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TITLE Lithium and Indium Quinoneoximic Complexes And their Application In Scintillation Counting

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LITHIUM AND INDIUM QUINONEOXIMIC COMPLEXES AND THEIR APPLICATION IN SCINTILLATION COUNTING

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

by

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The Polytechnic of
North London in
collaboration with
the National Physical
Laboratory

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To my parents and Andrew

"It is impossible to achieve the aim without suffering"

J. G. Bennett

Declaration

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

P. Gaganatsou

Paraskevi Gaganatsou

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ABSTRACT

Several complexes of lithium derived from 1,2-naphthoquinone 1-oxime and 1,2-naphthoquinone 2-oxime have been prepared and characterised using analytical, spectroscopic and thermal gravimetric techniques. I.r. studies indicate that the ligands in these complexes are essentially quinoneoximic in character. For the complex Li(1-nqo)(1-nqoH).EtOH the quinoneoximic character has been confirmed by X-ray crystallography.

All the lithium complexes were found to be stable towards atmospheric oxygen and water. Their reactivity towards dimethylacetylene dicarboxylate was investigated and compared to that of the copper quinoneoximato complexes. Each of the lithium complexes reacted readily with the acetylene dicarboxylate to give a novel nucleophilic addition product isomeric to the Diels-Alder adduct (1,4-oxazine) obtained from the copper complexes. Re-examination of the behaviour of the copper quinoneoximato complexes towards dimethylacetylene dicarboxylate has given an insight to the mechanism of the reaction and has shown that the copper complexes also act as catalysts in the conversion of 1,4-oxazine derivatives to 1,3-oxazoles.

Several lithium carboxylato and dithiocarbamato complexes have been prepared. For the dithiocarbamato complexes a new synthetic method involving the reaction of carbon disulphide and the amine with lithium chloride was developed during this study.

Solubility studies were carried out on several complexes of types Li(RCO_2), Li(R_2NCS_2)(R_2NCSSH), Li(nqo) and M$(qo)_n$ (M = Li, Na, K, Ni, Co) in polar and non-polar solvents. Maximum solubility was observed in pyridine, dimethylsulphoxide and ethanol.

The scintillation efficiency of pyridine, dimethylsulphoxide and ethanol was examined in commmercially available scintillator mixtures and in scintillator mixtures developed during this study. The scintillation efficiency of the lithium complexes derived from the mono-oximes of 1,2-naphthoquinone, carboxylic and dithiocarbamic acids was also investigated. The latter two set of complexes proved promising for loading liquid scintillation counters, when present as 'solid' in the scintillator mixture.

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ABBREVIATIONS

The following is a list of abbreviations employed in the text.

AR	Analar
b.p.	boiling point
DMAD	dimethylacetylene dicarboxylate
EGDE	ethylene glycol dimethyl ether
Fig.	figure
GPR	general purpose reagent
h	hour(s)
H.P.L.C.	high performance liquid chromatography
i.r.	infra-red
m.p.	melting point
m.s.	mass spectrum
n.m.r.	nuclear magnetic resonance
No.	number
1-nqoH	1,2-naphthoquinone 1-oxime
1-nqo$^-$	1,2-naphthoquinone 1-oximato anion
2-nqoH	1,2-naphthoquinone 2-oxime
2-nqo$^-$	1,2-naphthoquinone 2-oximato anion
nqo$^-$	1-nqo$^-$ or 2-nqo$^-$
nqoH	1-nqoