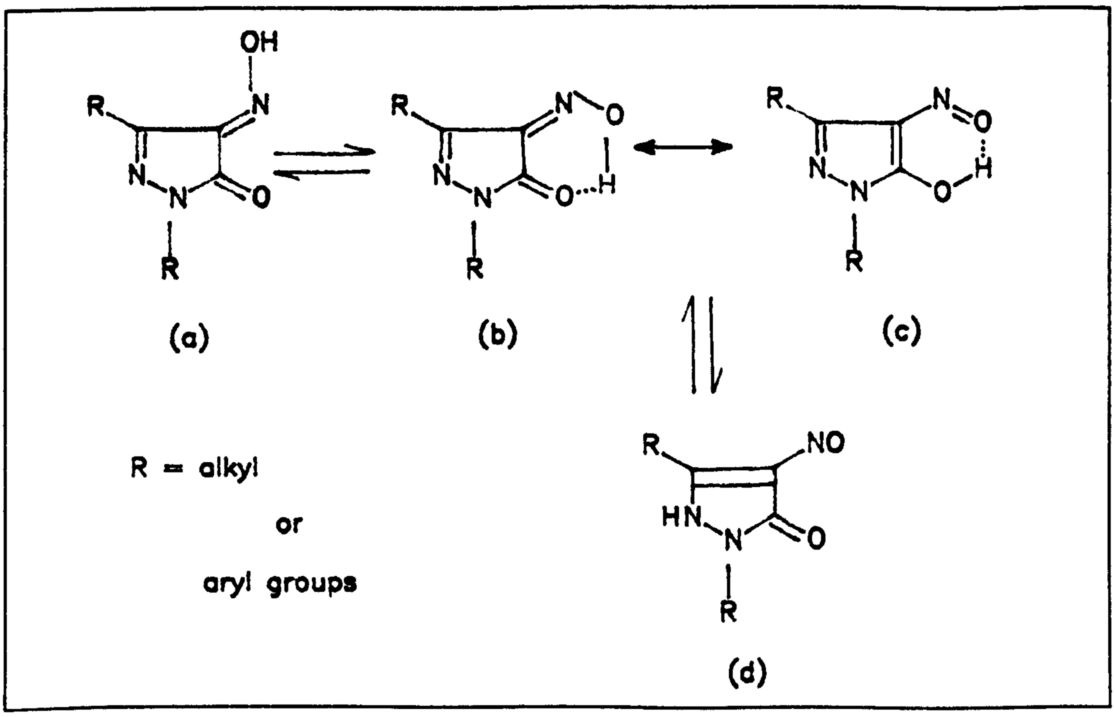
4.1 INTRODUCTION

Several studies of pyrazole-4,5-dione-4-oximes and their metal(II) complexes such as ML_2, $ML_2(LB)_2$ and $M(LH)_2X_2$ [LH = pyrazole-4,5-dione-4-oximes (see Table 4.1); M = Mg,[1] Cd,[1] Mn,[2,3] Fe,[3,4] Co,[5] Ni,[2,5] Cu,[5,6] Zn[1,3,5] VO,[3] UO_2,[3]; LB = NH_3, C_5H_5N; X = Cl, Br, ClO_4 and NO_3] have previously been reported. The reports are concerned mainly with the synthesis of the metal complexes, the pyridine and ammonia adducts of ML_2 and their characterisation by elemental and thermogravimetric analysis. The structural investigations of these complexes have received limited attention. On the basis of magnetic and Mössbauer studies, the iron complexes of the type FeL_2 are believed to be associated in the solid state.[4]

Similarly, association has been suggested for MnL_2 and VOL_2 complexes on the basis of magnetic studies.[3]

In this chapter a detailed account on the structure of some pyrazole-4,5-dione-4-oximato complexes as determined from their chemical, spectroscopic, magnetochemical and X-ray crystallographic studies are presented. Two ligands namely 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime and 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime have been employed in these studies.

As indicated in Chapter I, pyrazole-4,5-dione-4-oximes have structural similarities with 1,2-benzoquinone monooximes. Like 1,2-benzoquinone mono-oximes, pyrazole-4,5-dione 4-oximes can exhibit a complex tautomeric behaviour involving oximic (4.1a and 4.1b) and nitroso structures[7] (4.1c and 4.1d) (Scheme 4.1). The oximic forms can exist in either the *syn* (4.1b) or the *anti* (4.1a) configuration. The additional tautomeric nitroso form (4.1d) can be expected to arise by the rearrangement of either the oximic or the hydroxy proton.



SCHEME 4.1

In the earlier studies of 1,2-benzoquinone monooximes, infrared spectroscopy proved useful in distinguishing between *syn* and *anti* configurations. Generally, the compounds having an *anti* configuration are expected to exhibit νCO absorptions at higher frequencies to those adopting the *syn* configuration because of the intramolecular hydrogen-bonding present in the latter. In the case of the monooximes of 1,2-naphthaquinone the 1-isomer, whose *syn* structure has been established by X-ray crystallography, exhibits a νCO absorption at 1618 cm^{-1}[8] whereas the 2-isomer absorbs at a much higher frequency of 1668 cm^{-1}. This marked shift to lower frequency in the former isomer is due to intramolecular hydrogen bonding. On the basis of the above argument an *anti* structure has been suggested for the latter isomer.

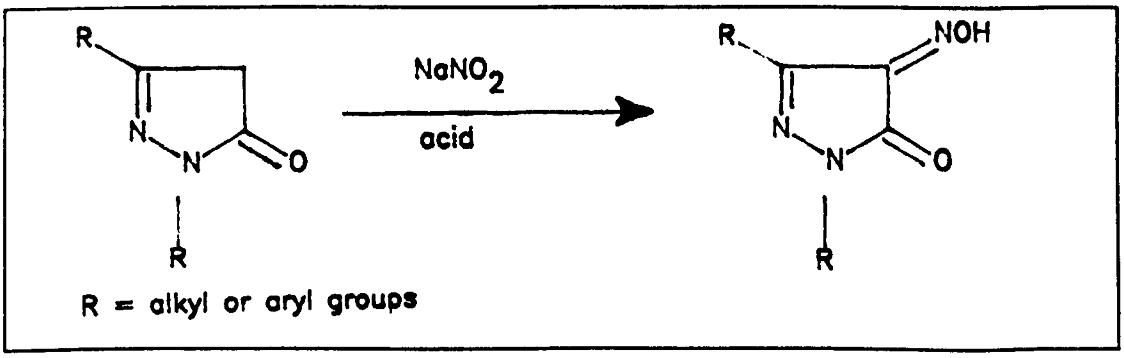
The structures of 5-alkoxy-1,2-benzoquinone 2-oximes have been assigned in a similar fashion. However in the case of 5-acylamino- and 5-alkylamino-1,2-benzoquinone 2-oximes the pattern is not so well-defined, a likely reason being that in such compounds other types of conjugation is possible (such tautomerism is discussed in Chapter III).

The pyrazole-4,5-dione-4-oximes, listed in Table 4.1, exhibit strong bands at 1690-1705 cm^{-1} assignable to νCO. By analogy to the 1,2-quinone monooxime system it can be suggested that pyrazole-4,5-dione-4-oximes exist in the *anti* configuration because of their νCO absorptions at high wavenumbers. Although there are no data on the solid state structures of pyrazole-4,5-dione-4-oximes, the *anti* structure has been established for the pyrazole-oxime ester, 4-[(N-benzyloxycarbonylvalyl)-oximino]-3-methyl-1-phenyl-2-pyrazolin-2-one[9] (Fig. 4.2).

TABLE 4.1 νCO Absorptions of Selected Pyrazole-4,5-dione-4-oximes

Pyrazole-4,5-dione-4-oxime	*νC=O (cm^{-1})*
1-PpoH	1705
3-PpoH	1690
MpoH	1691
poH	1704

Pyrazole-4,5-dione-4-oximes are usually prepared from their corresponding pyrazol-5-ones by the standard nitrosation method[10,11] involving sodium nitrite and acetic acid (Reaction 4.1).



REACTION 4.1

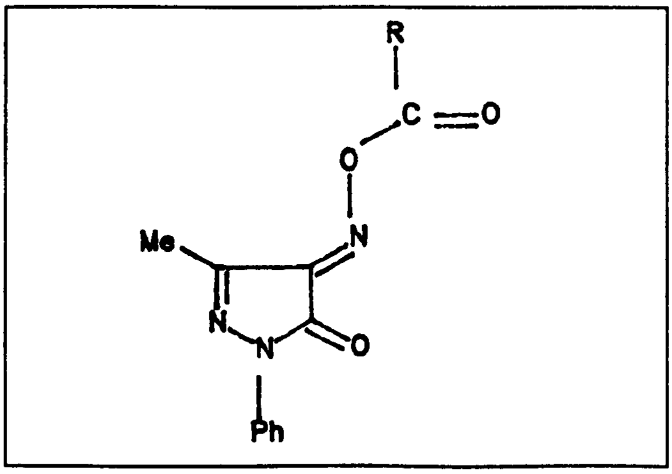
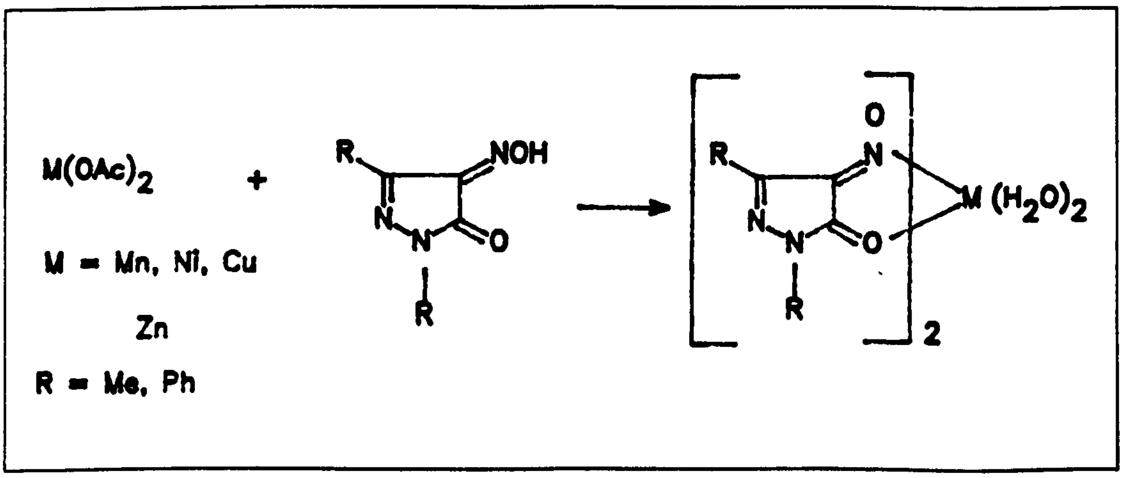


FIG. 4.2

4.2 SYNTHESIS AND CHARACTERISATION OF Mn^{II}, Ni^{II}, Cu^{II} AND Zn^{II} COMPLEXES OF PYRAZOLE-4,5-DIONE-4-OXIMES

Previously, transition and main group metal complexes of pyrazole-4,5-dione-4-oximes were prepared by the direct reaction of metal sulphates and nitrates with the oximes. In this study, the metal acetates are used (Reaction 4.2). The compounds are isolated as dihydrated complexes.



REACTION 4.2

The dihydrates $ML_2(H_2O)_2$ [M = Mn, Ni, Cu and Zn] react with pyridine to give adducts of type $ML_2(py)_2$. Thermal gravimetric analysis (Table 4.2) indicates that most of the adducts of manganese, nickel and copper complexes show quantitative loss of two moles of pyridine per mole of the complex at 120-190°C. This is followed by the decomposition of the parent complex at temperatures above 210°C. The behaviour of the zinc adducts, however, are different. The complex, $Zn(Mpo)_2(py)_2$, lose one mole of pyridine per mole of the complex at 120-130°C followed by the decomposition of $Zn(Mpo)_2(py)$ at *ca.* 300°C whereas $Zn(1\text{-}Ppo)_2(py)_2$ completely decompose at *ca.* 170°C. A behaviour similar to the latter complex is shown by $Ni(1\text{-}Ppo)_2(py)_2$. All the pyridine adducts afford the complex, ML_2, on macroscale pyrolysis at 145-150°C / 0.1 mm of Hg.

The ammonia, pyridine and aquo adducts of the complexes of type ML_2 have been reported earlier (*cf.* Table 1.3, Chapter I). Hovorka and Sücha reported that on pyrolysis, ammonia was lost at a higher temperature and less readily than pyridine or water to yield the anhydrous complexes. Consequently, it was concluded that ammonia was co-ordinated to the central metal atom whereas water and pyridine were present as solvents of crystallisation. However, this conclusion is contradicted by the single crystal X-ray analysis, carried out in the course of this study, of the diaquo and dipyridine adducts where it has been found that both the Lewis bases are coordinated to the metal atom.

TABLE 4.2 Thermal Gravimetric Analytical Data for $M(po)_2(py)_2$ [M = Mn, Ni, Cu, Zn; poH = MpoH, 1-PpoH]

Compound	*Wt. of sample(mg)*	*T^a (°C)*	*Wt. loss (mg)*		*Decomposition of complex (°C)*
			Found	*Calc*	
$Mn(Mpo)_2(py)_2$	150.8	120-170	48.2	48.3^c	323
$Mn(1\text{-}Ppo)_2(py)_2$	130.5	120-180	33.0	33.4^c	327
$Ni(1\text{-}Ppo)_2(py)_2$	125.3	-	-	-	160
$Ni(Mpo)_2(py)_2$	135.7	120-170	42.9	43.1^c	210
$Cu(Mpo)_2(py)_2$	115.1	120-180	36.3	36.8^c	250
$Cu(1\text{-}Ppo)_2(py)_2$	103.9	120-190	26.3	26.3^c	230
$Zn(Mpo)_2(py)_2$	114.1	120-130	17.5	17.9^b	300
$Zn(1\text{-}Ppo)_2(py)_2$	162.9	-	-	-	170

[a] Temperature of loss of pyridine [b] Weight loss calculated for one mole of pyridine
[c] Weight loss calculated for two moles of pyridine

In order to gain information regarding the structures of the complexes ML_2, $ML_2(py)_2$ and $ML_2(H_2O)_2$ [M = Mn, Ni, Cu and Zn; LH = MpoH, 1-PpoH] prepared during this work, their IR and LSIM spectra, room temperature magnetic moments and behaviour towards triphenylphosphine were studied. However, the electronic spectra of the transition metal complexes and NMR spectra of the zinc complexes proved uninformative. As noted earlier, two of these complexes were also characterised by X-ray crystallography.

Elucidation of the mode of bonding of pyrazole-4,5-dione-4-oximes to the metal atom: The infrared spectra of the hydrated complexes (eg. Figure 4.1) showed strong broad bands between 3500 - 3400 cm^{-1} assignable to νOH of the water molecules. The broadness of the band indicates that the νOH group is involved in hydrogen bonding. The presence of prominent νC=O absorptions between 1616 - 1646 cm^{-1} in both the hydrated complex and the pyridine adducts (eg. Figures 4.1 and 4.2 respectively) indicate that the ligand exists essentially in the oxime form. The values of νCO in the metal complexes are much lower than those observed in the corresponding free ligands suggesting that the ring carbonyl group is involved in bonding (Table 4.3). These features are also confirmed by the crystallographic study of Zn(Mpo)$_2$(H$_2$O)$_2$ and Mn(1-Ppo)$_2$(py)$_2$

FIGURE 4.1 Infra-red Spectrum of Zn(Mpo)$_2$(H$_2$O)$_2$

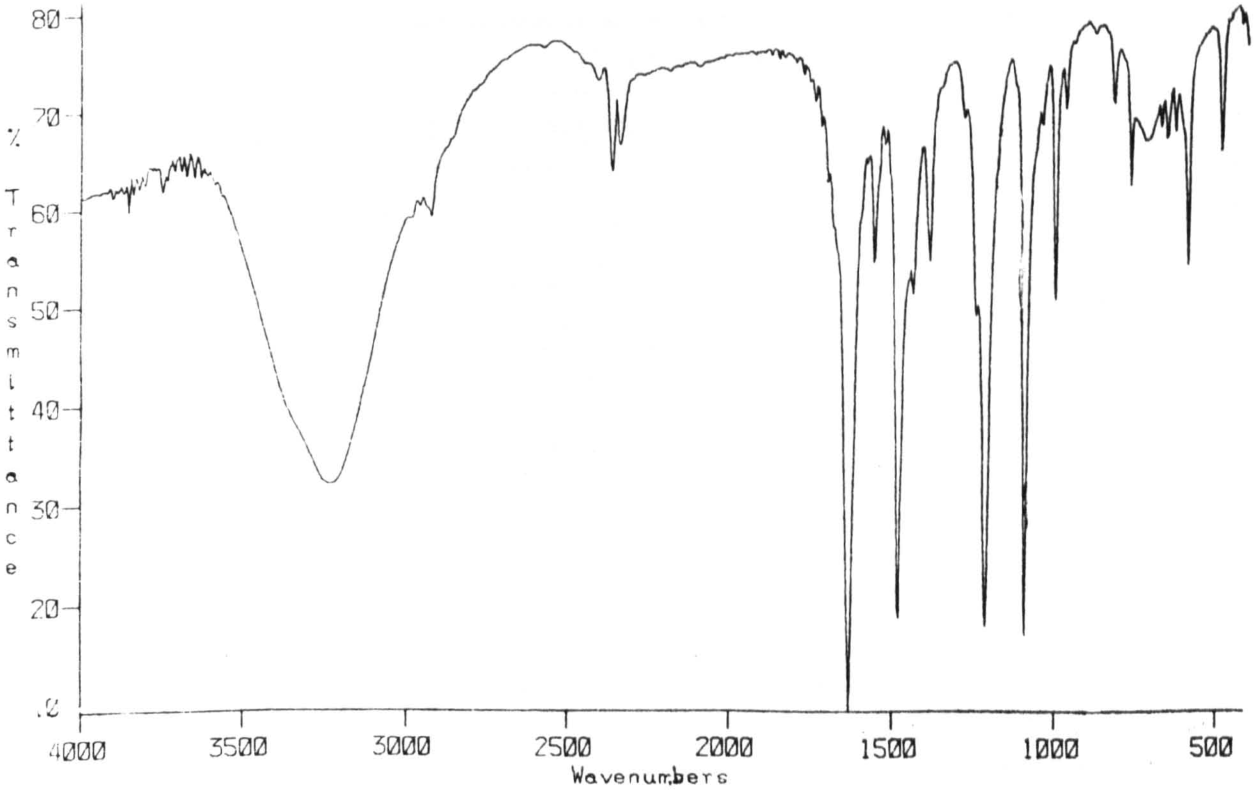


FIGURE 4.2 Infra-red Spectrum of $Cu(Ppo)_2(py)_2$

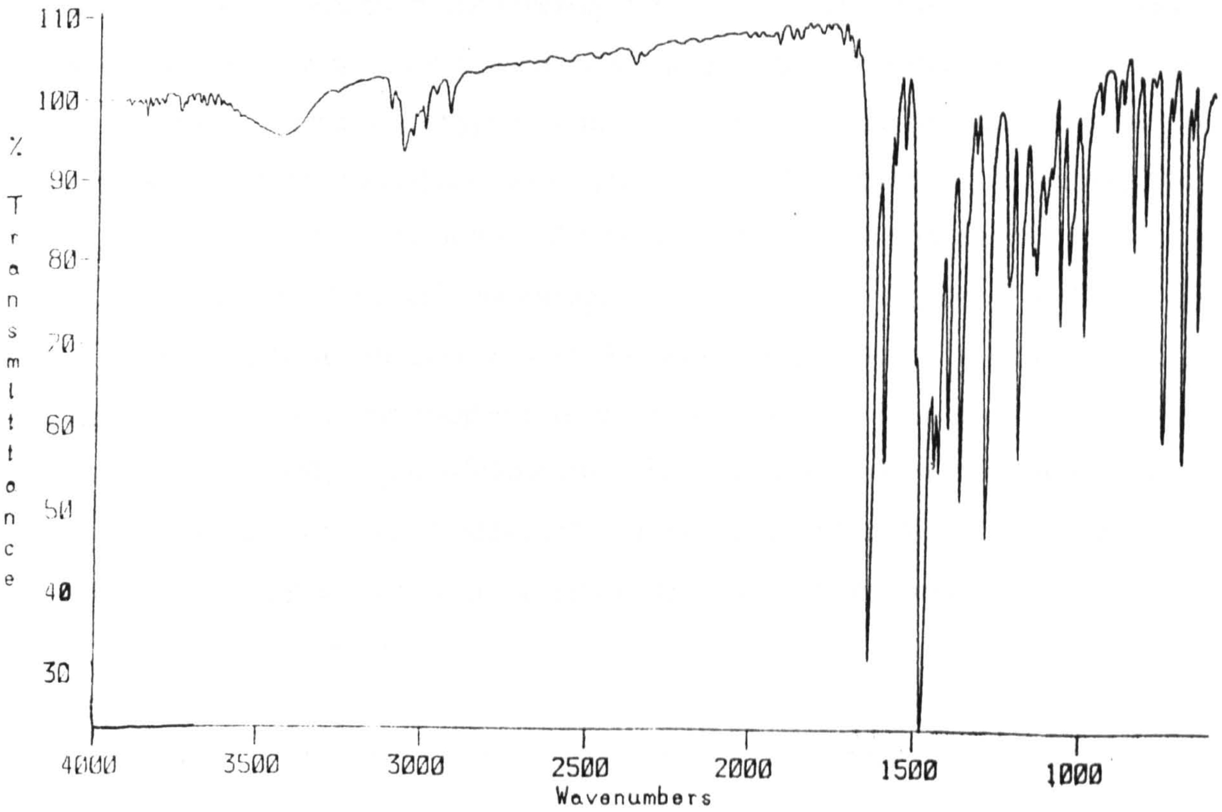


Table 4.3 νCO Absorptions in $ML_2(H_2O)_2$ and $ML_2(py)_2$

	$\nu C{=}O$ (cm^{-1}) for			*$\Delta\nu CO$ (cm^{-1}) in $ML_2(H_2O)_2/ML_2(py)_2$*
Compound	*LH*	*$ML_2(H_2O)_2$*	*$ML_2(py)_2$*	
MpoH	1691	-	-	-
$Mn(Mpo)_2(LB)_2$	-	1616	1631	75 / 60
$Ni(Mpo)_2(LB)_2$	-	1636	1633	55 / 58
$Cu(Mpo)_2(LB)_2$	-	1627	1646	64 / 45
$Zn(Mpo)_2(LB)_2$	-	1634	1633	57 / 58
1-PpoH	1705	-	-	-
$Mn(1\text{-}Ppo)_2(LB)_2$	-	1629	1635	76 / 70
$Ni(1\text{-}Ppo)_2(LB)_2$	-	1636	1637	69 / 68
$Cu(1\text{-}Ppo)_2(LB)_2$	-	1629	1640	76 / 65
$Zn(1\text{-}Ppo)_2(LB)_2$	-	1636	1638	69 / 67

All the νCO bands were strong and sharp LB = py or H_2O

Inorder to establish the mode of coordination of the NO group of pyrazole-4,5-dione-4-oximes to the metal atom, the investigations of the behaviour of selected complexes towards triphenylphosphine proved very useful. The NO group may bond to the metal through either the oxygen or nitrogen atom thereby forming a six or five membered chelate ring respectively (Figs. 4.3 and 4.4). Previous investigations have shown that in the majority of the 1,2-quinone monooximato complexes the ligand is bonded to the metal through the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group (Fig. 4.5). As evident from Fig. 4.5, the oximic oxygen atom is labile and this property is manifested by the facile reactions of such complexes towards triphenylphosphine. Their reactions with triphenylphosphine involves deoxygenation and leads to the formation of triphenylphosphine oxide along with other compounds depending upon the nature of the complexing metal (*cf.* Scheme 1.5, Chapter I).[12-14]

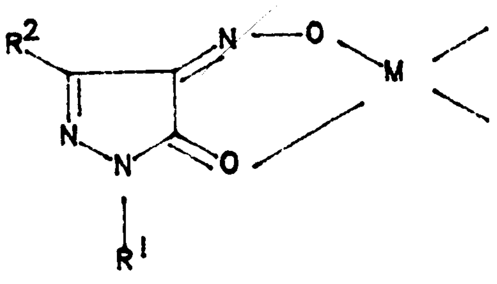


FIG. 4.3

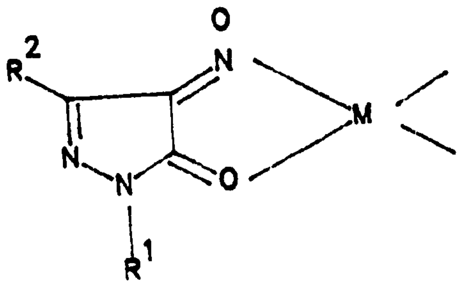


FIG. 4.4

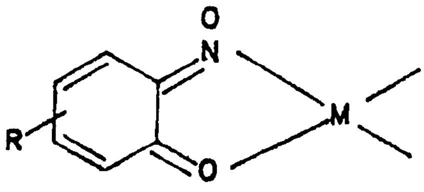


FIG. 4.5

In marked contrast, the pyrazole-4,5-dione-4-oximato complexes failed to react with triphenylphosphine. The lack of their reactions can be accounted for in terms of the unavailability of a labile oxygen atom which suggests that the oxygen atom of the

NO group is involved in bonding to the metal (Fig. 4.3). Significantly this has been confirmed by the X-ray crystal structure of $Zn(Mpo)_2(H_2O)_2$ and $Mn(1\text{-}Ppo)_2(py)_2$.

Structural Elucidation of the pyrazole-4,5-dione-4-oximato complexes: The magnetic moments of manganese(II), nickel(II) and copper(II) complexes of pyrazole-4,5-dione-4-oximes reported earlier are listed in Table 4.4. It has been generally observed that μ_{eff} for the hydrated complexes and their pyridine and ammonia adducts are higher than those of the corresponding anhydrous complexes. In the current study the room temperature magnetic susceptibilities of the complexes of the type $ML_2(H_2O)_2$, $ML_2(py)_2$ and ML_2 [M = Mn, Ni, Cu; LH= MpoH and 1-PpoH] have been measured and the calculated magnetic moments listed in Table 4.4 confirm the above observation.

The magnetic moments of the hydrated complexes and the pyridine adducts, obtained during this study and by other workers, are in good agreement with the spin only magnetic moments.[15] The magnetic moment values of all the manganese(II) complexes show that the metal is in a high spin state thereby indicating that the pyrazole-4,5-dione-4-oximes are weak O-O ligands. The hydrated and the pyridine adducts of all the complexes show that the compounds are magnetically dilute and hence monomeric in their solid state. By contrast, the observed room temperature magnetic moments of the anhydrous complexes are lower than those expected from their spin only formula. The lowering of the magnetic moments is more pronounced in the manganese(II) and nickel(II) complexes compared to the copper(II) complexes. The subnormal magnetic moments of the anhydrous complexes can be accounted for in terms of association and antiferromagnetic interaction between adjacent metal atoms as previously suggested for the related complexes, $Fe(po)_2$ and $Fe(1\text{-}Ppo)_2$[4] (Fig. 4.6). Similar lowering of magnetic moments on dehydration has also been observed in 1,2-benzoquinone monooximato complexes of manganese(II),[16] nickel(II)[17] and copper(II).[18] The association in pyrazole-4,5-dione-4-oximato complexes, like the complexes of 1,2-benzoquinone monooximes, could involve the interaction of the carbonyl oxygen atoms with the adjacent metal atoms. Convincing evidence of association is provided by the liquid secondary ion mass (LSIM) spectra of all the pyrazole-4,5-dione-4-oximato complexes prepared during this study.

The mass spectra of the manganese(II), nickel(II) and copper(II) complexes of pyrazole-4,5-dione-4-oximes of type ML_2 show dimetallic and trimetallic species such as $[M_2L_2]^+$, $[M_2L_3]^+$, $[M_3L_4]^+$ and $[M_3L_5]^+$ thereby indicating the presence of association in these complexes (Table 4.5 and Figures 4.3, 4.4). The presence of dimetallic and trimetallic ions has also been establised in the corresponding zinc complexes and, as noted in Chapter II, in alkali and alkaline earth metal complexes of 1,2-quinone monooximes.

TABLE 4.4 Room Temperature Magnetic Susceptibilities of Mn^{II}, Ni^{II} and Cu^{II} Complexes of Type $ML_2.nL'$ of Pyrazole-4,5-dione-4-oximes[a]

R^2	R^1	M^{II}	μ_{eff} (B.M.)			
			anh	$2H_2O$	2py	$2NH_3$
H	H	Ni	-	2.96[d]	2.97[d]	-
Me	H	Ni	-	3.01[d]	3.09[d]	-
Ph	H	Ni	-	2.77[d] ($1H_2O$)	3.12[d]	2.96[d]
H	Ph	Ni	2.44[d]	3.12[d]	2.97[d]	-
Me	$4-NO_2C_6H_4$	Ni	2.48[d]	-	3.01[d]	2.97[d]
Me	Ph	Ni	2.12[c]	3.12[b]	2.48[c]	-
Me	Me	Ni	2.39[c]	2.98[c]	2.83[c]	-
Me	Me	Cu	1.67[c]	2.06[c]	1.87[c]	-
Me	Ph	Cu	1.61[c]	1.70[c]	1.80[c]	-
Me	H	Mn	5.59[d]	5.81[d]	-	-
Ph	H	Mn	5.56[d]	5.80[d]	5.78[d]	-
Me	Ph	Mn	5.35[b]	-	5.72[c]	-
Me	Me	Mn	4.70[c]	-	5.91[c]	-
Ph	Ph	Mn	5.53[d]	_	_	_

[a] Substituents R^1, R^2 are present as in Fig. 4.3
[b] Confirmed by the present study
[c] Results obtained in the present study
[d] Data obtained from reference 19

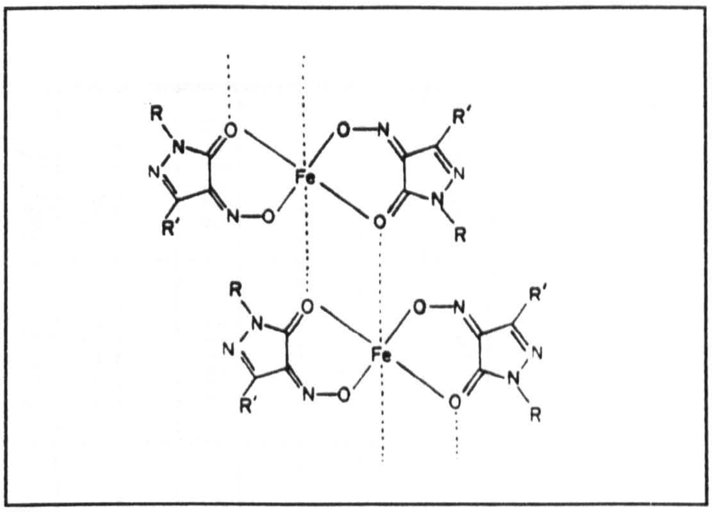


FIG. 4.6

FIGURE 4.3 The LSIM Spectrum of Ni(Mpo)$_2$(H$_2$O)$_2$

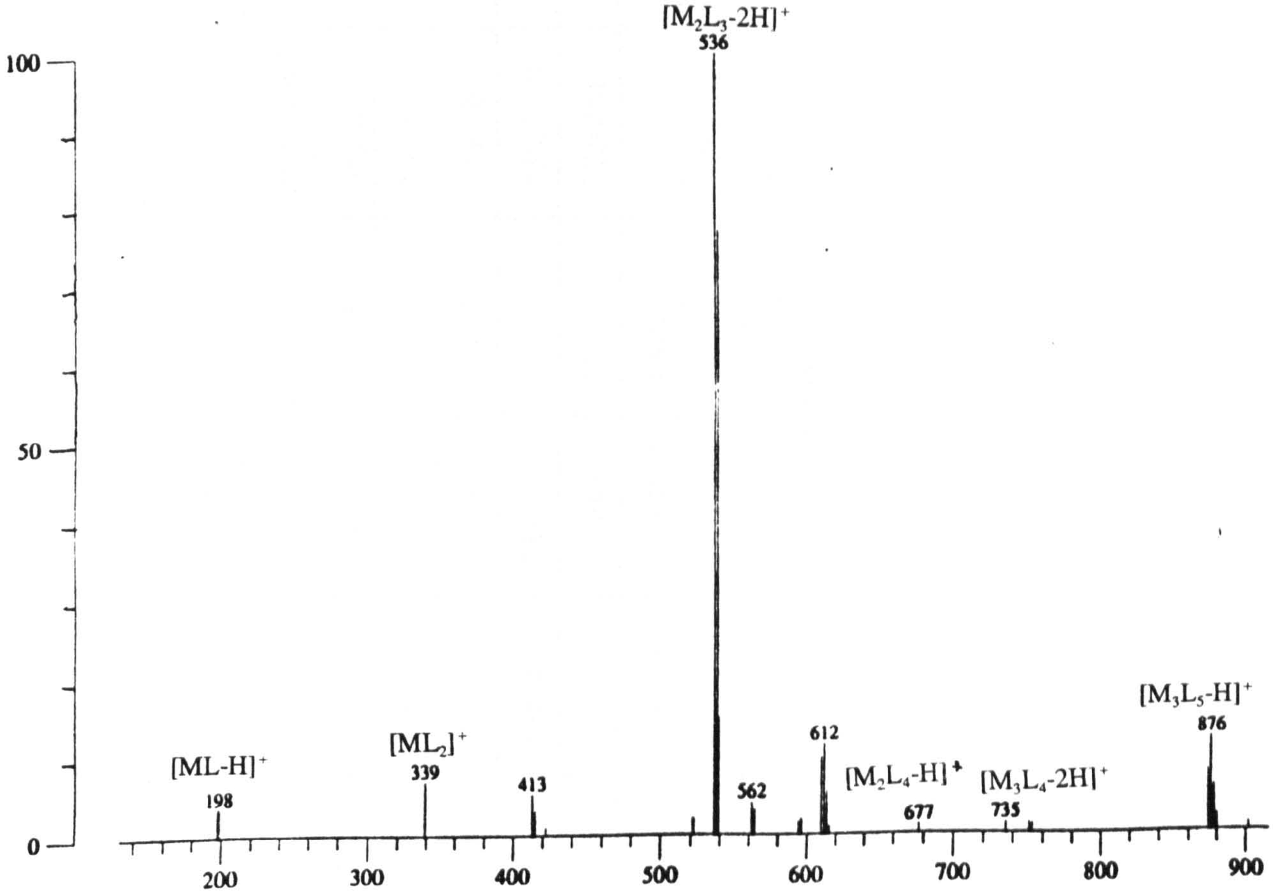


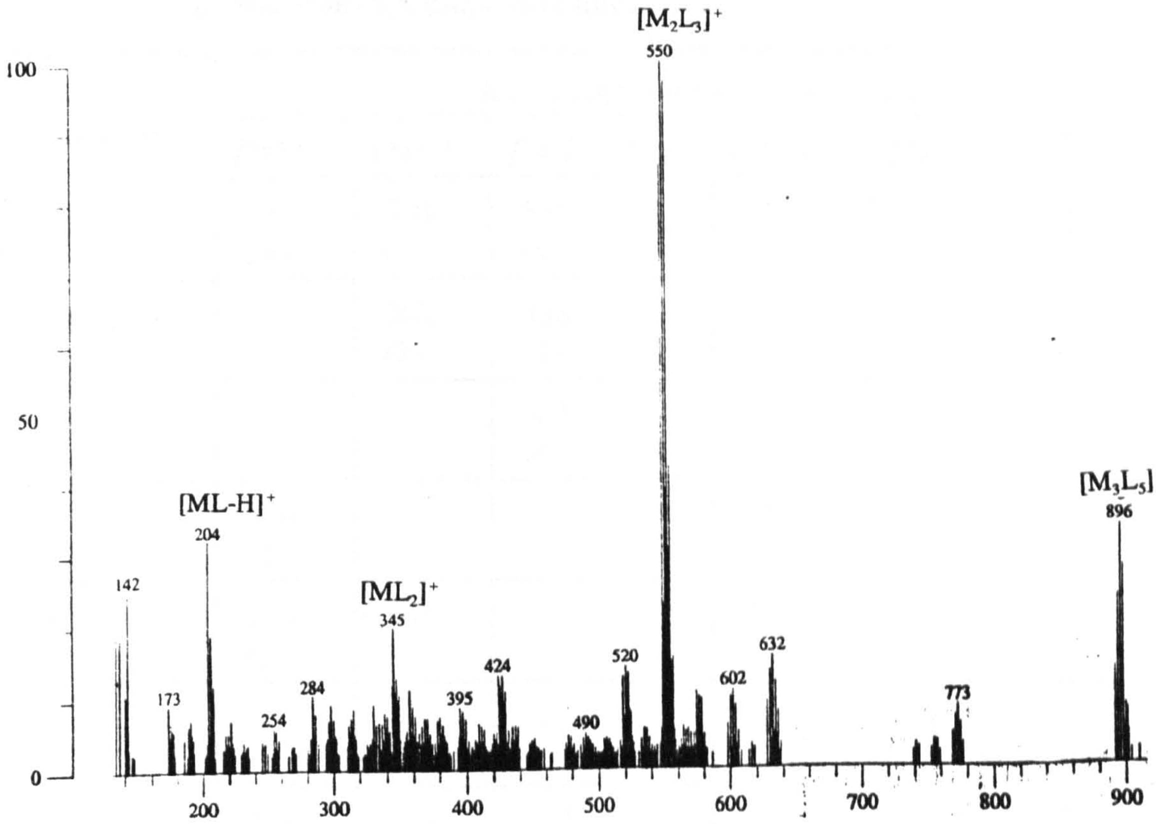
Table 4.5 m/z Values for Prominent Metal Containing Ions in the LSIM Spectra of Mn^{II}, Ni^{II}, Cu^{II} and Zn^{II} Complexes of Pyrazole-4,5-dione-4-oximes

Metal Complex	*Metal Containing Ions[a] (% Abundance)*							
	$[ML]^+$	*$[ML_2]^+$*	*$[M_2L_2]^+$*	*$[M_2L_3]^+$*	*$[M_3L_3]^+$*	*$[M_2L_4]^+$*	*$[M_3L_4]^+$*	*$[M_3L_5]^+$*
$Mn(Mpo)_2$	198(12)	334(5)	390(7)	530(8)	587(6)	-	726(3)	865(2)
$Mn(1\text{-}Ppo)_2$	256(13)	459(18)	514(17)	716(56)	-	-	-	-
$Ni(Mpo)_2$	198(4)	339(7)	-	536(100)	-	677(1)	735(1)	876 (12)
$Ni(1\text{-}Ppo)_2$	260(7)	463(6)	521(2)	722(28)	-	-	-	-
$Cu(Mpo)_2$	204(56)	344(100)	406(3)	-	-	689(3)	-	-
$Cu(1\text{-}Ppo)_2$	266(35)	467(16)	530(36)	732(12)	795(4)	-	-	-
$Zn(Mpo)_2$	204(32)	345(20)	410(4)	550(100)	616(3)	-	755(4)	896(34)

[a] These ions usually appear as cluster of ions composed of species such as ML_2, ML_2+H, ML_2-H

The isotopes of Mn, Ni, Cu and Zn used in the calculations are 55, 59, 63 and 65 respectively.

FIGURE 4.4 The LSIM Spectrum of $Zn(Mpo)_2(H_2O)_2$



The mass spectra also exhibit ions involving alkali metals and association of the matrix with the metal ions (Table 4.6). This observation is in agreement with an earlier suggestion that LSIM spectra reflects the composition of the species in the matrix and those arising from the primary ion source employed.[20] For example, some of the spectra show species such as $[M_2L_3+Na]^+$ and $[ML+K]^+$ which are 23 and 39 mass units greater than the expected values. Also matrix associated species such as $[MS]^+$, $[MS_2]^+$ and $[MLS]^+$, (where S = 2-nitrobenzyl alcohol) were observed (Table 4.6).

TABLE 4.6 m/z Values of Prominent Solvated and Alkali Metal Incorporated Ions in the LSIM Spectra of Mn^{II}, Ni^{II}, Cu^{II} and Zn^{II} Complexes of Pyrazole-4,5-dione-4-oximes

Metal Complexes	***Ion Assignment (% Abundance)***				
	$[MS]^+$	*$[MS_2]^+$*	*$[M_2L_3+Na]^+$*	*$[MLS]^+$*	*$[ML+K]^+$*
$Mn(Mpo)_2$	207 (30)	360 (11)	555 (4)	346 (10)	-
$Mn(1\text{-}Ppo)_2$	-	360 (23)	738 (3)	410 (2)	-
$Ni(Mpo)_2$	-	-	562 (4)	-	-
$Ni(1\text{-}Ppo)_2$	210 (2)	-	-	413 (6)	-
$Cu(Mpo)_2$	216 (26)	366 (4)	-	356 (39)	242 (9)
$Cu(1\text{-}Ppo)_2$	-	-	-	418 (4)	-
$Zn(Mpo)_2$	217 (5)	369 (4)	573 (3)	357 (11)	245 (4)
$Zn(1\text{-}Ppo)_2$	216 (7)	370 (15)	-	419 (2)	306 (9)

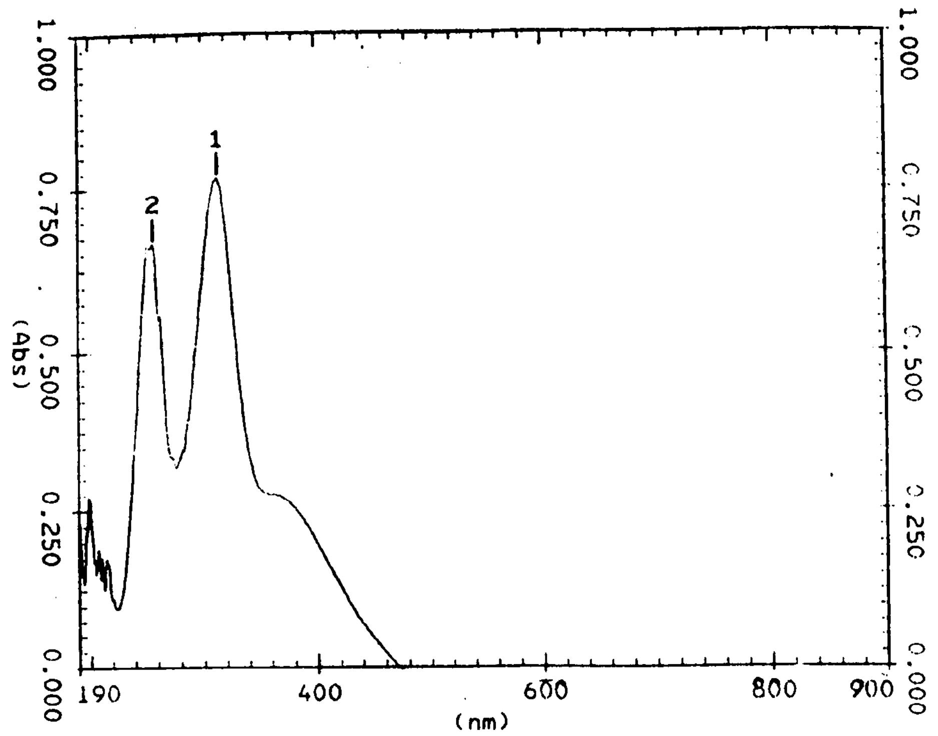
The LSIM spectra of some of the pyridine adducts contain ions of the type $ML_2(py)_2$. In addition, other pyridine containing ions of the type $[ML(py)]^+$, $[ML_2(py)]^+$ and $[M_2L_3(py)]^+$ were also observed (Table 4.7). The spectra also exhibit dimetallic ions such as $[M_2L_2]^+$ and $[M_2L_3]^+$. Similar LSIM spectra were observed for the pyridine adducts of 5-alkylamino-1,2-benzoquinone 2-oximato complexes of copper(II) and nickel(II).[21] Their formation can be explained by a pathway which involves an initial loss of pyridine and interaction of the ions to form the associated species which further react with pyridine to form species such as $[M_2L_4(py)_2]$ from which the ion $[M_2L_3(py)]^+$ could be generated.

TABLE 4.7 m/z Values for Prominent Ions in the LSIM Spectra of the Pyridine Adducts of the Mn^{II}, Ni^{II}, Cu^{II} and Zn^{II} Complexes of Pyrazole-4,5-dione-4-oximes

Metal Complexes	*Metal Containing Ions (% Abundance)*						
	$[ML]^+$	$[ML(py)]^+$	$[ML_2(py)_2]^+$	$[ML_2(py)]^+$	$[M_2L_2]^+$	$[M_2L_2(py)]^+$	$[M_2L_3]^+$
$Mn(1\text{-}Ppo)_2(py)_2$	256 (13)	335 (9)	617 (9)	-	514 (17)	-	716 (56)
$Ni(1\text{-}Ppo)_2(py)_2$	261 (9)	339 (24)	621 (6)	541 (4)	522 (25)	603 (12)	724 (59)
$Cu(Mpo)_2(py)_2$	204 (16)	282 (3)	501 (2)	422 (2)	406 (10)	485 (4)	546 (11)
$Cu(1\text{-}Ppo)_2(py)_2$	265 (74)	345 (36)	626 (6)	546 (8)	530 (100)	688 (3)	732 (22)
$Zn(Mpo)_2(py)_2$	204 (7)	-	503 (7)	425 (7)	412 (6)	-	550 (7)
$Zn(1\text{-}Ppo)_2(py)_2$	266 (54)	348 (23)	693 (4)	614 (10)	535 (20)	614 (10)	736 (100)

The solution electronic spectra of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime and 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime and their transition metal complexes were recorded in dimethylsulphoxide. The spectra show intense ligand charge-transfer bands in the U.V. region which tails into the visible region thereby masking any d-d transitions which may be expected (Figure 4.5). Consequently, the d-d transition bands could not be assigned.

FIGURE 4.5 UV/Vis Spectrum of $Cu(Mpo)_2(H_2O)_2$



The ^1H NMR study of $Zn(Mpo)_2(H_2O)_2$ and its pyridine adduct was determined in methanol. The NMR spectra showed the presence of the alkyl and aryl protons. The protons of the methyl group linked to the ring nitrogen atom appears at a downfield position of δ_H 3.3 compared to the other methyl protons which resonate at δ_H 2.3. The aromatic protons of the pyridine group in the adduct appear as a multiplet at δ_H 7.0 - 8.3. The paramagnetism of manganese(II), nickel(II) and copper(II) and the poor solubility of $Zn(1\text{-}Ppo)_2$ and its pyridine adduct in common organic solvents made them unsuitable for NMR studies.

4.3 SINGLE CRYSTAL X-RAY STRUCTURES OF DIAQUOBIS(1,2-DIMETHYL-1H-PYRAZOLE-4,5-DIONE-4-OXIMATO)ZINC(II) AND BIS(3-METHYL-1-PHENYL-1H-PYRAZOLE-4,5-DIONE-4-OXIMATO)MANGANESE(II).DIPYRIDINE

The single crystal structures of both transition and non-transition metal complexes of 1,2-quinone monooximes and their related ligands have been discussed in Chapter I with special emphasis on their mode of bonding and structural characteristics in the solid state. It has been found that in all the metal complexes, the ligand exists in the oximic and not in the nitroso form. The different types of bonding observed can be classified under three categories.

1) In the lithium and first row transition metal complexes of 1,2-benzoquinone monooximes, the metal is chelated to the ligand through the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group. Similar bonding is also observed in the iron complex of the violurate anion (Fig. 4.7).[22-25]

2) In the uranyl complex of 1,2-naphthaquinone 1-oxime the ligand is coordinated to the metal through the nitrogen and oxygen atoms of the oxime group.[26]

3) In the gold and platinum complexes of isoxazole-4,5-dione 4-oximes the metal is coordinated to the ligand through the nitrogen atom of the oxime group.[27]

However, there are no reports on the structural studies of the metal complexes of pyrazole-4,5-dione 4-oximes. So far these complexes have been represented by structures in which the ligand is bonded to the metal through the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group thereby forming a five-membered chelate ring. The only exception is the report on the Fe(II) complexes[4] where a six membered chelate ring is proposed involving the coordination of the ligand through the oxygen atoms of the oxime and carbonyl groups. To establish the structural characteristics and bonding mode of these complexes, single crystal X-ray studies of $Mn(1\text{-}Ppo)_2(py)_2$ and $Zn(Mpo)_2(H_2O)_2$ were carried out.

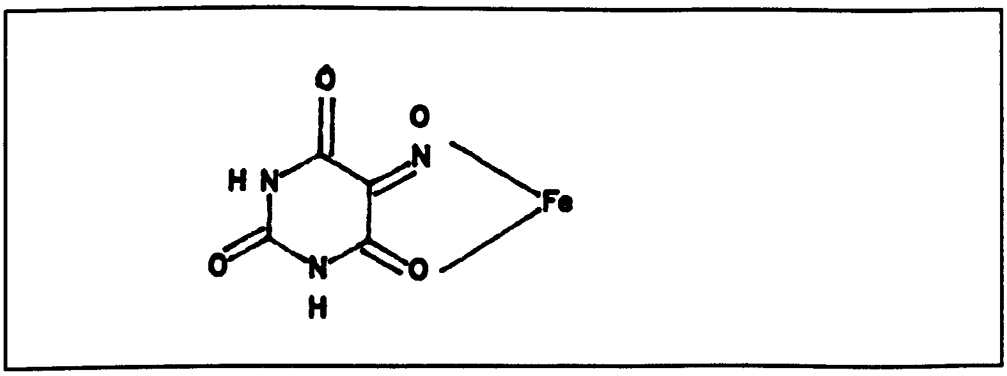


FIG. 4.7

4.3.1 Crystal Preparation

Diaquobis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)zinc(II) was prepared by the reaction of zinc acetate with 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime in aqueous ethanol. The orange powdery solid was recrystallised from aqueous methanol to give orange, needle-like crystals.

Diaquobis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)manganese(II), prepared by the reaction of manganese acetate with 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximes in aqueous ethanol, gave bis(3-methyl-1-phenyl-1H-pyrazol-4,5-dione-4-oximato)manganese(II)dipyridine on stirring with pyridine. The red prismatic crystals were obtained from the solution containing diaquobis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)manganese(II) and pyridine at 20°C.

4.3.2 Data Collection and Processing[28]

The unit cell parameters and the intensity data for $Zn(Mpo)_2(H_2O)_2$ and $Mn(1\text{-}Ppo)_2(py)_2$ were collected under ambient temperature on an CAD4 Enraf-Nonius diffractometer using graphite monochromatised CuKα radiation (λ = 1.5419 Å). The intensity data for both the structures were corrected for Lorentz-polarisation effects and for absorption.[29]

4.3.3 Structure Analysis and Refinement

The positions of the metal atoms in the structure of both the complexes were

Table 4.8 Details of Crystal Data and Data Collection

Complex	*$Zn(Mpo)_2.(H_2O)_2$*	*$Mn(Mpo)_2(py)_2$*
CRYSTAL DATA		
Chemical formula	$C_{10}H_{16}N_6O_6Zn$	$C_{30}H_{26}MnN_8O_4$
Mol. weight	381.65	617.53
Space group	$P2_1/n$	$P2_1/c$
Crystal system	monoclinic	monoclinic
a (Å)	5.126(2)	8.255(1)
b (Å)	14.636(3)	18.483(4)
c (Å)	11.198(2)	9.477(2)
α (deg)	90	90
β (deg)	110.14(2)	104.76(1)
γ (deg)	90	90
Z	2	2
V ($A^{\circ 3}$)	788.6(3)	1398.9(3)
Dx (mg m^{-3})	1.61	1.47
Radiation used	CuKα (λ = 1.5419 Å)	CuKα (λ = 1.5419 Å)
Crystal size (mm)	0.20×0.08×0.08	0.50×0.20×0.20
DATA COLLECTION		
Collection method	ω-2Θ	ω-2Θ
Absorption correction type	emperical	emperical
No. of independent reflections	1473	2709
No. of observed reflections	1016	2324
Criterion for observed	$I>3\ \sigma(I)$	$I>3\ \sigma(I)$
Θ_{max} (°)	70	70
Variation of standards	-3.9%	-1.0%

obtained from a Patterson synthesis with the remaining non-hydrogen atoms located from subsequent Fourier difference syntheses. Although the relevant hydrogen atoms were not located directly from the X-ray data, their positions were geometrically calculated to ride at respective carbon atoms at distances of C-H 1.08 Å with fixed thermal parameters of 0.08 $Å^2$. During the final cycles of refinement anisotropic thermal parameters were assigned to all the non-hydrogen atoms in both the structures. Final cycles of full-matrix refinement converged at R and Rw values as 0.052 and 0.052 for the zinc complex and 0.037 and 0.041 for the manganese complex with weights of $1/\sigma^2(Fo)$ assigned to individual reflections. Pertinent details are given in Table 4.8.

4.3.4. Results and Discussion

The single crystal structures of $Mn(1\text{-}Ppo)_2(py)_2$ and $Zn(Mpo)_2(H_2O)_2$ with the relevant atomic numbering are shown in Fig. 4.8 and Fig. 4.9 respectively. In both the complexes the metal atom is located on a site which corresponds to the centre of symmetry. The pentaatomic ring C1-C2-N2-N3-C3 is planar with the atoms N1, O1, O2, C4 and the substituent on N2 deviating from this plane. In case of $Mn(1\text{-}Ppo)_2(py)_2$, there are no intermolecular contacts shorter than 3 Å suggesting that the crystal packing results from Van der Waals forces. In $Zn(Mpo)_2(H_2O)_2$ the crystal packing is dominated by hydrogen bonds (as shown in Fig. 4.11). The hydrogen bonding involves the hydrogen atom of the water molecule of one complex moiety, the oximic oxygen atom of another moiety and the ring nitrogen atom of a third complex moiety. From the structural formulation it is evident that the metal is bonded to the ligand through the oxygen atoms of the oximato and carbonyl groups thereby forming a six membered chelate ring.

FIG. 4.8 A view of bis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)manganese(II)dipyridine with atomic numbering

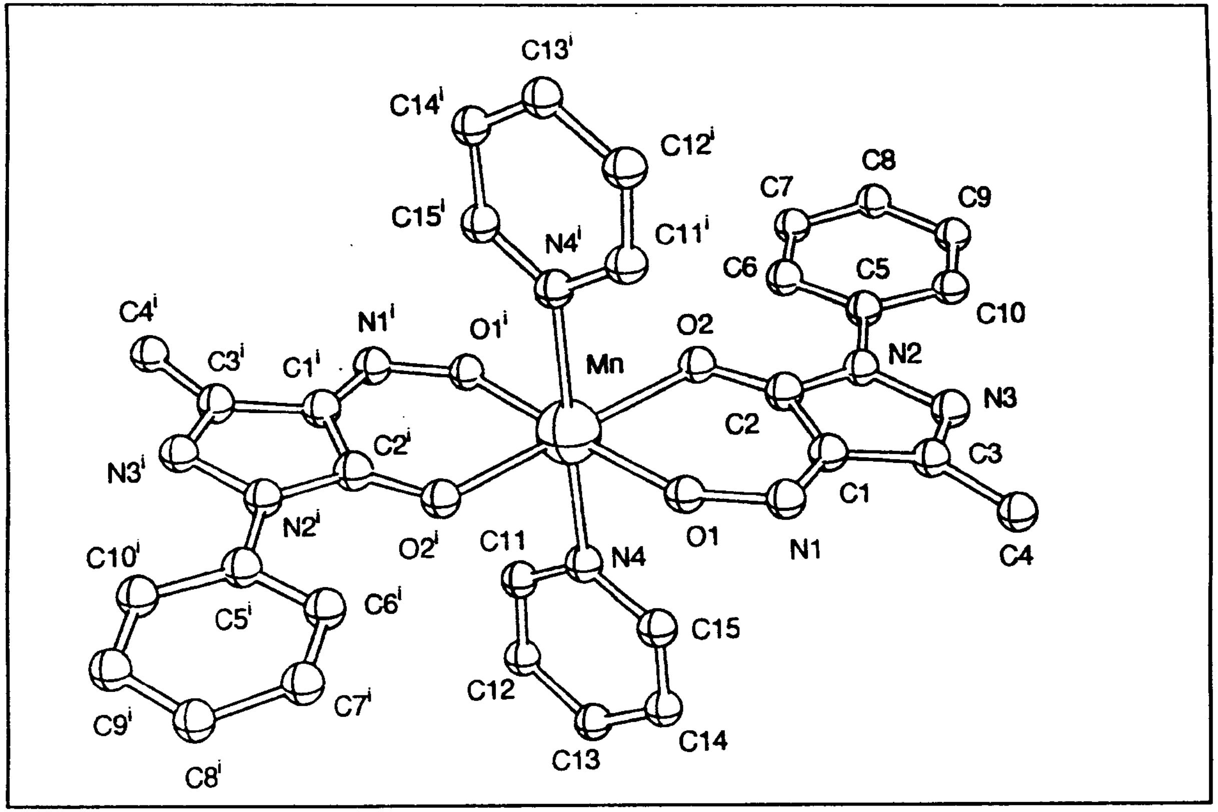
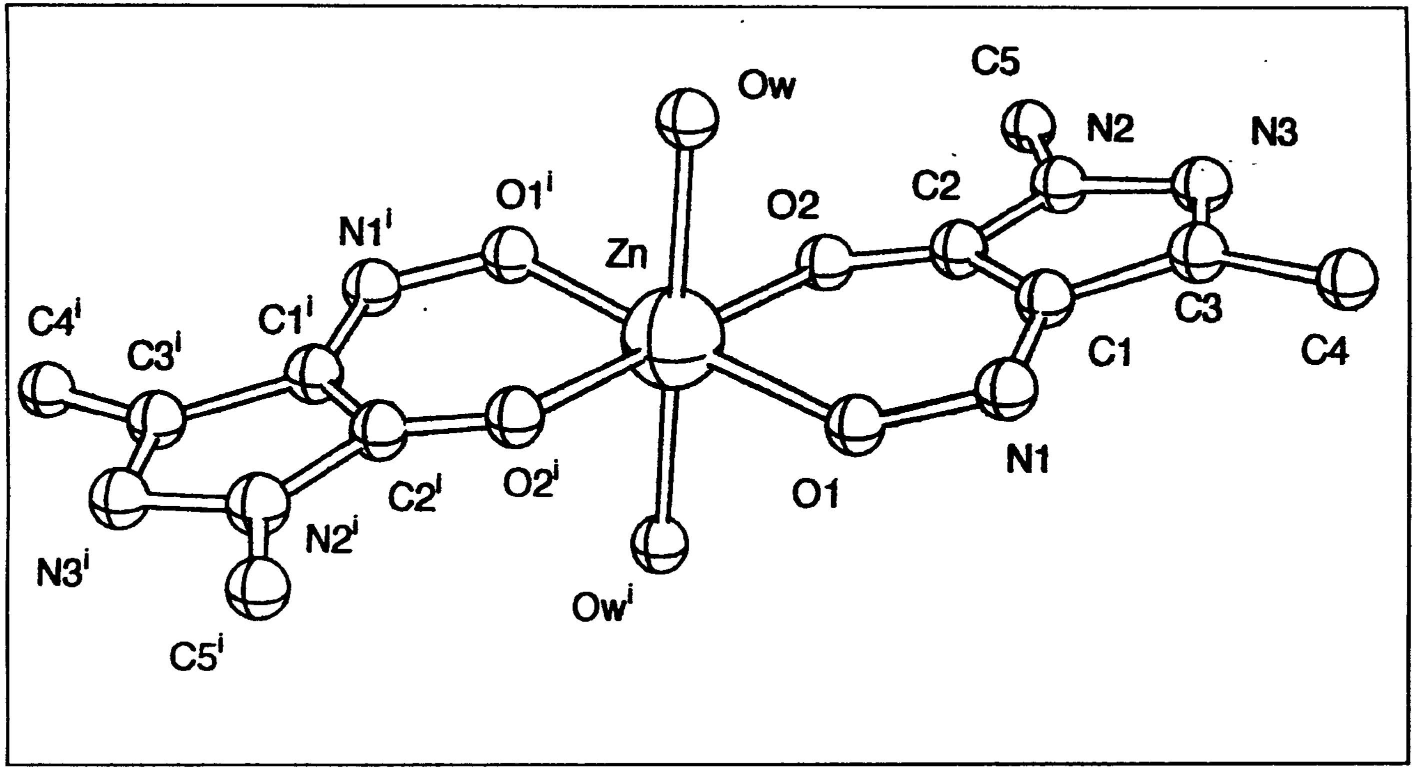


FIG. 4.9 A view of diaquobis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)zinc(II) with atomic numbering



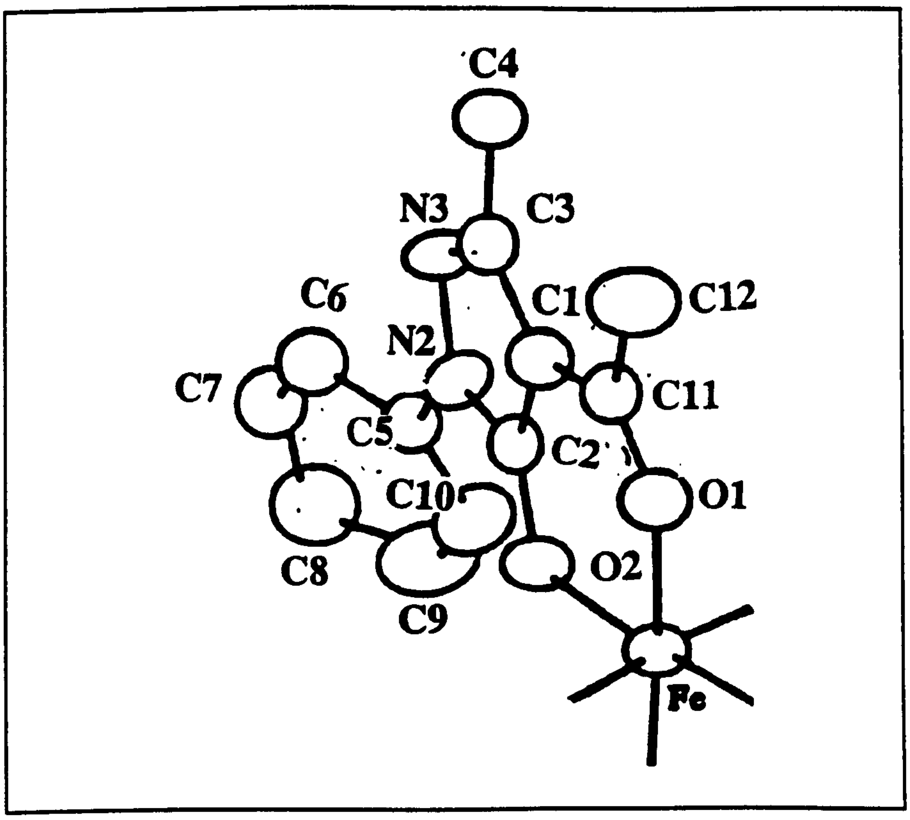


FIG. 4.10

An iron(III) complex of 3-methyl-1-phenyl-4-acetylpyrazol-5-one, Fe(Acpo)$_3$, (Fig. 4.10) has been reported.[30] This complex is comparable to the pyrazole-4,5-dione-4-oximato complexes since both these types of complexes contain the pyrazole moiety and six- membered chelate ring. In the case of the former, the ligand is bonded to the metal through the oxygen atoms of the ring and acetyl carbonyl group whereas in the latter, chelation occurs through the oxygen atoms of the ring and oximato groups thus forming six-membered chelate rings in both the cases (Figs. 4.8 - 4.10). However, the structural studies of Fe(Acpo)$_3$ show that the ligand exists in the enol form and complexation occurs by the loss of enolic proton.

In this section a comparative study of the bond lengths of different complexes has been attempted. Selected bond angles and bond distances of Mn(1-Ppo)$_2$(py)$_2$ and Zn(Mpo)$_2$(H$_2$O)$_2$ are given together with bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II).bipyridine [Cu(4-Clqo)$_2$by], diaquabis(1,2-naphthaquinone-2-oximato-ON)dioxouranium(VI)-Trichloromethane(½) [UO$_2$(1-nqo)$_2$(H$_2$O)$_2$].½CHCl$_3$

and $Fe(Acpo)_3$ in Tables 4.10 and 4.11 respectively. $[Cu(4\text{-}Clqo)_2by]$ is included in this discussion because it is known that the benzoquinone monooximato ligand is bonded to Cu^{II} through the nitrogen atom of the oxime group and the oxygen atom of the carbonyl group thus forming a five-membered chelate ring. But in the uranyl complex, 1-nqo$^-$ ligand is bonded to metal atom through the nitrogen and oxygen atoms of the oxime group therefore having a free CO group.

Apart from $Fe(Acpo)_3$ where the C2-O2 bond distance is 1.27 Å, the double bond character of C2-O2 in other complexes is indicated by its distances of 1.24-1.25 Å which is closely equal to the C=O bond lengths found in benzoquinone[31] and naphthaquinone compounds.[32] In $Fe(Acpo)_3$, the C2-O2 bond length is considerably longer and has been assigned single bond character. This has been attributed to the enolic character of the ligand.[30]

Also in $Fe(Acpo)_3$, the bonds C1-C2 and C3-N3 have significant double bond character.[33] But in a typical pyrazole-4,5-dione-4-oximato complex, the bond C3-N3 of the pyrazole-ring is expected to be considerably shorter than the corresponding C2-N2 due to the significant double bond character in the former. This structural feature has been confirmed in both the manganese(II) and zinc(II) complexes where the bond C3-N3 is found to be considerably shorter than C2-N2 (Table 4.11). Additionally the bond C1-C2 in both the manganese(II) and zinc(II) complexes are longer than that of the iron(III) compound. These structural differences further support the difference in the bonding mode of the Acpo$^-$ ligand against Ppo$^-$ and Mpo$^-$ ligands. In all the three complexes the attachment of the ligand occurs through the oxygen atom O2. But in $Fe(Acpo)_3$, the ligand Acpo$^-$ bonds to the metal through the loss of the enolic proton whereas the ligands Ppo$^-$ and Mpo$^-$ bond to the Mn(II) and Zn(II) metal atoms respectively *via* the coordination of the lone pair of electrons on the oxygen atom O2.

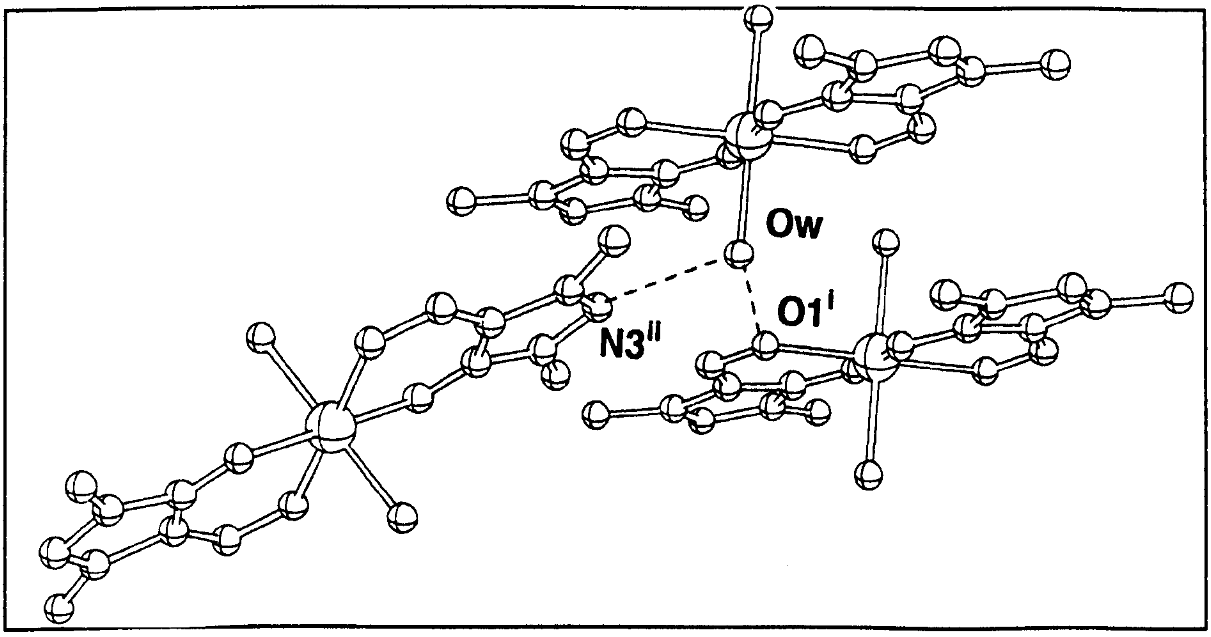


FIGURE 4.11

TABLE 4.10 Selected Bond Angles (°) in Different Oximato Complexes

Selected Atoms	*Bond Angles (°)*				
	$Zn(Mpo)_2 (H_2O)_2$	$Mn(Ppo)_2 (py)_2$	$Fe(Acpo)_3$	$Cu(4\text{-}Clqo)_2by$	$UO_2(1\text{-}nqo)_2(H_2O)_2$, ½$CHCl_3$
O2-C2-C1	131.3(5)	129.7(2)	130.3(5)	123.7(6)	122.0(1)
C2-O2-M	116.2(3)	121.9(2)	123.4(3)	107.7(5)	-
N1-C1-C2	131.8(5)	130.6(2)	122.6(5)	113.0(6)	116.0(1)
O1-N1-C1	115.9(4)	118.0(2)	-	118.1(6)	120.0(1)
N1-O1-M	128.5(3)	132.8(1)	-	-	76.9(5)

TABLE 4.11 Selected Bond Distances (Å) in different Oximato Complexes

Selected Bonds	*Intermolecular Bond Distances in*				
	$Zn(Mpo)_2(H_2O)_2$	$Mn(Ppo)_2(py)_2$	$Fe(Acpo)_3$	$Cu(4\text{-}Clqo)_2\,by$	$UO_2(1\text{-}nqo)_2(H_2O)_2.\frac{1}{2}CHCl_3$
M-O1	2.084(4)	2.164(2)	2.030(4)	-	2.37(1)
M-O2	2.045(3)	2.172(2)	2.013(4)	2.320(4)	-
N1-O1	1.296(6)	1.303(3)	-	1.2516	1.34(1)
C1-N1	1.350(6)	1.312(3)	-	1.364(7)	1.30(1)
C1-C2	1.457(7)	1.474(3)	1.428(7)	1.447(8)	1.50(1)
C2-O2	1.251(7)	1.242(3)	1.274(6)	1.235(6)	1.23(1)
C3-N3	1.295(7)	1.289(3)	1.306(8)	-	-
C3-C1	1.432(8)	1.440(4)	1.442(7)	-	-
N3-N2	1.392(7)	1.427(3)	1.393(7)	-	-
N2-C2	1.341(7)	1.364(3)	1.350(8)	-	

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CHAPTER V

REACTIONS OF PYRAZOLE-4,5-DIONE-4-OXIMES AND THEIR METAL COMPLEXES WITH DIMETHYL ACETYLENEDICARBOXYLATE

CONTENTS

5.1 INTRODUCTION

As noted in Chapter II, the Diels Alder reaction has been ultilised to illustrate the heterodiene character of 1,2-quinone monooximes. This is achieved through the synthesis of 1,4-benzoxazines (Fig. 5.1) by the reactions of the copper(II) and nickel(II) complexes of these ligands with dimethyl acetylenedicarboxylate.[1] However, the free ligands and their methyl ethers failed to react with dimethyl acetylenedicarboxylate even after prolonged reaction times. Subsequent work and current studies have established that the behaviour of 1,2-quinone monooximes and their metal complexes towards dimethyl acetylenedicarboxylate is far more complex than initially reported. For example, open chain addition products (Fig. 5.2) are obtainable from the reactions of the alkali and alkaline earth metal complexes with dimethyl acetylenedicarboxylate at -75 - 40°C (*cf.* Chapter II). Furthermore, two other cycloaddition products, namely the 1,3-oxazoles[2,3] (Fig. 5.3) and 1,4-benzoxazinones[4] (Fig. 5.4), can arise from the reactions of their copper(II) and nickel(II) complexes. The 1,3-oxazole was initially reported to be recovered when copper(II) complexes of 1,2-quinone monooximes were refluxed with dimethyl acetylenedicarboxylate in anhydrous methanol.[3] Later it was shown that these compounds were the oxidation products of the corresponding 1,4-oxazine, the oxidation being promoted by the unreacted metal complex in the reaction system.[2]

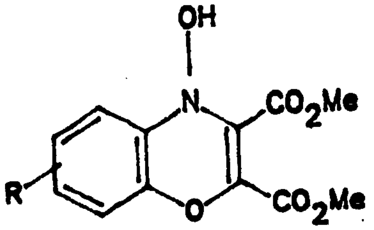


FIG. 5.1 1,4-benzoxazine

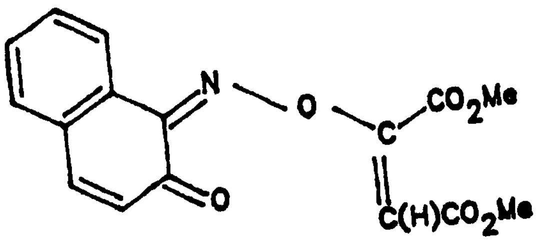


FIG. 5.2 O-(1′,2′-dicarbomethoxy ethenyl)-1,2-naphthaquinone 1-oxime

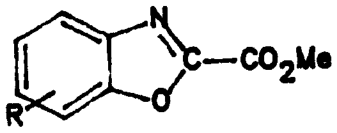


FIG. 5.3 1,3-oxazole

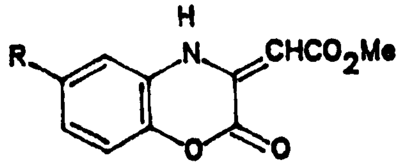
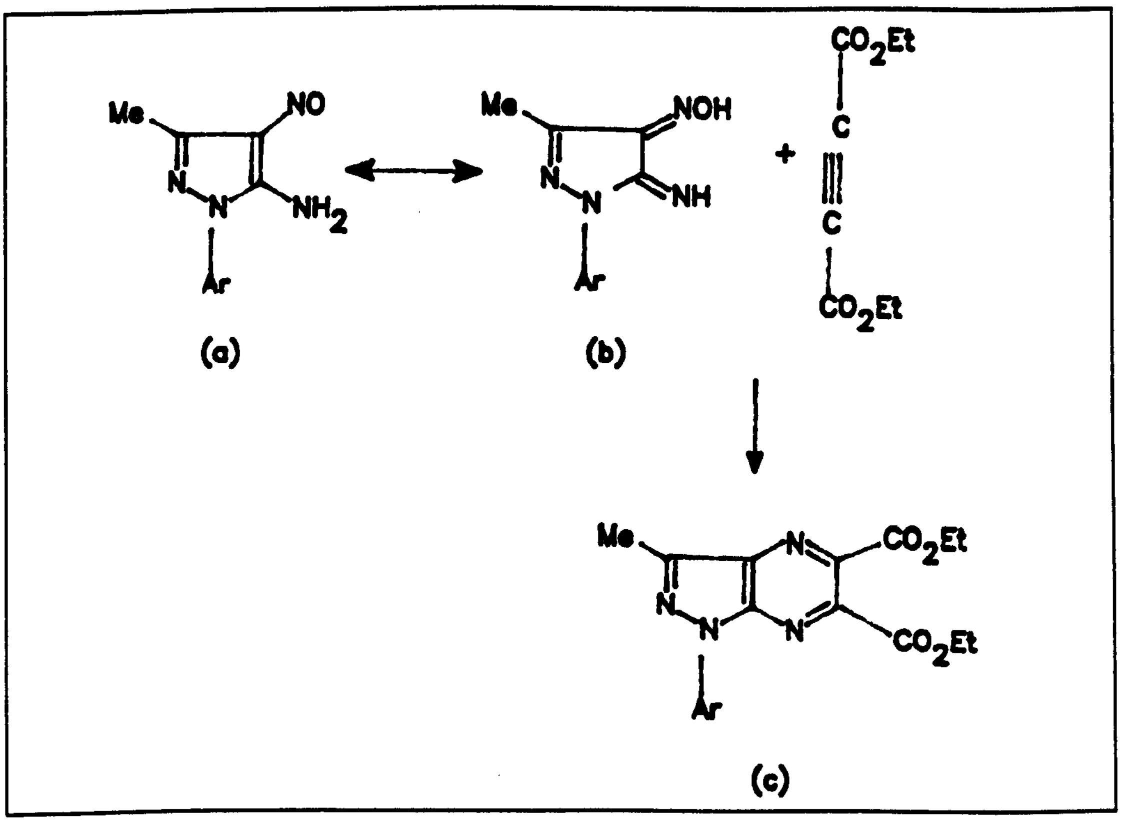


FIG. 5.4 1,4-benzoxazinone

Cycloaddition reactions are also observed in the reactions of 4-nitroso-5-aminopyrazoles (5.5a), which can exhibit tautomerism involving the 1,2-iminooxime form (5.5b), with diethyl acetylenedicarboxylate to form a pyrazine derivative (5.5c, Scheme 5.5). In this particular case, however, the cycloaddition is accompanied by intramolecular dehydration.[5]

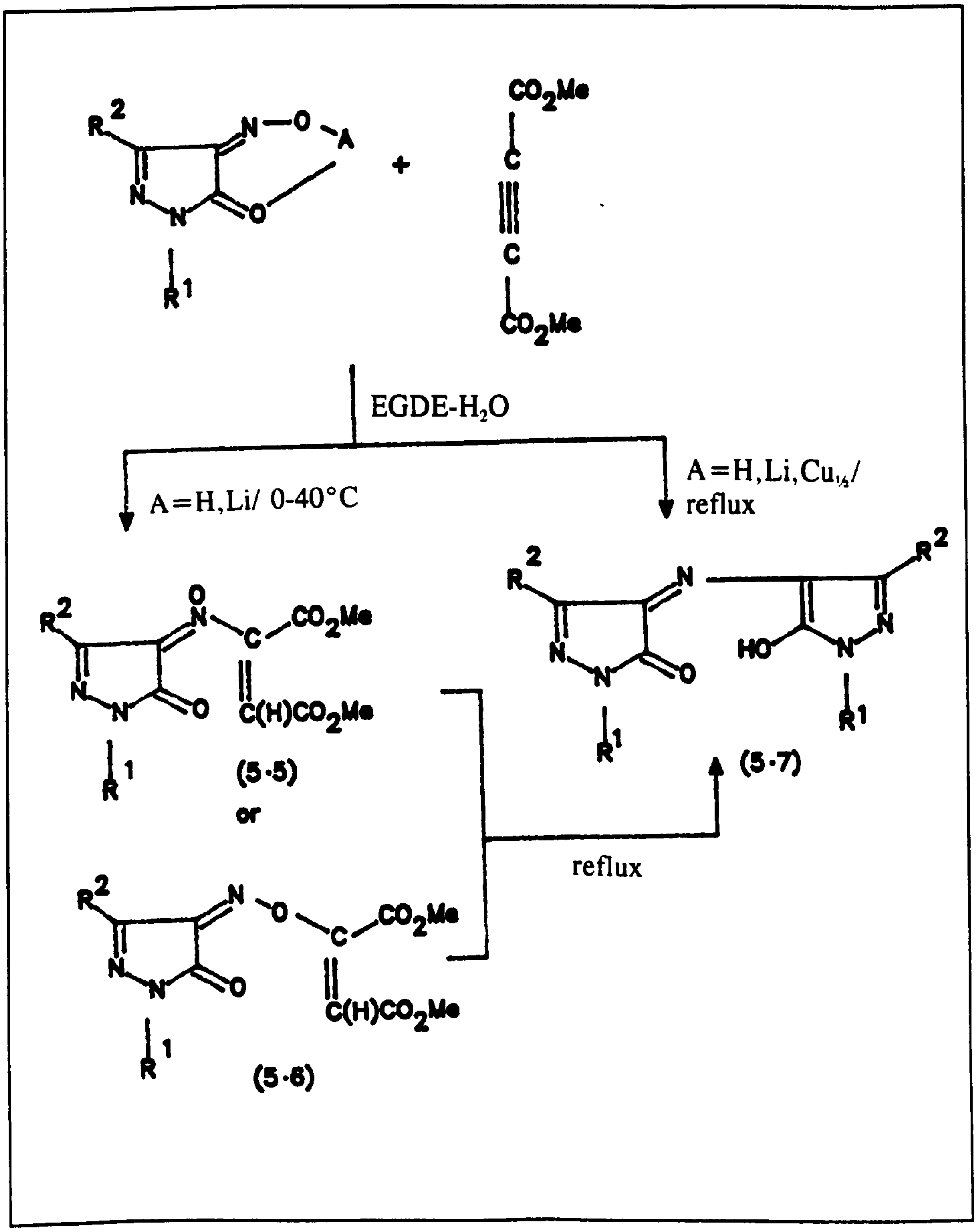
The results of this study on the reactions of pyrazole-4,5-dione-4-oximes and their metal complexes with dimethyl acetylenedicarboxylate are presented below (§ 5.2). In brief, these investigations indicate that the formation of the open chain adducts is preferred but these adduct may subsequently react further to form condensation products.



SCHEME 5.5

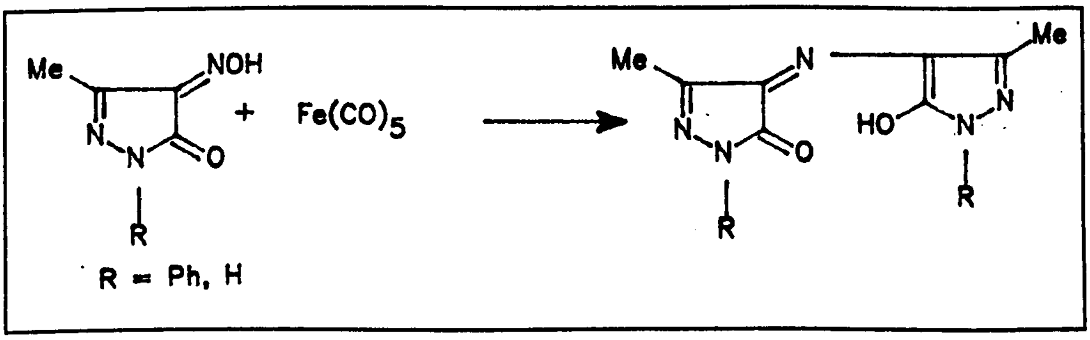
5.2 REACTIONS OF PYRAZOLE-4,5-DIONE-4-OXIMES AND THEIR METAL COMPLEXES WITH DIMETHYL ACETYLENEDICARBOXYLATE

During this study, the reactions of pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate were investigated both at low temperatures, *ie.*, 0, 20, 40°C and under reflux. Four oximes, namely 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime (1-PpoH), 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (MpoH), 1-methyl-3-phenyl-1H-pyrazole-4,5-dione-4-oxime (3-PpoH) and 3-methyl-1H-pyrazole-4,5-dione-4-oxime (poH) were used. In each case two different products were isolated depending on the reaction temperature. At low temperatures open chain adduct formation occurs which could either be the compound 5.5 or its isomer 5.6 (Scheme 5.6). Under reflux conditions, a Schiff base condensation product (Fig. 5.7, Scheme 5.6) resulted.



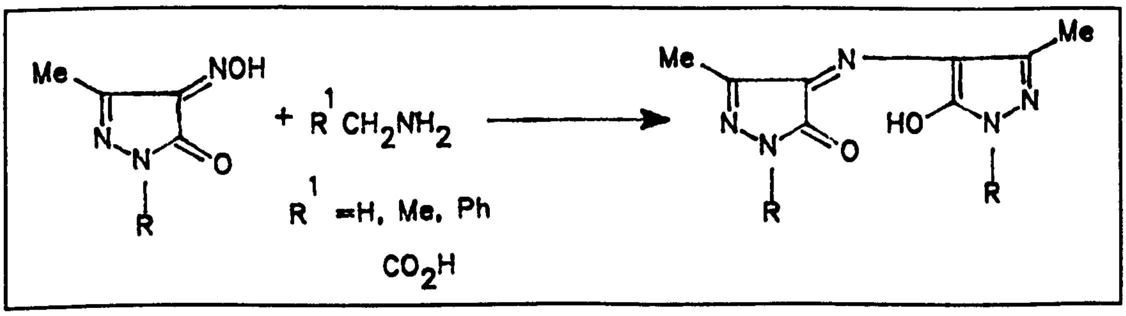
SCHEME 5.6

Open chain adducts were also formed by the reactions of the lithium complexes of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime with dimethyl acetylenedicarboxylate at low temperatures (Scheme 5.6). In contrast, the copper(II) complexes of 1,3-dimethyl and 3-methyl-1-phenyl-1H-pyrazol-4,5-dione-4-oximes failed to react under similar conditions. However, under reflux both the lithium(I) and copper(II) complexes reacted to form the condensation product, Fig. 5.7 (Scheme 5.6). Such compounds, which are known as rubazonic acids, have also been obtained by the reaction of pyrazol-5-one oximes with iron pentacarbonyl[6] (Reaction 5.1) and with



REACTION 5.1

amino acids and primary amines[7] (Reaction 5.2).



REACTION 5.2

In order to examine whether the condensation products, 5.7, obtained at elevated temperatures, can also arise from the open chain adducts 5.5/ 5.6, the latter were heated under reflux in aqueous ethylene glycol dimethyl ether for 2-3 hours. In all cases, the condensation products were isolated in good yield (Scheme 5.6), thus clearly indicating the convertibility of the open chain adducts to the condensation products at elevated temperatures.

The reactions of pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate were initially studied at 20°C. In the case of MpoH and 3-PpoH, the respective adducts were obtained in good yield but with 1-PpoH and poH, the yields were relatively low (Table 5.1). In an attempt to increase the yield of these products, the reactions were subsequently carried out at the higher temperature of 40°C and at the lower temperature of 0°C. In all cases it was observed that lower temperatures led to higher yield. However, the yields of the products arising from 1-PpoH were relatively poor even at 0°C.

TABLE 5.1 The effect of temperature on the overall yield of the open chain adducts

Compound used	***% yield of the open chain adducts formed at (°C)***		
	0	***20***	***40***
1-PpoH	29	18	15
3-PpoH	94	65	49
MpoH	60	49	42
poH	-	27	-
Li(Mpo)	-	58	-

The characterisation of the open chain adducts was achieved by elemental analysis and spectroscopic studies. The results of the spectroscopic studies are presented and discussed in Section 3 of this chapter. However, at this stage a brief summary of the NMR and IR spectra supporting the formation of the open chain adducts (5.5 or 5.6) rather than the cycloadduct (5.8) is given:

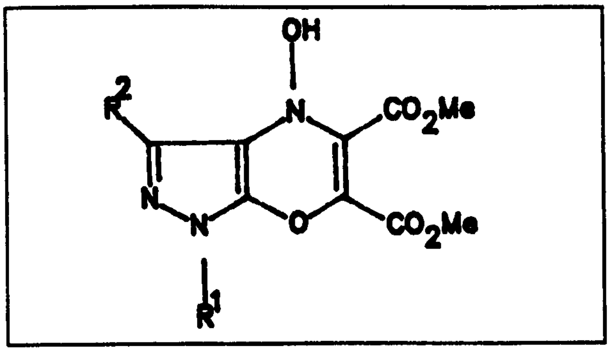


FIG. 5.8

The ^1H NMR spectra of all the products arising from the reactions of pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate at low temperatures show a sharp *singlet* in the range δ_H 6.40-6.66 due to a vinylic proton ($>C=C\underline{H}$-), suggesting their formulation as the open chain adducts (5.5 or 5.6). In the ^{13}C NMR spectra, the presence of a signal in the range δ_C 112-114 also indicates the presence of an alkene ($=\underline{C}H$) carbon atom. Further evidence for the open chain structure is obtained from the IR spectra which indicate the presence of three prominent C=O stretchings and the absence of any absorptions due to the νOH group. Attempts to distinguish between the structures 5.5 and 5.6 from the NMR chemical shift emperical calculations of the vinylic proton proved inconclusive.

In order to distinguish between the two possible open chain structures, the reaction of the products with triphenylphosphine at 20°C was investigated by thin layer chromatography. The reaction readily afforded triphenylphosphine oxide thereby possibly indicating the presence of a reactive NO group and therefore suggesting the formulation 5.5 as the likely product.

5.4 ANALYSIS OF THE SPECTROSCOPIC DATA OF THE OPEN CHAIN ADDUCTS

The electron impact mass spectra of the open chain adducts obtained by the reactions of pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate at 0 - 40°C show prominent parent ion peaks. The fragmentation pattern, which involves the loss of CH_3OH, CO, $CH_3O^{\bullet}$ and [O-C-C=O] groups, does not give any substantial evidence to differentiate between the three proposed structures (5.5, 5.6 and 5.8). Also the mass spectra of all the compounds isolated show the fragment ion 5.9 which can arise by the gradual fragmentation of any of the three compounds (5.5, 5.6 or 5.8). The mass spectrometry study of the addition compounds was inconclusive. The possible structure of the compounds cannot be elucidated from these spectral studies alone.

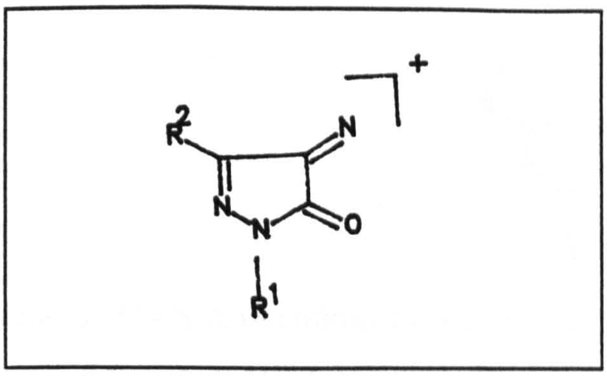
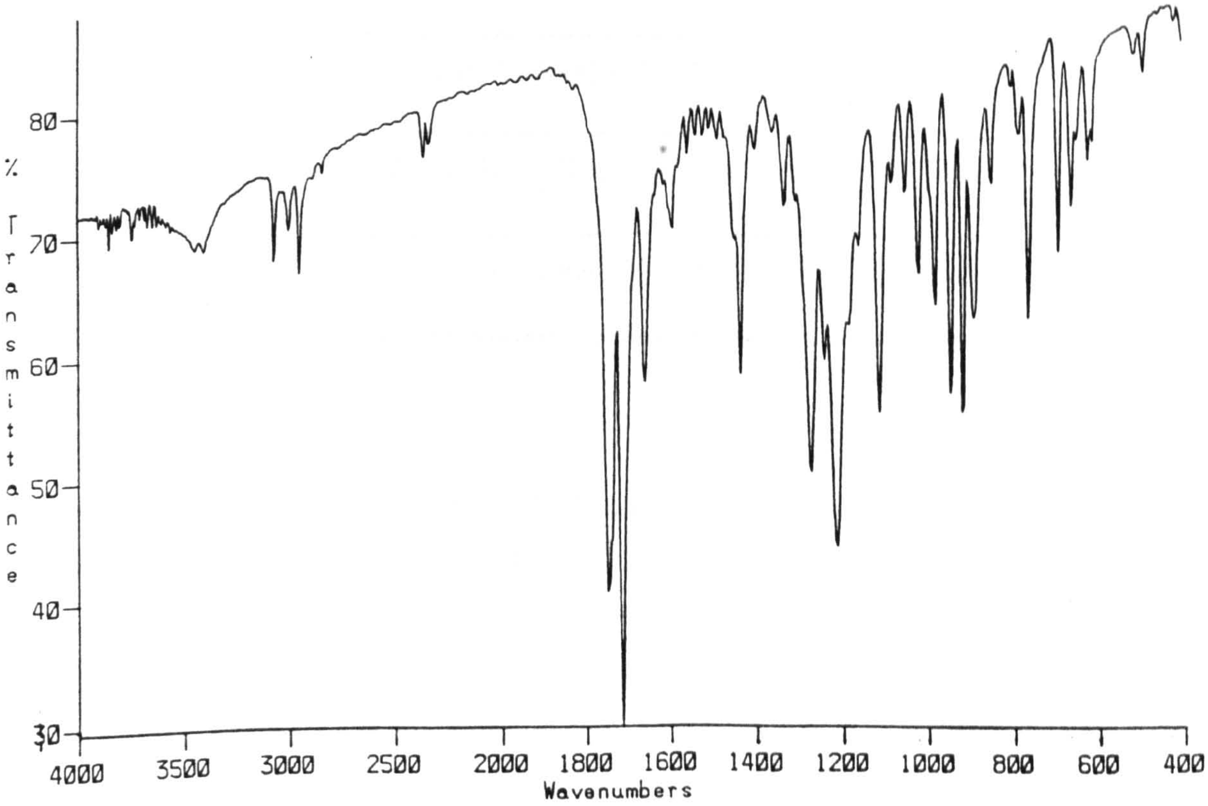


FIG. 5.9

FIGURE 5.1 Infrared Spectrum of A^2 when R^1=Me, R^2=Ph



The infrared spectrum of the addition product, isolated by the reaction of 1-methyl-3-phenyl-1H-pyrazole-4,5-dione-4-oxime with dimethyl acetylenedicarboxylate at 0 - 40°C, is shown in Figure 5.1. The spectrum shows four prominent absorptions in the region 1746 - 1620 cm^{-1}. These absorptions are attributed to C=O and C=N stretches since C=N stretching frequencies of pyrazol-5-ones have been reported in the region of 1600 - 1630 cm^{-1}.[8] Table 5.2 gives the C=O and C=N stretchings of the four addition products obtained at low temperature.

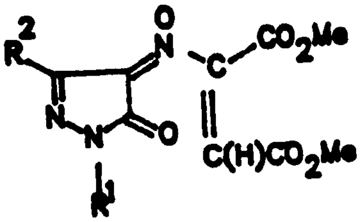


TABLE 5.2 νC=O and νC=N Absorptions in the IR Spectra of the Addition Products obtained at low temperatures

Addition compounds	*νC=O (cm^{-1})*	*νC=N (cm^{-1})*
A^1 (R^1=Ph,R^2=Me)	1746(sh), 1732(s, sh), 1718(sh)	1663(sh)
A^2 (R^1=Me,R^2=Ph)	1746(sh), 1730(sh), 1712(s, sh)	1656(sh)
A^3 (R^1,R^2=Me)	1723(s, sh), 1713(s, sh), 1664(sh)	1620(sh)
A^4 (R^1=H,R^2=Me)	1734(s, sh), 1664(sh), 1610(sh)	1596(sh)

s = strong, sh = sharp

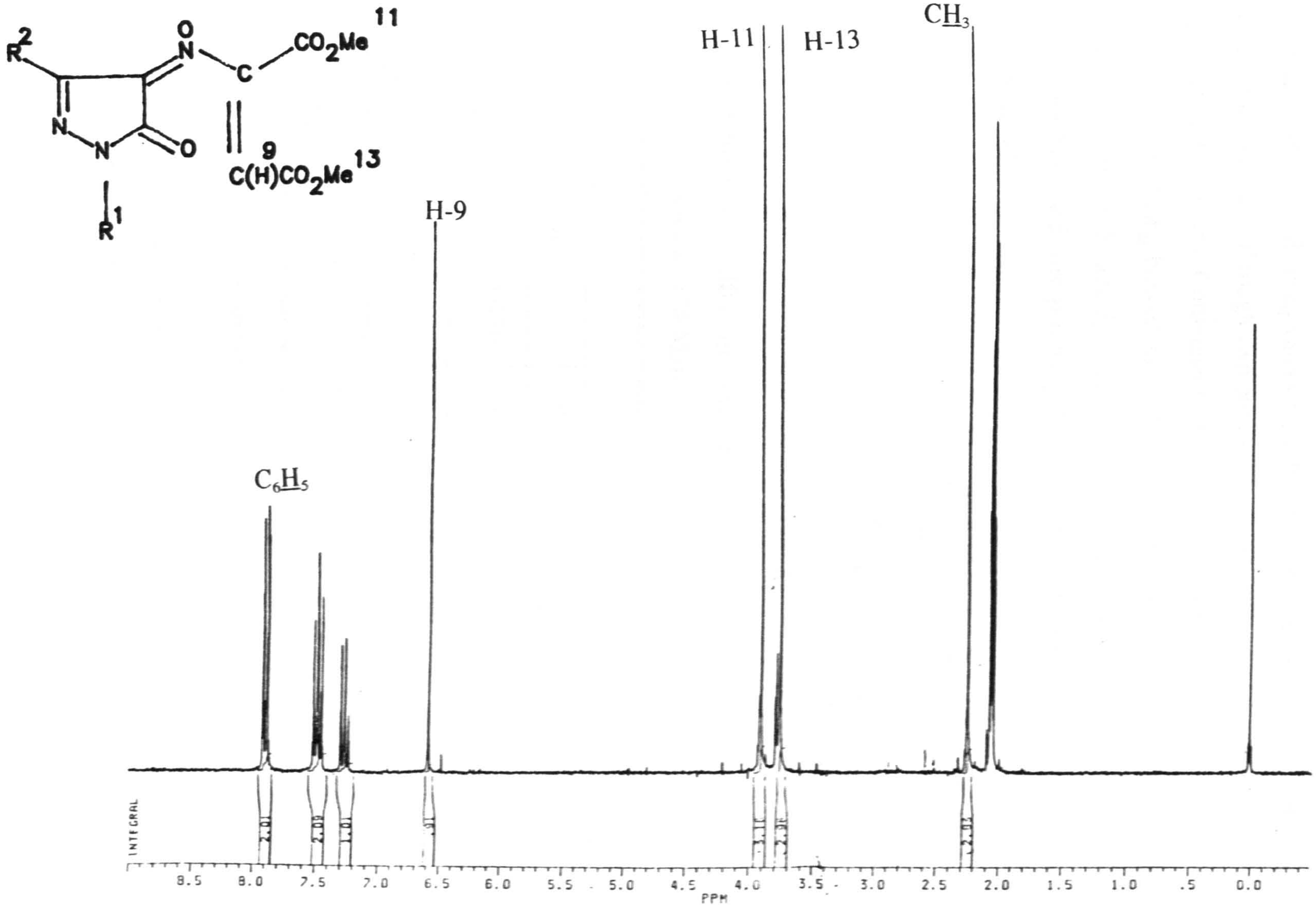
The infrared spectra of the four addition products, obtained by the reaction of 1,3-disubstituted-1H-pyrazole-4,5-dione-4-oxime with dimethyl acetylenedicarboxylate at low temperatures, indicate three intense carbonyl absorptions. The νCO absorptions at higher wavenumbers (1664 - 1746 cm^{-1}) are due to the C=O stretchings of the carbomethoxy groups.[9] This infrared evidence supports the formulation of the open chain adducts rather than the closed chain oxazine since the latter consists of only two carbonyl groups.

The open chain structure of the addition product is more strongly supported by NMR spectroscopy. The NMR spectra of the addition products, obtained by the reaction of 1-PpoH with dimethylacetylene dicarboxylate at 20°C, has been investigated in detail.

The ^{1}H-NMR spectrum of the addition products, formed by the reaction of 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime with dimethyl acetylenedicarboxylate, is shown in Figure 5.2. The phenyl protons appear as *multiplets* at δ_H 7.2 - 7.9. Of the three sets of methyl protons, those attached to the pyrazolone ring appear as a *singlet* at δ_H 2.25. These protons appear at a comparatively downfield position compared to methyl (CH_3-$\underline{H}$) protons attached to a saturated carbon atom, possibly due to the deshielding effect of the β- and γ-nitrogen atoms. The methyl protons of the carbomethoxy groups appear further downfield as two *singlets* at δ_H 3.8 and 3.9 due to the strong deshielding effect of the adjacent oxygen atoms. The *singlet* at δ_H 6.6 indicates the presence of the vinylic proton since a vinylic proton attached to a carbomethoxy group resonates at δ_H 5.8 - 6.7.[9] Although qualitative HPLC studies indicate that all of the four addition compounds exist as a mixture of two isomers, the ^{1}H and ^{13}C NMR spectra of A^1, A^2 and A^3 indicate the compounds to be single-components but those of A^4 show it to be an isomeric mixture. One possibility could be that the two isomers for A^1, A^2 and A^3 coincidentally resonate at the same chemical shift *ie.* the chemical shifts for each isomer in the mixture is identical.

The ^{13}C-^{1}H COSY and the ^{13}C NMR spectra of A^1 (Figures 5.3 and 5.4 respectively) exhibit three resonances for the five aromatic protons thereby indicating the presence of two sets of identical aromatic protons and carbon atoms. The protons H-2 and H-6 and H-3 and H-5 and their corresponding carbon atoms are in the same environment respectively and hence their resonances coincide. The ^{13}C-^{1}H COSY spectrum has been used to identify the signal arising from the resonance of the vinylic carbon atom (C-9) which appears at δ_C 114.10.

FIGURE 5.2 ^{1}H-NMR Spectrum of A^1 when R^2 = Me, R^1 = Ph in $(CD3)_2CO$ at 250 MHz



A distinction could not be made between the resonances of the two carbomethoxy protons using the ^{1}H NMR spectrum of A^1 alone. With the help of the ^{13}C-^{1}H COSY spectrum, assignment of their δ_H values have been accomplished. C-11 is linked to the oximic nitrogen atom through two carbon atoms whereas C-13 is linked to it through three carbon atoms. Consequently C-11 resonate downfield (δ_C 53.61) to C-13 (δ_C 52.39). H-11 being bonded to C-11 will also resonate downfield [δ_H 3.9] to H-13 [δ_H 3.8]. Selected δ_H and δ_C values for the other three addition products are given in Tables 5.3 and 5.4 respectively (based on their ^{13}C NMR, C-H COSY and ^{13}C DEPT spectra).

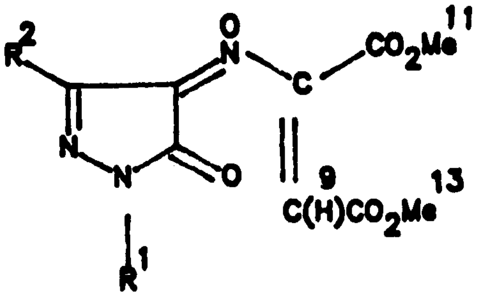


TABLE 5.3 Chemical Shifts of Protons of the Addition Products in CDCl$_3$ and at 250 MHz

Addition Products	*δ_H/ppm*				
	R^2	*R^1*	*H-9*	*H-11*	*H-13*
A^2 (R^1=Me,R^2=Ph)	7.35-7.85(m)	3.47(s)	6.55(s)	3.90(s)	3.67(s)
A^3 (R^1,R^2=Me)	2.08(s)	3.26(s)	6.52(s)	3.88(s)	3.73(s)
A^{4*} (R^1=H,R^2=Me)	2.14(s), 2.46(s)	9.53(d)	6.47(s), 6.54(s)	3.89(d)	3.78(d)

*spectrum exhibiting an isomeric mixture

Both the open chain addition products and the oxazine have methyl, methine and quarternary carbon atoms. The structure of the addition product has been further consolidated by ^{13}C-DEPT spectra. In the ^{13}C-DEPT 135 spectrum, the methyl and methine carbon atoms appear on the positive side while the methylene carbon atoms appear inverted. Quarternary carbons do not appear in such spectra. In the oxazine, there are eight methyl and methine carbon atoms while in both the open chain

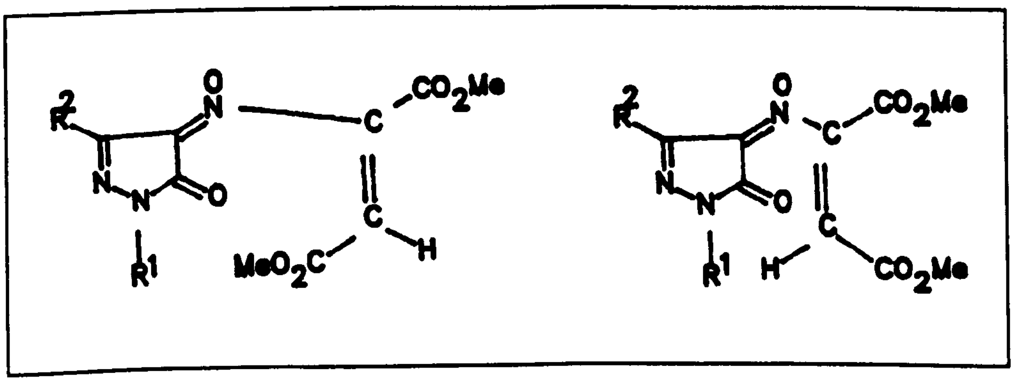
TABLE 5.4 Chemical Shifts of Carbon Atoms of the Addition Products in $CDCl_3$

Addition Products	*δ_C/ppm*				
	R^2	*R^1*	*C-9*	*C-11*	*C-13*
A^2 (R^1=Me,R^2=Ph)	31.87(s)	127.24-130.37(m)	112.87(s)	53.34(s)	52.17(s)
A^3 (R^1,R^2=Me)	12.42(s)	31.52(s)	113.87(s)	53.54(s)	52.31(s)
A^{4*} (R^1=H,R^2=Me)	12.64(s) 17.33(s)	-	113.11(s) 114.05(s)	53.47- 53.29(m)	52.39- 53.24(m)

*spectrum exhibiting an isomeric mixture

structures there are nine methyl and methine carbons. The ^{13}C-DEPT 135 spectrum of the addition product, A^1, where R^2 = Me and R^1 = Ph, exhibits nine peaks on the positive side of the axis thereby confirming the open chain structure.

From the spectroscopic and chemical evidence, the product can be assigned the highly probable structure 5.5, the two geometric isomers being 5.5a and 5.5b.



5.5a 5.5b

FIGURE 5.3. ^{13}C-^{1}H COSY NMR Spectrum of A^1 where R^2 = Me, R^1 = Ph in $CDCl_3$

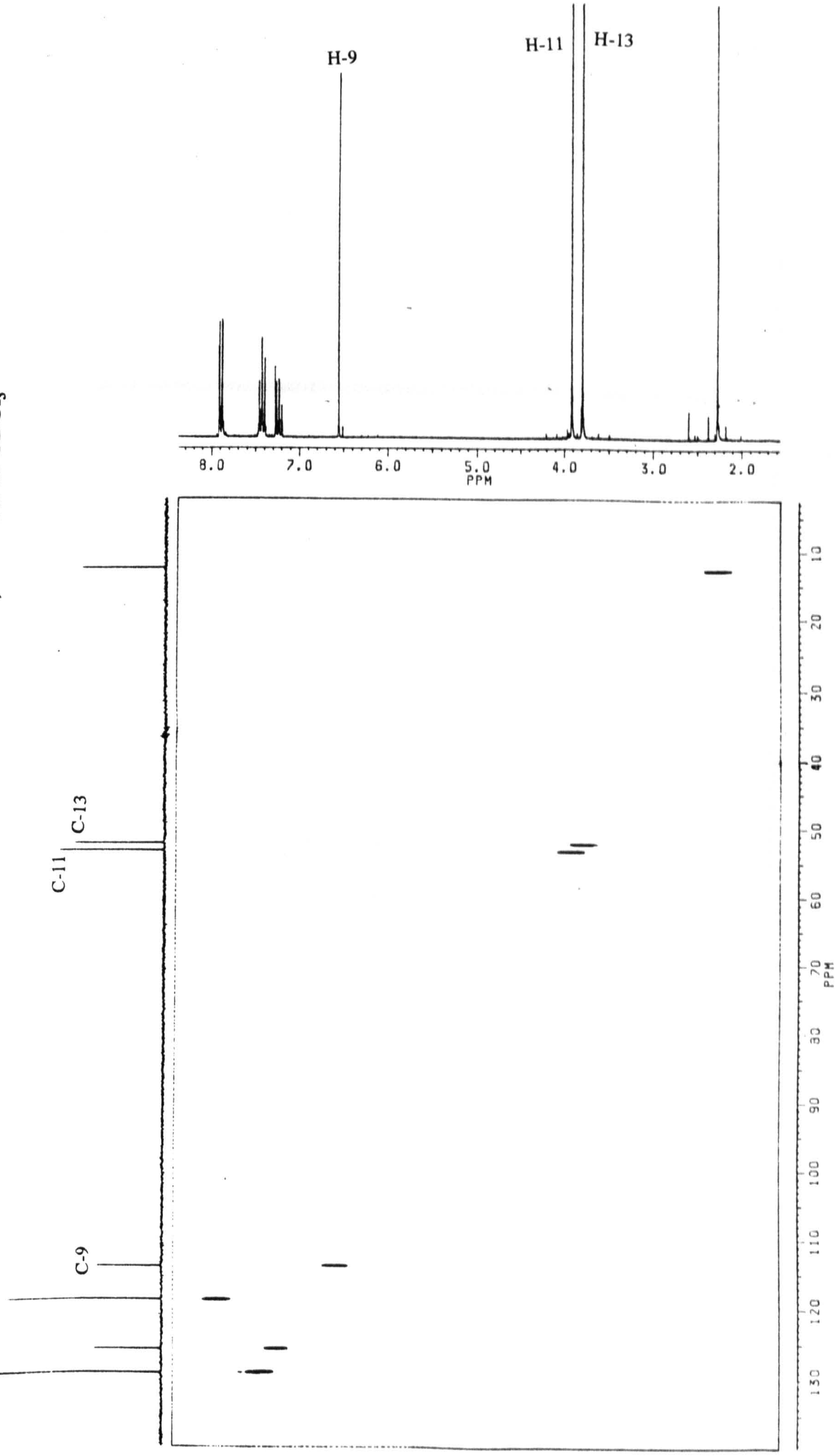
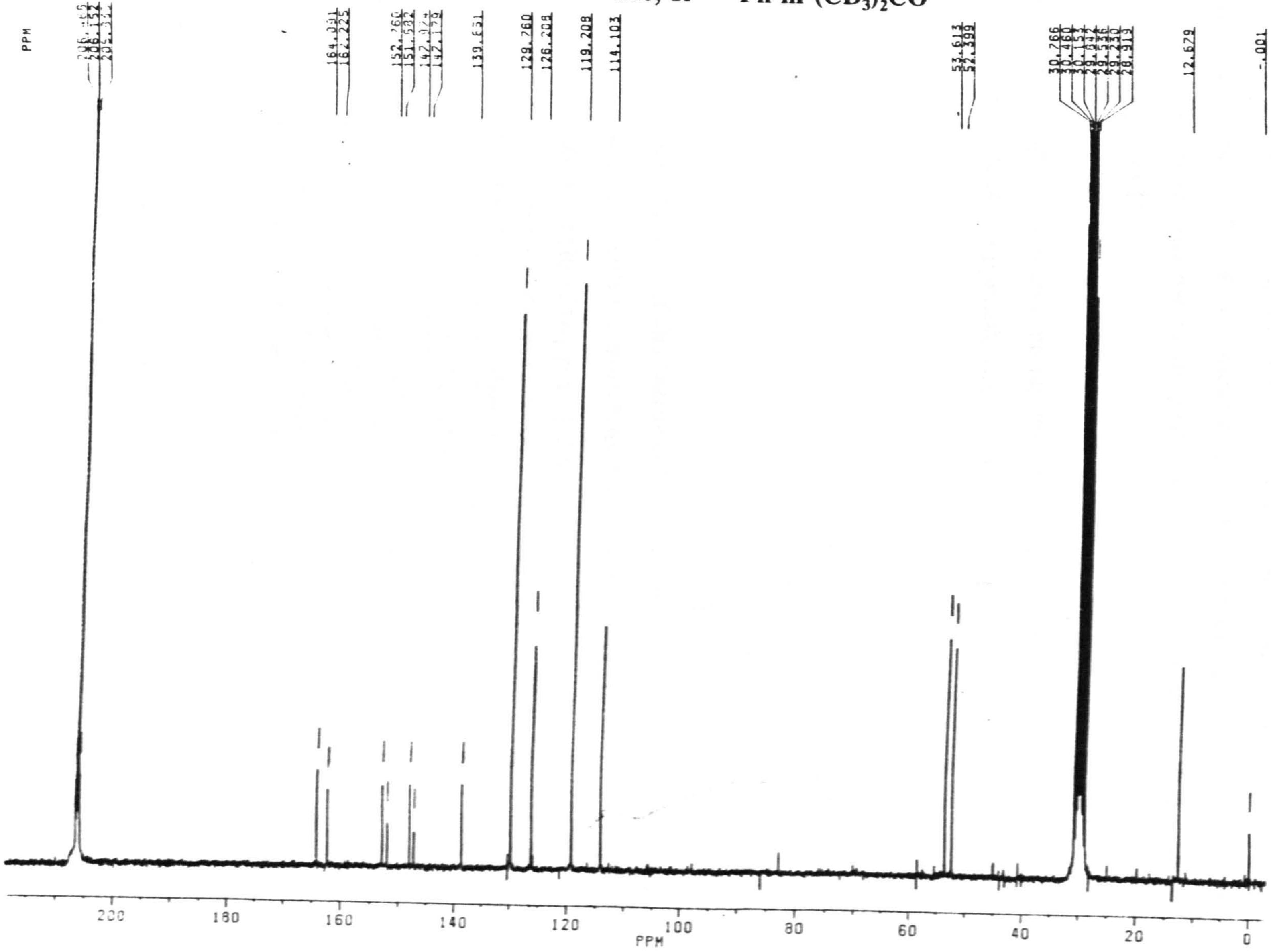


FIGURE 5.4 ^{13}C NMR Spectrum of A^1 where R^2 = Me, R^1 = Ph in $(CD_3)_2CO$



5.4 ANALYSIS OF THE SPECTROSCOPIC DATA OF THE CONDENSATION PRODUCTS

The structure of these compounds have been established by spectroscopic studies which are discussed below. The electron impact mass spectra of the condensation products show prominent parent ion peaks and fragment ions corresponding to the loss of CO and OH•.

The infrared spectrum shows strong absorptions due to the phenolic OH, C=O groups and C=N of the pyrazole ring as shown in Table 5.5.

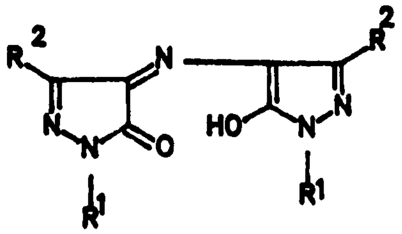


TABLE 5.5 Assignments of the Infrared Bands in the Spectra of 2,4-dehydro-4[(1,3-disubstituted-5-hydroxy-1H-pyrazol-4-yl)imino]2,4-disubstituted-3H-pyrazol-3-one

Condensation Product	*νOH (cm^{-1})*	*νC=O (cm^{-1})*	*νC=N (cm^{-1})*
P^1 (R^1=Ph, R^2=Me)	3440(br)	1731(s,sh)	1619(sh)
P^2 (R^1=Me, R^2=Ph)	3435(br)	1642(sh)	1562(sh)
P^3 (R^1,R^2=Me)	3430(br)	1743(sh)	1639(sh)
P^4 (R^1=H, R^2=Me)	3128(br)	1653(sh)	1604(sh)

(sh)=sharp (s)=strong (br)=broad

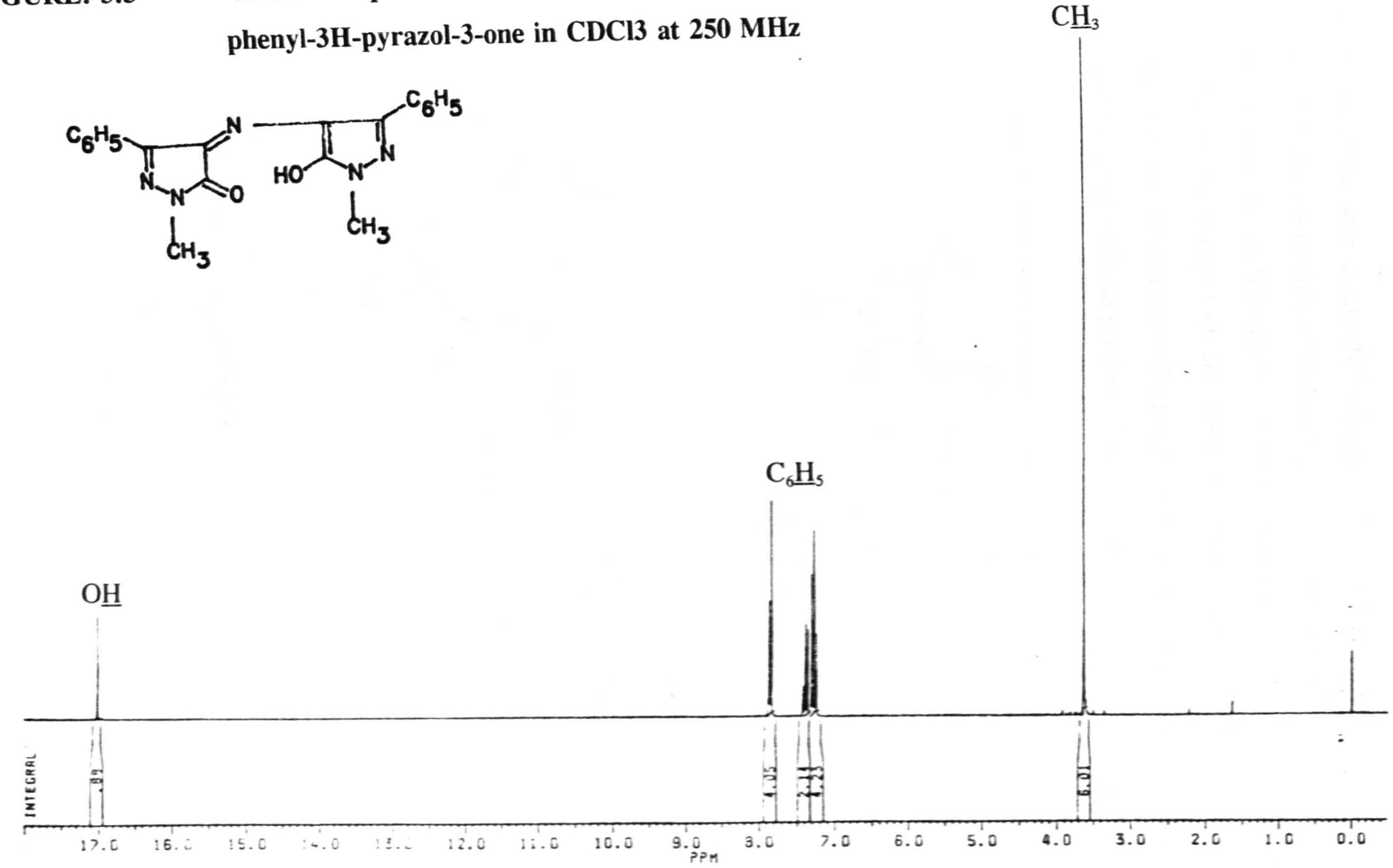
The C=N stretching of the oxime group, which usually appears as a weak band in the range of 1690-1640 cm^{-1}, is difficult to identify as it is overlapped by the strongly intense C=C vibrations. It is noteworthy to mention that the peak due to the phenolic hydroxyl group is broad and at lower wavenumbers (3440-3128 cm^{-1}) (the free phenolic hydroxyl group appears at 3650-3590 cm^{-1}) indicating intramolecular hydrogen - bonding to the carbonyl oxygen making up part of an eight - membered ring. Also the $\nu C=O$ stretching in these compounds appears at higher values in comparison to the free ligand (§Chapter 4). This may be due to the reduction in the bond order of the C=O group in the free ligand resulting from the tautomeric behaviour thereby resulting in the lengthening of the carbon-oxygen bond.

Finally, the structure of the product is established by NMR spectroscopy.The ^{1}H-NMR spectrum of 2,4-dehydro-4[(5-hydroxy-1-methyl-3-phenyl-1H-pyrazol-4-yl)imino]-2-methyl-5-phenyl-3H-pyrazol-3-one is given in Figure 5.5. The methyl protons appear at δ_H 3.65 (6H, s). The aromatic protons appear as *multiplets* at δ_H 7.15 - 7.95 and the phenolic OH proton appears as a *singlet* at a very downfield position at δ_H 17.00 (1H, s) (Ar-O$\underline{H}$ protons normally appear at δ_H 4.5-10.0) thereby indicating a strong intramolecular hydrogen bonding between the carbonyl oxygen and phenolic OH group forming an eight - membered ring (supporting the observations made in their infrared studies). The signals arising due to methyl, aromatic and phenolic OH protons in the other three products are tabulated in Table 5.6.

TABLE 5.6 ^{1}H NMR Chemical Shifts of the Condensation Products in $CDCl_3$ at 250 MHz

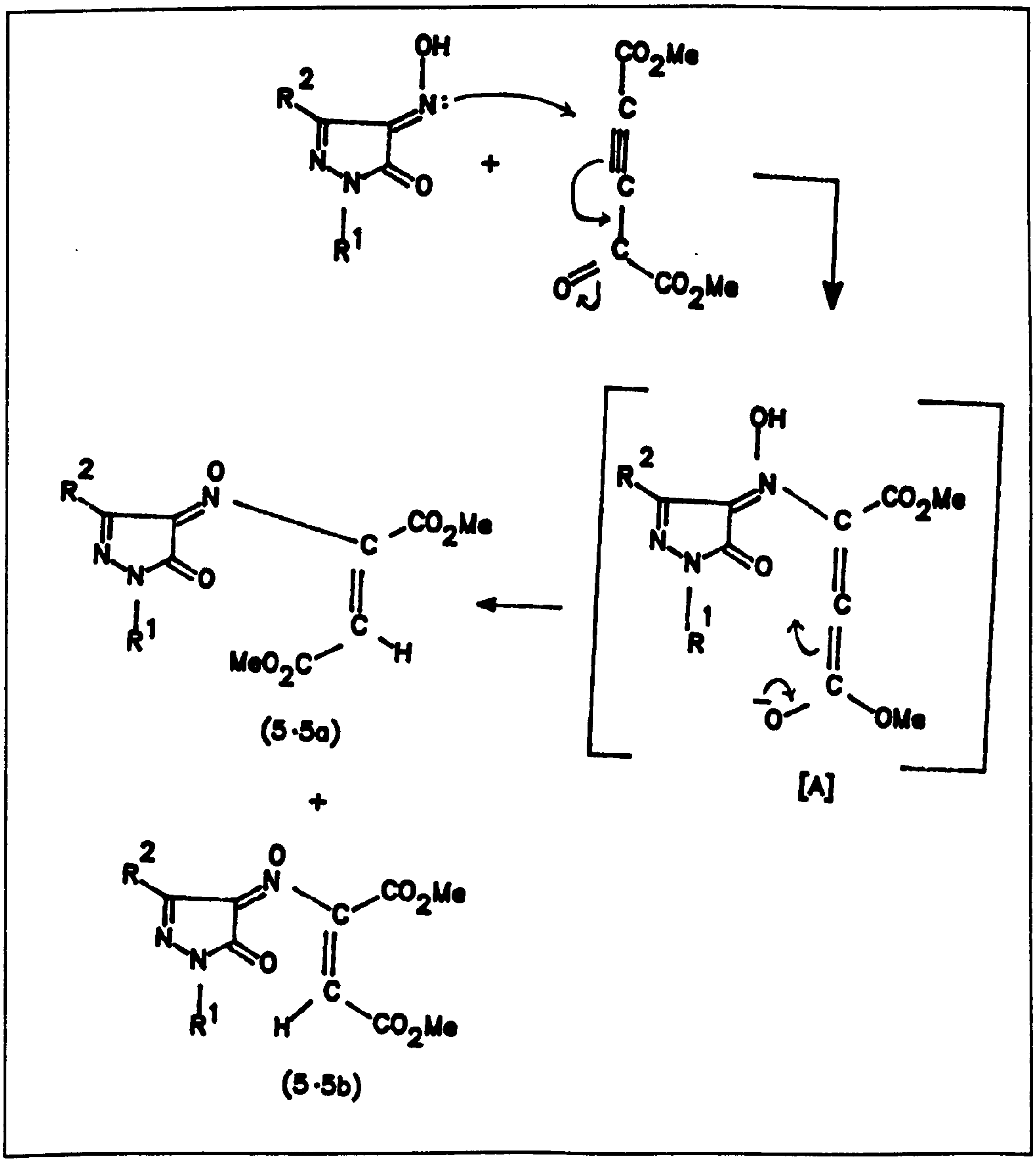
Condensation Products	*δ_H/ppm*		
	R^2	***R^1***	***phenolic OH***
P^1 (R^1=Ph,R^2=Me)	2.26(s)	6.54-7.93(m)	17.46(s)
P^3 (R^1,R^2=Me)	2.22(s)	3.50(s)	17.34(s)
P^4 (R^1=H,R^2=Me)	2.24(s)	12.70(s)	16.75(s)

FIGURE. 5.5 ^{1}H NMR Spectrum of 2,4-dehydro-4[(5-hydroxy-1-methyl-3-phenyl-1H-pyrazol-4-yl)imino]-2-methyl-5-phenyl-3H-pyrazol-3-one in CDCl3 at 250 MHz



5.5 MECHANISTIC APPRAISAL OF THE REACTIONS

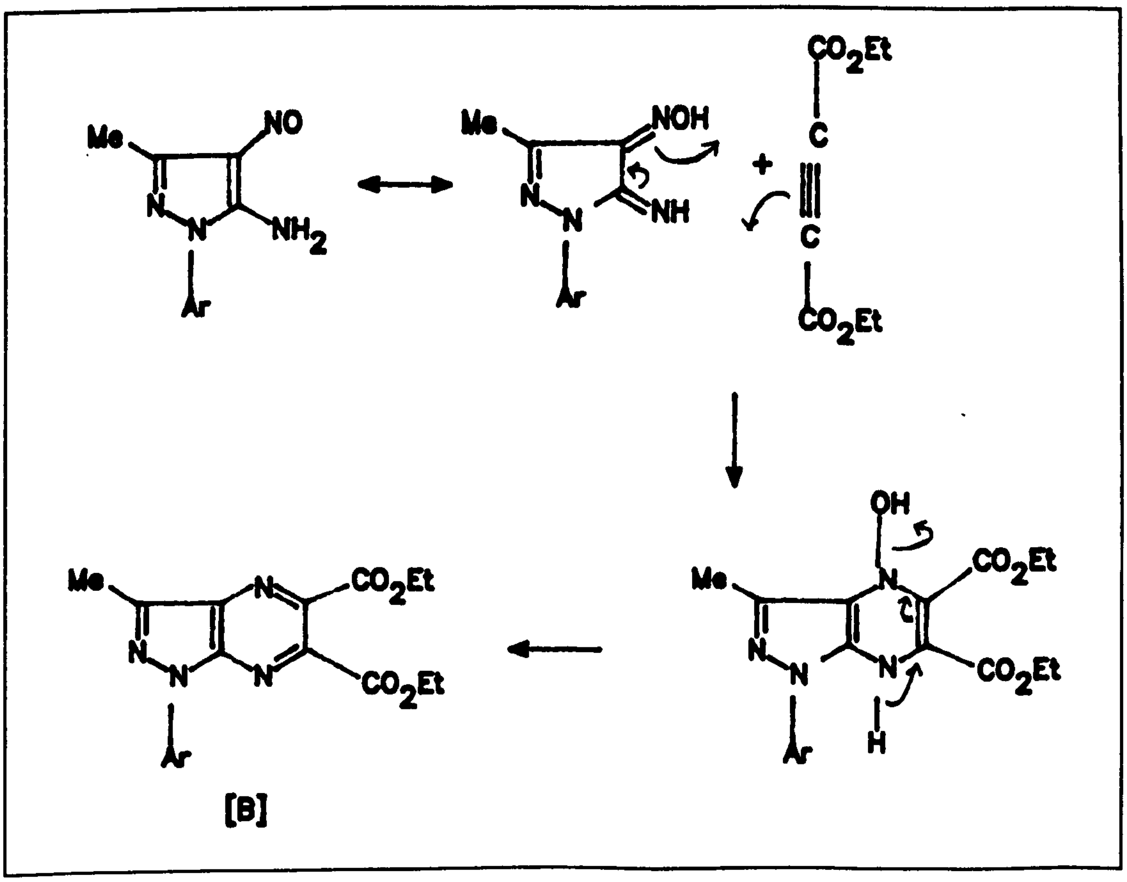
The formation of the open-chain Michael type addition product, from the reactions of pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate, can be rationalised as outlined in Scheme 5.7. The mechanism involves the nucleophilic attack by the oximic nitrogen on the electron-deficient alkyne carbon atom. This leads to the formation of an intermediate ([A], Scheme 5.7) which undergoes proton migration to form the addition product. Two isomers of the latter are expected due



SCHEME 5.7

to geometric isomerism at the vinylic carbon atom. A similar mechanism can also be suggested for the reaction of the lithium complexes of 1,3-dimethyl-1H-pyrazole-4,5-dione 4-oximes with dimethyl acetylenedicarboxylate.

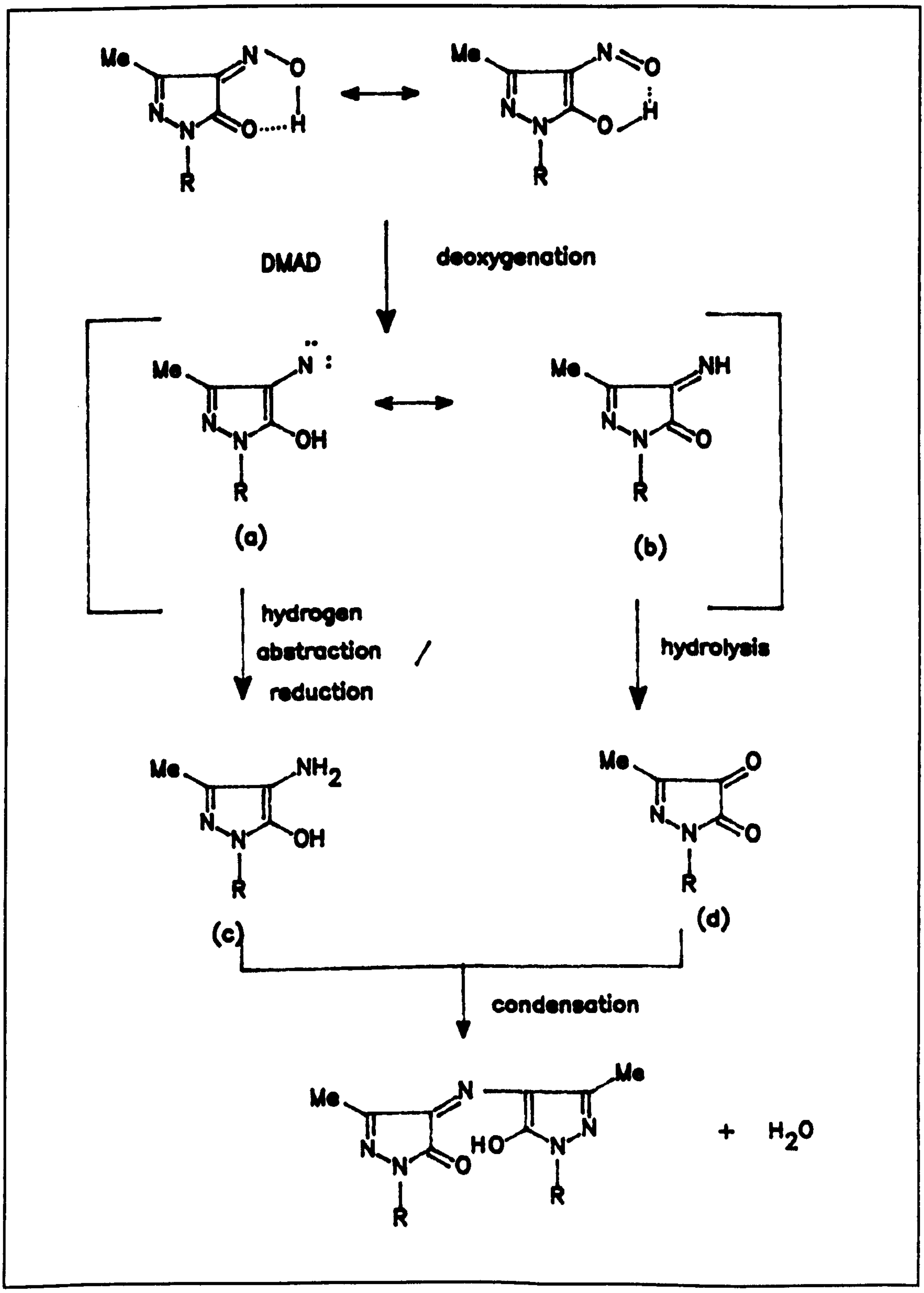
The formation of the pyrazine ([**B**], Scheme 5.8), from the reaction of pyrazole-5-imino-4-oximes with diethyl acetylenedicarboxylate, can be explained by a mechanism which is initiated by the oximic nitrogen atom in a Diel-Alder fashion followed by dehydration (Scheme 5.8). The same reaction was previously explained by an approach involving the attack by the imino nitrogen atom followed by electronic rearrangement and dehydration.[5]



SCHEME 5.8

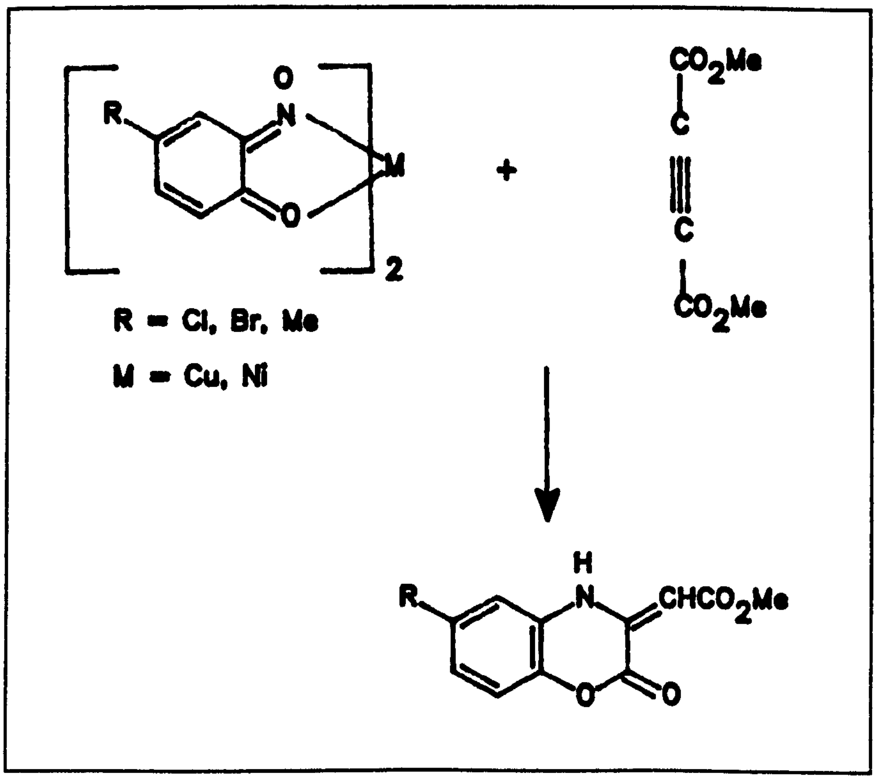
The formation of the condensation products, by the reaction of pyrazole-4,5-dione-5-oxime with dimethyl acetylenedicarboxylate under reflux, can be rationalised in terms of the formal deoxygenation of the ligand by dimethyl acetylenedicarboxylate

(Scheme 5.9) as suggested for the analogous reaction of the oximes with iron pentacarbonyl.[6] The ability of dimethylacetylene dicarboxylate to act as a



SCHEME 5.9

deoxygenating reagent has been noted earlier in their reactions with 4-chloro-, 4-bromo- and 4-methyl-1,2-benzoquinone 2-oximes to form 1,4-benzoxazinones (Reaction 5.3).[4] The mechanism proposed in Scheme 5.9 involves *STEP 1* an initial step of deoxygenation of pyrazole-4,5-dione-4-oxime by dimethylacetylene dicarboxylate resulting in the intermediate nitrene (5.9a) - quinone imine (5.9b). *STEP 2* The nitrene intermediate undergoes hydrogen abstraction/reduction to form the amine (5.9c) and the quinone-imine tautomer undergoes hydrolysis to form the dione (5.9d). *STEP 3* Condensation of the amine (5.9c) with the dione (5.9d) gives the desired condensation product.

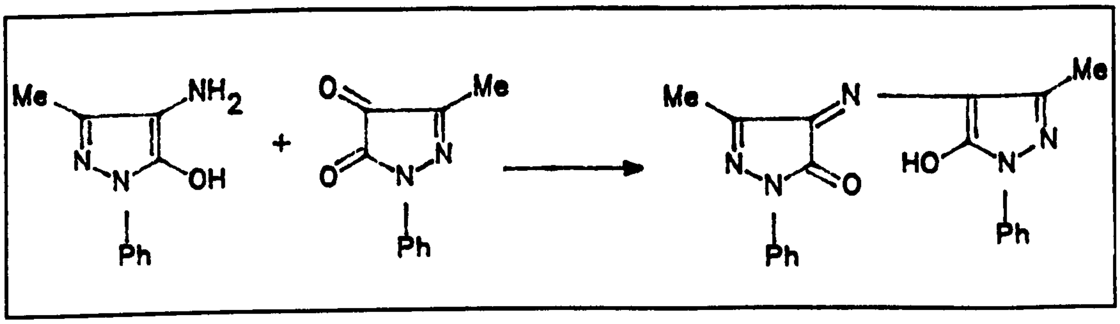


REACTION 5.3

The involvement of dimethyl acetylenedicarboxylate as the deoxygenating agent in *STEP 1* is indicated by the lack of any reaction when pyrazole-4,5-dione-4-oxime was refluxed in the absence of dimethyl acetylenedicarboxylate for 4 hours.

Support for *STEP3* is provided by the established synthesis of 2,4-dehydro-4[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-

one by the condensation of 4-amino-5-hydroxy-3-methyl-1-phenyl-1H-pyrazole (5.9c, R = Ph) with 3-methyl-1-phenyl-1H-pyrazol-4,5-dione[10] (5.9d, R = Ph) (Reaction 5.4).



REACTION 5.4

A related alkyne, acetylenedicarboxylic acid, was also found to exhibit similar deoxygenating ability. When 1-methyl-3-phenyl- and 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime was refluxed with acetylenedicarboxylic acid for 24 hours, the condensation product was obtained. However, acetylene dicarboxylic acid did not react with pyrazole-4,5-dione-4-oximes at room temperature.

The reactions of 1,2-quinone monooximes and pyrazole-4,5-dione-4-oximes with dimethyl acetylenedicarboxylate can be summarised as follows: at mild temperatures (0 - 40°C), both the oximes give the open chain adducts which are isomeric to each other. However, at higher temperatures completely different products are obtained. 1,2-Quinone monooximes result in cycloadducts at higher temperatures whereas pyrazole-4,5-dione-4-oximes give Schiff base condensation products. Also the open chain adducts formed from 1,2-naphthaquinone 1-oxime can be converted to the corresponding 1,4-oxazine when heated under reflux but similar reactions with the adducts formed from pyrazole-4,5-dione-4-oximes give the corresponding condensation products.

5.6 REFERENCES

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CHAPTER VI

EXPERIMENTAL

CONTENTS

6.1 GENERAL

All the reagents used in this study were of G.P.R. grade. Solvents were used as purchased, except when used for chromatographic purposes they were redistilled. For column chromatography, silica gel (0.0063 - 0.200 mm, 70 - 230 mesh) obtained from BDH Merck was used as the stationary phase. Thin layer chromatography (TLC) was performed using commercially supplied silica gel plates.

The monooximes of 1,2-naphthaquinone were obtained commercially from Aldrich Chemical Company Ltd. 5-Ethylamino-4-methyl-1,2-benzoquinone 2-oxime was prepared by the method described by Thomas.[1] The nitrosation of pyrazole-5-ones were achieved by the standard nitrosation procedure using sodium nitrite / acetic acid.[2] The pyridine adducts of the manganese(II), nickel(II), copper(II) and zinc(II) were prepared by the method employed by Hovorka and Sücha.[3]

6.2 ANALYTICAL

Infra-red Spectra

Infra-red spectra, in the region 4000 - 400 cm^{-1}, were recorded on a *Bio-rad FTS-40* spectrophotometer. The spectra were recorded mainly as KBr discs.

NMR Spectra

High resolution fourier transform ^1H NMR spectra were recorded on a *Bruker AM250* NMR spectrometer at 250 MHz for ^1H and 60.1 MHz for ^{13}C. Trimethylsilane was used as the internal standard.

Melting points

Melting points were recorded on an *Electrothermal* digital melting point aparatus.

Mass spectra

Mass spectra for both EI and LSIMS methods were recorded on a *Kratos Analytical* mass spectrometer. The LSIM spectra of the metal complexes were recorded by using a caesium ion source. Glycerol or 3-nitrobenzyl alcohol was used as matrix.

Magnetic moment measurements

Room temperature magnetic susceptibilities were measured by using a Johnson Matthey balance. The instrument was calibrated with a mercury tetrathiocyanatocobaltate(II), the measurements were carried out in duplicate and the magnetic susceptibilities were corrected for diamagnetism of the ligand.[4]

HPLC measurements

HPLC measurements were carried out by Drew Scientific Data Station using a Philips Unicam PU4000 HPLC with a UV detector at a wavelength of 254 cm^{-1} connected to the column which was Spherisorb C18 (250 mm long and 4 mm in internal diameter). The flow rate was 1 cc/min and the volume of injection used was 20 μL. The eluant used was 60% aqueous methanol.

X-Ray Crystallography

X-ray crystallography data were collected on a Philips PW1100 four-circle diffractometer and Enraf-Nonius CAD-4 diffractometer using Mo-Kα and Cu-Kα radiation respectively.

Elemental Analysis

Carbon, hydrogen and nitrogen analysis were carried out on a *Carlo Erba 1160* microanalytical aparatus.

6.3 REACTIONS

1) Reactions of 1,2-quinone monooximes with alkali metal hydroxides in aqueous ethanol in the molar ratio of 1:1

(For % yield, analytical and other data, see Table 6.1)

a) 1,2-naphthaquinone 1-oxime / sodium and potassium hydroxides

A solution of 1,2-naphthaquinone 1-oxime (1.50 g, 8.6 mmol) in aqueous ethanol (75 cm^3) was added dropwise and with continuous stirring to a solution of sodium hydroxide (0.34 g, 8.6 mmol) in aqueous ethanol (20 cm^3). The resultant mixture was heated to 65°C for 3 h and then filtered under suction to give green (1,2-naphthaquinone 1-oximato)sodium(I).dihydrate (1.51 g) which was washed with ethanol (15 cm^3) and petroleum ether (b.p. 40 - 60°C) (25 cm^3) and dried at 25°C / 1.0 mm.

Similarly potassium hydroxide (0.48 g, 8.6 mmol) and 1,2-naphthaquinone 1-oxime (1.50 g, 8.6 mmol) gave green (1,2-naphthaquinone 1-oximato)potassium(I).½ethanol (1.44 g).

b) 1,2-naphthaquinone 2-oxime / sodium and potassium hydroxides

A solution of 1,2-naphthaquinone 2-oxime (3.20 g, 18.5 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of sodium hydroxide (0.70 g, 18.5 mmol) in aqueous ethanol (15 cm^3). The resultant solution was heated to 65°C for 3 h. On slow evaporation, the mixture gave brown (1,2-naphthaquinone 2-oximato)sodium(I).dihydrate (3.04 g) which was washed with ethanol (15 cm^3) and petroleum ether (b.p. 40 - 60°C) (30 cm^3) and dried at 25°C / 1.0 mm.

Similarly, 1,2-naphthaquinone 2-oxime (3.20 g, 18.5 mmol) and potassium hydroxide (1.10 g, 18.5 mmol) in aqueous ethanol yielded (1,2-naphthaquinone 2-oximato)potassium(I).½ethanol) (2.90 g).

c) 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime / lithium, sodium and potassium hydroxide

A solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (3.49 g, 19.4 mmol) in aqueous ethanol (100 cm^3) was added to a solution of lithium hydroxide monohydrate (0.85 g, 19.4 mmol) in aqueous ethanol (15 cm^3) dropwise and with continuous stirring. The reaction mixture was heated to 65°C for 3 h and slow evaporation of the resulting solution gave red crystalline *aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)lithium(I)* (2.75 g) which was filtered off and washed with petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 5-ethylamino-4-methyl-1,2-benzoquinoe 2-oxime (3.50 g, 19.4 mmol) and sodium hydroxide (0.78 g, 19.4 mmol) in aqueous ethanol (115 cm^3) gave red *(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)sodium(I).dihydrate* (3.32 g).

A similar reaction of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (3.50 g, 19.4 mmol) and potassium hydroxide (1.10 g, 19.4 mmol) in aqueous ethanol (115 cm^3) yielded red *(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)potassium(I). dihydrate* (3.50 g).

TABLE 6.1 **Yield, Analytical and Other Data for the Alkali Metal Complexes formed by the reaction of metal hydroxide and the ligand in the molar ratio of 1:1**

Formula	*% yield*	*Analysis Found (Calc.) (%)*				*Melting point (°C)*
		C	*H*	*N*	*M*	
(1-nqo)Na.2H_2O	75	50.9 (51.9)	4.2 (4.3)	5.8 (6.1)	9.4 (10.0)	308-311 (decomp.)
(1-nqo)K.½EtOH	71	56.8 (56.4)	3.9 (3.8)	6.0 (6.0)	16.0 (16.7)	293-294 (decomp.)
(2-nqo)Na.2H_2O	71	51.1 (51.9)	4.2 (4.3)	6.0 (6.1)	9.5 (10.0)	301-303 (decomp.)
(2-nqo)K.½EtOH	67	55.4 (56.4)	3.2 (3.8)	5.2 (6.0)	15.9 (16.7)	290-292 (decomp.)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)*	74	52.8 (53.5)	6.6 (6.4)	13.7 (13.9)	1.9 (1.7)	180-181
(5-Et-4-Meqo)Na.2H_2O*	72	44.8 (45.2)	6.3 (6.3)	11.5 (11.8)	9.2 (9.6)	200-202
(5-Et-4-Meqo)K.2H_2O*	71	42.0 (42.4)	5.7 (5.9)	10.2 (10.9)	14.9 (15.3)	214-215

*New compounds

2) *Reactions of 1,2-quinone monooximes with alkali metal hydroxides in aqueous ethanol in the molar ratio of 2:1*
(For % yield, analytical and other data, see Table 6.2)

a) <u>1,2-naphthaquinone 1-oxime / sodium and potassium hydroxides</u>

A solution of 1,2-naphthaquinone 1-oxime (3.50 g, 20.2 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of sodium hydroxide (0.40 g, 10.1 mmol) in aqueous ethanol (15 cm^3). The resultant solution was heated to 65°C for 4 h and filtered under suction to give green (1,2-naphthaquinone 1-oxime)(1,2-naphthaquinone 1-oximato)sodium(I).ethanol (2.51 g) which was washed with ethanol (15 cm^3) and petroleum ether (b.p. 40 - 60°C) (30 cm^3) and dried at 20°C / 1.0 mm.

Similarly 1,2-naphthaquinone 2-oxime (3.50 g, 20.2 mmol) and potassium hydroxide (0.60 g, 10.1 mmol) in aqueous ethanol (115 cm^3) yielded the green (1,2-naphthaquinone 1-oxime)(1,2-naphthaquinone 1-oximato)potassium(I).ethanol (3.04g).

b) 1,2-naphthaquinone 2-oxime / sodium and potassium hydroxide

A solution of 1,2-naphthaquinone 2-oxime (3.50 g, 20.2 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of sodium hydroxide (0.40 g, 10.1 mmol) in aqueous ethanol (15 cm^3). The mixture was heated to 65°C for 4 h and filtered under suction to give brown (1,2-naphthaquinone 2-oxime)(1,2-naphthaquinone 2-oximato)sodium(I).ethanol (2.63 g) which was washed with ethanol (5 cm^3) and petroleum ether (b.p. 40 - 60°C) (25 cm^3) and dried at 25°C / 1.0 mm.

(1,2-naphthaquinone 2-oxime)(1,2-naphthaquinone 2-oximato)potassium(I).ethanol (2.52 g) was obtained by the similar reaction of 1,2-naphthaquinone 2-oxime (3.50g, 20.2 mmol) and potassium hydroxide (0.60 g, 10.1 mmol) in ethanol (115 cm^3).

c) 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime / lithium, sodium and potassium hydroxide

A solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (1.37 g, 7.5 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of lithium hydroxide monohydrate (0.16 g, 3.8 mmol) in aqueous ethanol (15 cm^3) and the solution was heated to 65°C for 4 h. The slow evaporation of the mixture gave red crystalline *bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)lithium(I).1½*H_2O (1.13 g) which was washed with petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (2.60 g, 14.4 mmol) and sodium hydroxide (0.30 g, 7.5 mmol) in aqueous ethanol (115 cm^3) gave red *aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)sodium(I)* (2.08 g).

Analogous reaction of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (1.90 g, 10.5 mmol) and potassium hydroxide (1.10 g, 19.4 mmol) in aqueous ethanol (115 cm^3) gave red *aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)potassium(I)* (1.55 g).

TABLE 6.2 Yield, Analytical and Other Data for the Alkali Metal Complexes formed by the reaction of metal hydroxide and the ligand in the molar ratio of 1:2

Formula	*% yield*	*Analysis Found (Calc.) (%)*				*Melying point (°C)*
		C	*H*	*N*	*M*	
Na(1-nqo)(1-nqoH)(EtOH)	60	62.3 (63.8)	3.1 (4.6)	7.1 (6.8)	6.5 (5.5)	300 -301 (decomp.)
K(1-nqo)(1-nqoH)(EtOH)	70	61.0 (61.4)	3.1 (4.4)	6.9 (6.5)	10.4 (9.0)	240 - 242 (decomp.)
Na(2-nqo)(2-nqoH)(EtOH)	63	61.3 (63.8)	3.9 (4.6)	7.0 (6.8)	6.0 (5.5)	170 -171 (decomp.)
K(2-nqo)(2-nqoH)(EtOH)	58	62.8 (61.4)	3.5 (4.4)	6.9 (6.5)	9.6 (9.0)	331 -332 (decomp.)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O*	78	56.0 (55.4)	6.4 (6.7)	14.7 (14.4)	1.2 (1.2)	146 - 147
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)*	72	52.6 (53.7)	6.1 (5.7)	13.7 (13.9)	5.3 (5.7)	141 - 142
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)*	71	50.8 (51.6)	6.0 (6.0)	12.4 (13.4)	9.0 (9.3)	180 -181

*New compounds

3) *Reactions of 1,2-quinone monooximes with alkali metal hydroxides in aqueous ethanol in the molar ratio of 3:1*

(For % yield, analytical and other data, see Table 6.3)

a) 1,2-naphthaquinone 1-oxime / lithium, sodium and potassium hydroxides

A solution of 1,2-naphthaquinone 1-oxime (1.38 g, 8.0 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of lithium hydroxide monohydrate (0.11 g, 2.6 mmol) in aqueous ethanol (15 cm^3) and heated to 65°C for 4 h. On slow evaporation of the solution, the green (1,2-naphthaquinone 1-oxime)(1,2-naphthaquinone 1-oximato)lithium(I).ethanol (1.11 g) was obtained which was washed with ethanol (15 cm^3) and petroleum ether (b.p. 40 - 60°C) (25 cm^3) and dried at 25°C/ 1.0 mm.

Similarly 1,2-naphthaquinone 1-oxime (1.47 g, 8.50 mmol) and sodium hydroxide (0.11 g, 2.8 mmol) in aqueous ethanol (115 cm^3) gave (1,2-naphthaquinone 1-oxime)(1,2-naphthaquinone 1-oximato)sodium(I).ethanol (0.61 g).

(1,2-naphthaquinone 1-oxime)(1,2-naphthaquinone 1-oximato)potassium(I).ethanol (0.88 g) was obtained by the reaction of 1,2-naphthaquinone 1-oxime (1.74 g, 10.1 mmol) and potassium hydroxide (0.18 g, 3.2 mmol) in aqueous ethanol (115 cm3).

b) 1,2-naphthaquinone 2-oxime / lithium hydroxide

A solution of 1,2-naphthaquinone 2-oxime (1.50 g, 8.7 mmol) in aqueous ethanol (100 cm^3) and lithium hydroxide monohydrate (0.12 g, 2.9 mmol) in aqueous ethanol (15 cm^3) were heated to 65°C for 4 h. The slow evaporation of the resultant solution gave brown (1,2-naphthaquinone 2-oxime)(1,2-naphthaquinone 2-oximato)lithium(I). ethanol (0.77 g) which was washed with ethanol (5 cm^3) and petroleum ether (b.p. 40 - 60°C) (25 cm^3) and dried at 25°C / 1.0 mm.

c) 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime / lithium, sodium and potassium hydroxide

A solution of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (3.90 g, 21.5 mmol) in aqueous ethanol (150 cm^3) was added portionwise and with continuous stirring to a solution of lithium hydroxide monohydrate (0.30 g, 7.1 mmol) in aqueous ethanol (25 cm^3) and the resultant solution was heated to 65°C for 4 h. On slow evaporation of the solution red crystalline *bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)lithium(I).1½*H_2O (3.7 g) was obtained which was washed with petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

A similar reaction of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (1.28 g, 7.1 mmol) and sodium hydroxide (0.90 g, 2.3 mmol) in aqueous ethanol (115 cm^3) gave red *aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)sodium(I)* (0.89 g).

Simiarly 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (0.94 g, 5.2 mmol) and potassium hydroxide (0.10 g, 1.8 mmol) in aqueous ethanol (115 cm^3) gave red *aquo(5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)potassium(I)* (0.56 g).

4) Reaction of 1,2-naphthaquinone 1-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime with barium hydroxide octahydrate in aqueous ethanol in the molar ratio of 2:1

A solution of 1,2-naphthaquinone 1-oxime (1.11 g, 6.4 mmol) in aqueous ethanol (180 cm^3) was added to a solution of barium hydroxide octahydrate (1.00 g, 3.3 mmol) in aqueous ethanol (25 cm^3) portionwise and with continuous stirring. The reaction mixture was heated to 65°C for 4 h and filtered under suction to give green *bis(1,2-naphthaquinone 1-oximato)barium(II).dihydrate* [1.4 g, 84%; Found: C, 46.3, H, 2.9, N, 5.2%. $BaC_{20}H_{16}N_2O_6$ requires C, 46.4, H, 3.1, N, 5.1%. νCO 1620 cm^{-1}, m.p. 310-311°C(decomp.) νOH 3444 cm^{-1}] which was washed with ethanol (10 cm^3) and petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

TABLE 6.3 Yield, Analytical and Other Data for the Alkali Metal Complexes formed by the reaction of metal hydroxide and the ligand in the molar ratio of 1:3

Formula	*% yield*	*Analysis* *C*	*Found (Calc.) (%)* *H*	*N*	*M*
Li(1-nqo)(1-nqoH)(EtOH)	70	68.1 (66.3)	4.2 (4.5)	7.9 (7.0)	1.9 (1.8)
Na(1-nqo)(1-nqoH)(EtOH)	35	63.7 (63.8)	3.2 (4.6)	7.4 (6.8)	6.3 (5.5)
K(1-nqo)(1-nqoH)(EtOH)	41	58.7 (61.4)	3.2 (4.4)	7.0 (6.5)	9.6 (9.0)
Li(2-nqo)(2-nqoH)(EtOH)	45	63.5 (66.3)	4.1 (4.5)	7.0 (7.0)	1.8 (1.8)
Li(5-Et-4-Meqo)(5-Et-4-MeqoH)$_2$.1½H_2O*	90	55.8 (55.4)	6.3 (6.7)	14.1 (14.4)	1.1 (1.2)
Na(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)*	63	53.5 (53.7)	5.6 (5.7)	13.8 (13.9)	5.8 (5.7)
K(5-Et-4-Meqo)(5-Et-4-MeqoH)(H_2O)*	52	51.5 (51.6)	6.0 (6.0)	13.0 (13.4)	9.0 (9.3)

*New compounds

Similarly 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (2.00 g, 11.0 mmol) barium hydroxide octahydrate (1.64 g, 5.5 mmol) gave red *bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)barium(II).dihydrate* [2.3g, 79%; Found: C, 39.9, H, 4.6, N, 10.4%. $BaC_{18}H_{26}N_4O_6$ requires C, 40.5, H, 4.9, N, 10.5%; m.p. 280°C (decomp.); νCO 1625 cm^{-1}, νOH 3450 cm^{-1}].

5) *Reaction of 1,2-naphthaquinone 1-oxime and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime with magnesium acetate tetrahydrate in aqueous ethanol in different molar ratios*

A solution of 1,2-naphthaquinone 1-oxime (2.97 g, 17.2 mmol) in aqueous ethanol (100 cm^3) was added to a suspension of magnesium acetate tetrahydrate (1.85 g, 8.6

mmol) in aqueous ethanol (25 cm^3) dropwise and with continuous stirring at 65°C for 4 h. The slow evaporation of the solution gave green *bis(1,2-naphthaquinone 1-oximato)magnesium(II).dihydrate* [2.90 g, 83%; Found: C, 58.9, H, 3.5, N, 6.2%, $C_{20}H_{16}N_2MgO_6$ requires C, 59.4, H, 3.9, N, 6.9%; m.p 328°C (decomp.) νCO 1625 cm^{-1}, νOH 3550 cm^{-1}] which was washed with ethanol (5 cm^3) and petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (1.06 g, 5.9 mmol) and magnesium acetate tetrahydrate (0.64 g, 2.9 mmol) in aqueous ethanol (115 cm^3) gave yellow *bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)magnesium(II).dihydrate* [0.7g, 59%; Found: C, 51.7, H, 6.1, N, 13.6 Mg, 5.6%. $C_{18}H_{26}N_4MgO_6$ requires C, 51.4, H, 6.2, N, 13.3 Mg, 5.7%; m.p 310 - 311°C (decomp.); νCO 1625 cm^{-1}, νOH 3247 cm^{-1}].

Analogous reaction of 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime (1.53 g, 8.5 mmol) and magnesium acetate tetrahydrate (0.61 g, 2.8 mmol) gave the yellow *bis(5-ethylamino-4-methyl-1,2-benzoquinone 2-oximato)magnesium(II).dihydrate* [1.1g, 62%; Found: C, 53.0, H, 6.1, N, 12.8 Mg, 5.4%. $C_{18}H_{26}N_4MgO_6$ requires C, 51.4, H, 6.2, N, 13.3 Mg, 5.7%].

5) Reaction of lithium, sodium and potassium hydroxide with 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime in aqueous ethanol in the molar ratio of 1:1 (See Table 6.4 for % yield, analytical and other data)

A solution of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.42 g, 1.0 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of lithium hydroxide monohydrate (0.42 g, 1.0 mmol) in aqueous ethanol (25 cm^3) and the solution was heated at 65°C for 4 h. Concentration of the resultant solution gave yellow *(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)lithium(I).dihydrate* (1.47 g) which was washed with ethanol (5 cm^3) and petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.47 g, 10.4 mmol) in aqueous ethanol and sodium hydroxide (0.42 g, 10.5 mmol) gave yellow *(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)sodium(I).dihydrate* (1.70 g).

Analogous reaction of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (0.85 g, 6.0 mmol) and potassium hydroxide (0.36 g, 6.5 mmol) gave yellow *(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)potassium(I).monohydrate* (0.92 g).

6) *Reaction of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime with lithium, sodium and potassium hydroxide in aqueous ethanol in the molar ratio of 2:1*

(See Table 6.4 for % yield, analytical and other data)

A solution of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.55 g, 10.9 mmol) in aqueous ethanol (100 cm^3) was added dropwise and with continuous stirring to a solution of lithium hydroxide monohydrate (0.23 g, 5.5 mmol) in aqueous ethanol (15 cm^3). The resultant solution was heated at 65°C for 4 h and its slow evaporation gave yellow *bis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime)lithium(I).dihydrate* (1.31 g) which was washed with petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.69 g, 11.9 mmol) and sodium hydroxide (0.23 g, 5.8 mmol) gave yellow *(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime)sodium(I).dihydrate* (0.88 g)

Analogous reaction of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.46 g, 10.3 mmol) and potassium hydroxide (0.29 g, 5.6 mmol) gave yellow *(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime)potassium(I)dihydrate* (0.90 g).

TABLE 6.4 Yield, Analytical and Other Data for the Alkali Metal Complexes formed by the reaction of metal hydroxide and the ligand in the molar ratio of 1:2

Formula	*% yield*	*Analysis Found (Reqd.) (%)*				*Melting point (°C)*
		C	*H*	*N*	*M*	
Li(Mpo).$2H_2O$	80	32.2 (32.8)	4.9 (5.5)	19.9 (22.9)	3.6 (3.8)	238-240
Li(Mpo)(MpoH). $2H_2O$	78	36.7 (37.0)	3.9 (4.3)	22.1 (25.9)	2.0 (2.2)	131-133
Na(Mpo).$2H_2O$	82	28.8 (27.6)	4.7 (5.5)	16.1 (19.4)	10.5 (10.5)	292-293
Na(Mpo)(MpoH). $2H_2O$	73	32.3 (35.3)	4.0 (4.7)	20.0 (24.7)	6.2 (6.8)	299-300
K(Mpo).H_2O	78	29.4 (30.5)	3.5 (4.0)	17.0 (21.3)	16.9 (19.7)	296-297
K(Mpo)(MpoH). $2H_2O$	72	33.5 (33.7)	4.0 (4.5)	21.5 (24.7)	10.1 (10.9)	288-289

7) Reaction of magnesium acetate tetrahydrate and barium hydroxide octahydrate with 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (MpoH) in the molar ratio of 1:2

A solution of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.0 g, 7.1 mmol) in aqueous ethanol (100 cm^3) was added to a solution of magnesium acetate tetrahydrate (0.76 g, 3.5 mmol) in aqueous ethanol (25 cm^3) dropwise and with continuous stirring. The mixture was heated at 65°C for 4 h and its slow evaporation gave yellow *bis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)magnesium(II).dihydrate* [1.0g, 83%; Found: C, 35.3, H, 4.7, N, 24.8, Mg, 6.9% $C_{10}H_{16}MgN_6O_6$ requires C, 35.3, H, 4.7, N, 24.7, Mg, 7.1%; m.p. 240°C (decomp.) νCO 1649 cm^{-1}, νOH 3241 cm^{-1}] which was washed with ethanol (5 cm^3) and petroleum ether (b.p. 40 - 60°C) (40 cm^3) and dried at 25°C / 1.0 mm.

Similarly 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (1.00 g, 7.1 mmol) and barium hydroxide octahydrate (1.11 g, 3.5 mmol) in aqueous ethanol (115 cm^3) gave yellow *bis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)barium(II).dihydrate* [1.20g, 75%; Found: C, 26.3, H, 3.4, N, 18.7, Ba, 29.9%. $BaC_{10}H_{16}N_6O_6$ requires C, 26.5, H, 3.5, N, 18.5, Ba, 30.2%; m.p. 305-307°C (decomp.); νCO 1624 cm^{-1}, νOH 3429-3388 cm^{-1}].

8) *Reaction of magnesium acetate tetrahydrate and barium hydroxide octahydrate with 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime (1-PpoH) in the molar ratio of 1:2*

3-Methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime (1.00 g, 4.9 mmol) in ethanol (100 cm^3) and magnesium acetate tetrahydrate (0.52 g, 2.5 mmol) in aqueous ethanol (25 cm^3) were reacted as in experiment 7 to give yellow *bis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)magnesium(II).dihydrate* [0.75 g, 65%; Found: C, 51.8, H, 4.4, N, 18.1, Mg, 5.0% $C_{20}H_{20}MgN_6O_6$ requires C, 51.7, H, 4.3, N, 18.1, Mg, 5.2%; m.p. 320 (decomp.) νCO 1650 cm^{-1}, νOH 3421 cm^{-1}]

Similarly 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime (1.00 g, 4.9 mmol) and barium hydroxide octahydrate (0.78 g, 2.5 mmol) gave yellow *bis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)barium(II).dihydrate* [0.90 g, 63%; Found: C, 39.2, H, 2.8, N, 13.4, Ba, 23.5%. $BaC_{20}H_{20}N_6O_6$ requires C, 41.6, H, 3.5, N, 14.6, Ba, 23.7%; m.p. 235-236°C (decomp.); νCO 1650 cm^{-1}, νOH 3410 cm^{-1}].

9) *Reaction of (1,2-napthaquinone 1-oximato)sodium(I).dihydrate with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1*

DMAD (1.46 g, 10.3 mmol) dissolved in EGDE (10 cm^3) was added to a suspension of (1,2-naphthaquinone 1-oximato)sodium(I).dihydrate (1.12 g, 5.1 mmol) in EGDE-water (7:1) (50 cm^3) and the mixture was stirred at -75°C for 4 h. Filtration under gravity gave a white solid (0.02g) and a dark brown filtrate (multicomponent by t.l.c.). The residue obtained after removal of the solvent was chromatographed on silica. Elution with toluene gave a yellow eluate from which orange yellow (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (0.92 g, 58%) (m.p. 101 - 103°C) (Lit.[5] 104 - 106°C) (identified by comparative ir study) was obtained on concentration. Further elution with dichloromethane, ethyl acetate, acetone and methanol gave multicomponent eluates.

Simiarly (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime was also obtained by using the same quantities of the reagents at 0, 20 and 50°C for 3, 2 and 1½ h in 56, 53 and 5% yield respectively.

10) Reaction of (1,2-naphthaquinone 1-oximato)potassium(I).½ethanol with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1.

DMAD (1.37 g, 9.6mmol) in EGDE (10 cm^3) was added to a suspension of (1,2-naphthaquinone 1-oximato)potassium(I).½EtOH (1.10 g, 4.8mmol) in EGDE - water (7:1) (50 cm^3) and stirred for 4 h at -75°C. Using the isolation technique described in experiment 9, (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (0.75 g, 50%) (identified by comparative t.l.c. and i.r.) was obtaineded.

Similarly (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime was obtained by using the same quantities of the reagents at 0, 20 and 50°C for 3, 2 and 1½ h in 48, 34 and 6% yield respectively.

11) Reaction of bis(1,2-naphthaquinone 1-oximato)barium(II).dihydrate with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:2.

DMAD (0.60 g, 4.2mmol) in EGDE (10 cm^3) was added to a suspension of bis(1,2-naphthaquinone 1-oximato)barium(II).dihydrate (1.10 g, 2.1mmol) in EGDE - water (50 cm^3) (7:1) and stirred at 0°C for 4 h. Using the isolation technique described in experiment 9, (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (0.56 g, 84%) (identified by comparative t.l.c. and i.r.) was obtained.

Similarly (*cis* and *trans*) O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (0.37 g, 55%) was obtained by using the same quantities of the reagents at 20°C for 2 h.

12) Effect of temperature on O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime

A solution of O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime (0.50 g, 1.6 mmol) in EGDE - water (40 cm^3) (7:1) was heated under reflux for 6 h. The resultant brown solution was concentrated under nitrogen and chromatographed on silica. Elution with toluene gave yellow 2,3-dimethoxycarbonyl-4-hydroxy-1,4-naphthoxazine (0.20 g, 40%) m.p. 156 -157°C (Lit^6 159 - 160°C) (identified by comparative t.l.c. and i.r.).

Similarly 2,3-dimethoxycarbonyl-4-hydroxy-1,4-naphthoxazine (50%) resulted when a solution of O-(1′,2′-dicarbomethoxyethenyl)-1,2-naphthaquinone 1-oxime in toluene (60 cm^3) was heated under reflux for 4 h.

13) Synthesis of the M^{II} complexes of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime and 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime [M^{II} = Mn, Ni, Cu, Zn]

A solution of pyrazole-4,5-dione-4-oxime (14.0 mmol) in aqueous ethanol (40 cm^3) was added to a solution of the metal acetate (7.0 mmol) in water (15 cm^3). After stirring for 2 h, *diaquobis(pyrazole-4,5-dione-4-oximato)metal(II)* (See Table 6.5 for product formula, % yield and analysis) was obtained.

14) Macroscale pyrolysis of bis(pyrazole-4,5-dione-4-oximato)metal(II).dipyridine

Bis(pyrazole-4,5-dione-4-oximato)metal(II).dipyridine (*ca.* 0.4 g) was heated at 150-160°C/1.0 mm for 14 h to give bis(pyrazole-4,5-dione-4-oximato)metal(II) (See Table 6.6 for % yield, melting point and analytical data).

TABLE 6.5 Analytical Data for the metal complexes of MpoH and 1-PpoH

Complex	Yield (%)	Analysis Found (Calcd.) (%)			
		C	H	N	M
$Mn(Mpo)_2(H_2O)_2$	69	32.0 (32.3)	4.0 (4.3)	22.4 (22.6)	14.3 (14.8)
$Mn(Ppo)_2(H_2O)_2$	67	48.3 (48.5)	3.9 (4.0)	16.5 (16.9)	11.0 (11.1)
$Ni(Mpo)_2(H_2O)_2$	65	31.5 (32.0)	4.0 (4.3)	22.0 (22.4)	15.1 (15.7)
$Ni(Ppo)_2(H_2O)_2$	74	47.5 (48.1)	3.9 (4.0)	16.2 (16.8)	11.2 (11.8)
$Cu(Mpo)_2(H_2O)_2$	66	32.0 (31.6)	3.8 (4.2)	23.6 (22.2)	16.3 (16.6)
$Cu(Ppo)_2(H_2O)_2$	69	47.1 (47.7)	3.9 (3.6)	16.7 (16.6)	12.0 (12.5)
$Zn(Mpo)_2(H_2O)_2$	51	30.7 (31.5)	3.9 (4.2)	21.3 (22.0)	16.8 (17.1)
$Zn(Ppo)_2(H_2O)_2$	65	47.4 (47.5)	3.8 (4.0)	16.9 (16.6)	12.5 (12.9)

TABLE 6.6 Analytical Data for the anhydrous metal complexes of MpoH and 1-PpoH

Complex	*Yield (%)*	*Decomp temp. (°C)*	*Analysis Found (Calcd.) (%)*			
			C	*H*	*N*	*M*
$Mn(Mpo)_2$	98	320-323	35.5 (35.8)	3.4 (3.6)	26.0 (25.0)	16.1 (16.4)
$Mn(Ppo)_2$	98	325-327	52.1 (52.3)	3.4 (3.5)	17.7 (18.3)	11.5 (11.9)
$Ni(Mpo)_2$	99	207-210	35.0 (35.3)	3.5 (3.5)	25.6 (24.7)	17.1 (17.4)
$Ni(Ppo)_2$	97	350-352	51.8 (51.8)	3.5 (3.6)	18.3 (18.1)	12.2 (12.7)
$Cu(Mpo)_2$	98	250-251	35.0 (35.0)	3.5 (3.5)	24.6 (24.5)	17.9 (18.4)
$Cu(Ppo)_2$	97	230-231	51.3 (51.3)	3.5 (3.4)	17.9 (18.0)	13.0 (13.5)
$Zn(Mpo)_2$	98	298-300	34.7 (34.8)	3.9 (3.5)	24.3 (24.3)	18.5 (18.8)
$Zn(Ppo)_2$	99	351-352	51.1 (51.4)	3.4 (3.4)	17.9 (17.9)	13.5 (13.9)

15) Reaction of 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oxime (1-PpoH) with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 at low temperatures

A solution of 1-PpoH (0.50 g, 2.5mmol) and DMAD (0.35 g, 2.5mmol) in EGDE - water (45 cm^3) (8:1) were stirred at 0°C for 3 h. The reaction mixture was dried under nitrogen and the resultant red oil was chromatographed on silica. Elution with toluene gave orange (*cis* and *trans*) *N-(1′,2′-dicarbomethoxyethenyl)-3-methyl-1-phenyl-4-oximino-1H-pyrazol-4,5-dione* (0.25 g, 29%) m.p. 101 - 103°C (Found: C, 56.0; H, 4.4; N, 12.2%. $C_{16}H_{15}N_3O_6$ requires C, 55.7; H, 4.4; N, 12.2%) m/z 345 (M^+); ν_{max} (KBr): 1746, 1732, 1718 (C=O), 1663 (CN) cm^{-1}; δ_H [$(CD)_3CO$ (250 MHz)] 2.25 (3H, s, C$\underline{H}_3$), 3.78 and 3.91 (3H, s, OC$\underline{H}_3$), 6.57 (1H, s, C$\underline{H}$), 7.25-

7.91 (5H, m, $C_6\underline{H}_5$). Further elution with ethyl acetate yielded a dark red oil (multicomponent by t.l.c.).

Similarly the same quantities of reactants afforded (*cis* and *trans*) *N-(1',2'-dicarbomethoxyethenyl)-3-methyl-1-phenyl-4-oximino-1H-pyrazol-4,5-dione* (0.15 g, 18%) (identified by comparative t.l.c. and i.r.) at 20°C for 2 h.

At 40°C, (*cis* and *trans*) *N-(1',2'-dicarbomethoxyethenyl)-3-methyl-1-phenyl-4-oximino-1H-pyrazol-4,5-dione* (0.10 g, 15%) (identified by comparitive t.l.c. and i.r.) was obtained when stirred for 1½ h.

16) Reaction of 1-methyl-3-phenyl-1H-pyrazole-4,5-dione-4-oxime (3-PpoH) with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 at low temperatures

A solution of 3-PpoH (0.50 g, 2.5 mmol) in EGDE - water (50 cm^3) (7:1) and DMAD (0.35 g, 2.5 mmol) in EGDE (5 cm^3) was stirred at 0°C for 3 h. Using the isolation procedure described in experiment 15, *N-(1',2'-dicarbomethoxyethenyl)-1-methyl-3-phenyl-4-oximino-1H-pyrazol-4,5-dione* (0.80 g, 94%) m.p. 120 - 123°C (Found: C, 55.6, H, 4.4, N, 12.0%. $C_{16}H_{15}N_3O_6$ requires C, 55.7, H, 4.4, N, 55.7, H, 4.4, N, 12.2%) m/z 345 (M^+); ν_{max} (KBr): 1746, 1730, 1712 (C=O), 1656 (CN) cm^{-1}; δ_H($CDCl_3$) (250 MHz) 3.45 (3H, s, $C\underline{H}_3$), 3.65-3.95 (3H, s, $OC\underline{H}_3$), 6.55 (1H, s, $C\underline{H}$), 7.35-7.85 (5H, m, $C_6\underline{H}_5$) has been obtained.

N-(1',2'-dicarbomethoxyethenyl)-1-methyl-3-phenyl-4-oximino-1H-pyrazol-4,5-dione (0.55 g, 65%) (identified by comparitive t.l.c. and i.r.) was obtained by reacting the same quantities of the reactants at 20°C for 2 h.

Similarly *N-(1',2'-dicarbomethoxyethenyl)-1-methyl-3-phenyl-4-oximino-1H-pyrazol-4,5-dione* (0.42 g, 49%) was obtained from the same quantities of the reactants at 40°C for 1½ h.

17) *Reaction of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (MpoH) with dimethyl acetylenedicarboxylate in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 at low temperatures*

A solution of MpoH (0.50 g, 3.5mmol) in EGDE - water (50 cm^3) (7:1) was added to DMAD (0.50 g, 3.5mmol) in EGDE (5 cm^3) and stirred at 0°C for 3 h. Using the isolation procedure described above, *cis* and *trans O-(1′,2′-dicarbomethoxyethenyl)-1,3-dimethyl-4-oximino-1H-pyrazol-4,5-dione* (0.60 g, 60%) m.p. 66 - 69°C (Found: C, 46.6; H, 4.6; N, 14.8%. $C_{11}H_{13}N_3O_6$ requires C, 46.6; H, 4.6; N, 14.8%) m/z 283 (M^+); ν_{max} (KBr): 1723, 1713, 1664 (C=O), 1620 (CN) cm^{-1}; $\delta_H(CDCl_3)$ (250 MHz) 2.10 and 3.45 (3H, s, $C\underline{H}_3$), 3.70-3.95 (3H, s, $OC\underline{H}_3$), 6.55 (1H, s, $C\underline{H}$); was obtained.

Using the same quantities of the reactants at 20 and 40°C for 2 and 1½ h respectively, *cis* and *trans O-(1′,2′-dicarbomethoxyethenyl)-1,3-dimethyl-4-oximino-1H-pyrazol-4,5-dione* was obtained at 49 and 42% yield.

18) *Reaction of 3-methyl-1H-pyrazole-4,5-dione-4-oxime (poH) with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 at 20°C.*

To a solution of poH (0.5g, 3.9 mmol) in EGDE - water (40 cm^3) (7:1), DMAD (0.55 g, 3.9 mmol) in 5 cm^3 was added and the mixture was stirred at 20°C for 3 h. Using the isolation procedure described in experiment 15, (*cis* and *trans*) *O-(1′,2′-dicarbomethoxyethenyl)-3-methyl-4-oximino-1H-pyrazol-4,5-dione*(0.28g,27%)m.p. 82 - 84°C (Found: C, 44.7, H, 4.1, N, 15.6%. $C_{10}H_{11}N_3O_6$ requires C, 44.6, H, 4.1, N, 15.6%.) m/z 269 (M^+); ν_{max} (KBr): 1734, 1654, 1610 (C=O), 1596 (CN) cm^{-1}; $\delta_H(CDCl_3)$ (250 MHz) 2.10-2.55 (3H, s, $C\underline{H}_3$), 9.5 (1H, s, $N\underline{H}$) 3.70-3.95 (3H, s, $OC\underline{H}_3$), 6.40-6.65 (1H, s, $C\underline{H}$) was obtained

19) *Reaction of (1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato) lithium(I). dihydrate with dimethyl acetylenedicarboxylate in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 at 20°C*

A suspension of (1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)lithium(I).dihydrate

(0.50 g, 2.7 mmol) in EGDE - water (50 cm^3) was added to DMAD (0.38g, 2.6 mmol) in EGDE (5 cm^3) and the reaction mixture was stirred at 20°C for 4 h. Using the isolation procedure described in experiment 15 (*cis* and *trans*) *N-(1',2'-dicarbomethoxyethenyl)-1,3-dimethyl-4-oximino-1H-pyrazol-4,5-dione*
(0.49 g, 58%) was formed.

20) *Reactions of pyrazole-4,5-dione-4-oxime with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1 under refluxing condition*

DMAD (0.35 g, 2.5 mmol) in EGDE (5 cm^3) and 3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximes (0.50 g, 2.5 mmol) in EGDE - water (40 cm^3) (7:1) were heated under reflux for 3 h. The residue obtained after removal of the solvent was chromatographed on silica. Elution with toluene gave red 2,4-dehydro-4[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-onewas isolated (0.17 g, 20%) m.p. 185 - 187°C (Lit[2] 185 - 187°C) (Found: C, 67.1; H, 4.7; N, 19.7%. Calcd. for $C_{20}H_{17}N_5O_2$ C, 66.9; H, 4.7; N, 19.5%) m/z 359 (M^+); ν_{max} (KBr): 1731 (C=O), 1619 (CN), 3440 (OH) cm^{-1}; δ_H($CDCl_3$) (250 MHz) 2.26 (6H, s, C$\underline{H}_3$), 6.54-7.93 (12H, m, $C_6\underline{H}_5$) 17.46 1H, s, O$\underline{H}$).

By using the same experimental procedure and isolation technique, the following reactions were also carried out.

1-methyl-3-phenyl-1H-pyrazole-4,5-dione-4-oxime (0.50 g, 2.5 mmol) reacted with dimethyl acetylenedicarboxylate (0.35 g, 2.5mmol) to give *2,4-dehydro-4[(5-hydroxy-1-methyl-3-phenyl-1H-pyrazol-4-yl)imino]-2-methyl-5-phenyl-3H-pyrazol-3-one* (0.17g, 20%) m.p. 200 - 203°C (Found:C, 66.8, H, 4.8, N, 19.5%. $C_{20}H_{17}N_5O_2$ requires C, 66.9, H, 4.7, N, 19.5%) m/z 359 (M^+); ν_{max} (KBr): 1642 (C=O), 3435 (OH) cm^{-1}; δ_H($CDCl_3$) (250 MHz) 3.65 (6H, s, C$\underline{H}_3$), 7.15-7.95 (12H, m, $C_6\underline{H}_5$) 17.00 1H, s, O$\underline{H}$).

1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (0.50 g, 3.5 mmol) was reacted with dimethyl acetylenedicarboxylate (0.50 g, 3.5mmol) to give *2,4-dehydro-4-[(1,3-*

dimethyl-5-hydroxy-1H-pyrazol-4-yl)imino]-2,5-dimethyl-3H-pyrazol-3-one (0.15g, 18%) m.p. 208 - 210°C (Found: C, 51.5; H, 5.4; N, 28.5%. Calcd. for $C_{10}H_{13}N_5O_2$ C, 51.1; H, 5.5; N, 29.8%) m/z 235 (M^+); ν_{max} (KBr): 1743 (C=O), 3430 (OH) cm^{-1}; $\delta_H(CDCl_3)$ (250 MHz) 3.50 and 2.22 (6H, s, C$\underline{H}_3$), 17.34 (1H, s, O$\underline{H}$).

3-Methyl-1H-pyrazole-4,5-dione-4-oxime (0.50 g, 3.9 mmol) reacted with dimethyl acetylenedicarboxylate (0.55g, 3.9mmol) to give *2,4-dehydro-4[(5-hydroxy-3-methyl-1H-pyrazol-4-yl)imino]-5-methyl-3H-pyrazol-3-one* m.p. 294°C (decomp.) (Found: C, 46.4, H, 4.5, N, 30.6%. $C_8H_9N_5O_2$ requires C, 46.4, H, 4.4, N, 33.8%) m/z 207 (M^+); ν_{max} (KBr): 1653 (C=O), 3128 (OH) cm^{-1}; $\delta_H(CDCl_3)$ (250 MHz) 2.24 (6H, s, C$\underline{H}_3$), 12.70 (2H, s, N$\underline{H}$), 17.34 (1H, s, O$\underline{H}$).

21) *Reactions of diaquobis(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)copper(II) [Cu(Mpo)$_2$(H$_2$O)$_2$] with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio* ∮ 2

[$Cu(Mpo)_2(H_2O)_2$] (0.50 g, 1.3 mmol) and DMAD (0.37 g, 2.6 mmol) were stirred in ethylene glycol dimethyl ether - water (7:1) (40 cm^3) at 20°C for 6 hours. Filtration of the reaction mixture gave unreacted $Cu(Mpo)_2(H_2O)_2$ (0.49g, 98% recovery) (identified by comparative ir study).

The same quantities of the reactants were heated in ethylene glycol dimethyl ether under reflux for 6 hours. Filtration afforded a black solid (0.13g) (ill-defined ir spectrum) and red filtrate. The residue obtained after the removal of solvent from the filtrate was chromatographed on silica. Elution with toluene gave red *2,4-dehydro-4-[(1,3-dimethyl-5-hydroxy -1H-pyrazol-4-yl)imino]-2,5-dimethyl-3H-pyrazol-3-one* (0.27 g, 80%) (identified by comparatived t.l.c. and i.r.).

22) *Reactions of diaquobis(3-methyl-1-phenyl-1H-pyrazole-4,5-dione-4-oximato)copper(II) $[Cu(1\text{-}Ppo)_2(H_2O)_2]$ with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:2*

$[Cu(1\text{-}Ppo)_2(H_2O)_2]$ (0.50 g, 1.0 mmol) and DMAD (0.0.28 g, 2.0 mmol) were stirred in ethylene glycol dimethyl ether - water (7:1) (40 cm^3) at 20°C for 6 h. Filtration of the reaction mixture under gravity gave unreacted $Cu(1\text{-}Ppo)_2(H_2O)_2$ (0.49g, 98% recovery) (identified by comparative ir study).

The same quantities of the reactants were heated in ethylene glycol dimethyl ether under reflux for 6 h. Filtration under suction afforded a black solid (0.13 g) (ill-defined ir spectrum) and red filtrate. The residue obtained after the removal of solvent from the filtrate was chromatographed on silica. Elution with toluene gave red *2,4-dehydro-4-[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-one* (0.21 g, 58%) (identified by comparative t.l.c. and i.r.).

23) *Reactions of (1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)lithium(I).dihydrate with dimethyl acetylenedicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1*

(1,3-dimethyl-1H-pyrazole-4,5-dione-4-oximato)lithium(I).dihydrate (0.50 g, 2.7 mmol) and DMAD (0.37 g, 2.6 mmol) were heated under reflux in ethylene glycol dimethyl ether - water (7:1) (40 cm^3) for 6 h. The residue obtained after the removal of solvent from the filtrate was chromatographed on silica. Elution with toluene gave red *2,4-dehydro-4-[(1,3-dimethyl-5-hydroxy-1H-pyrazol-4-yl)imino]-2,5-dimethyl-3H-pyrazol-3-one* was recovered (0.30 g, 38%) (identified by comparatived t.l.c. and i.r.).

24) *Reaction of pyrazole-4,5-dione-4-oximes with acetylenedicarboxylic acid (ADA) in ethylene glycol dimethyl ether (EGDE) - water in the molar ratio of 1:1*

A solution of 1,3-dimethyl-1H-pyrazole-4,5-dione-4-oxime (0.50 g, 3.5 mmol) in EGDE - water (40 cm^3) (7:1) and ADA (0.40 g, 3.5 mmol) in EGDE (10 cm^3) was stirred at 20°C for 24 hours. T.l.c. of the resultant solution indicated the absence of any reaction. 0.45 g (90%) of MpoH was recovered.

In the second experiment, the same quantities of the reactants were heated under reflux for 24 h. The residue obtained after removal of the solvent was chromatographed using silica. Elution with toluene gave *2,4-dehydro-4-[(1,3-dimethyl-5-hydroxy-1H-pyrazol-4-yl)imino]-2,5-dimethyl-3H-pyrazol-3-one* (0.10 g, 12%) (identified by comparative t.l.c. and ir) was obtained.

Similarly 3-methyl-1-phenyl-1H-pyrazol-4,5-dione-4-oxime (1-PpoH) (0.50 g, 2.5 mmol) with ADA (0.29 g, 2.5 mmol) in DME - water under reflux resulted in the formation of *2,4-dehydro-4[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-one* (0.15 g, 17%) (identified by comparative t.l.c. and ir)

25) *Effect of temperature on O-(1′,2′-dicarbomethoxyethenyl)-4-oximino-1H-pyrazole-4,5-dione*

(1′,2′-dicarbomethoxyethenyl)-1,3-dimethyl-4-oximino-1H-pyrazole-4,5-dione (0.50g, 1.8 mmol) dissolved in EGDE- water (40 cm^3) was heated under reflux for 6 h. The residue obtained after the removal of solvent was chromatographed using silica. Elution with toluene yielded *2,4-dehydro-4[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-one* (0.27 g, 64%) (identified by comparative t.l.c. and i.r.) on removal of the solvent.

Similarly N-(1′,2′-dicarbomethoxyethenyl)-3-methyl-1-phenyl-4-oximino-1H-pyrazole-4,5-dione (0.50 g, 1.4 mmol) gave *2,4-dehydro-4[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-one* (0.30 g, 58%) (identified by comparative t.l.c. and i.r.).

2,4-dehydro-4[(5-hydroxy-1-methyl-3-phenyl-1H-pyrazol-4-yl)imino]-2-methyl-5-phenyl-3H-pyrazol-3-one (0.35 g, 67%) was obtained by refluxing a EGDE-water solution of N-(1′,2′-dicarbomethoxyethenyl)-1-methyl-3-phenyl-4-oximino-1H-pyrazol-4,5-dione (0.50 g, 1.4 mmol).

Under the same refluxing condition, ($1^{/}$,$2^{/}$-dicarbomethoxyethenyl)-3-methyl-4-oximino-1H-pyrazol-4,5-dione (0.50 g, 1.9 mmol) resulted in *2,4-dehydro-4[(5-hydroxy-3-methyl-1H-pyrazol-4-yl)imino]-2-methyl-5-phenyl-3H-pyrazol-3-one* (0.25 g, 65%).

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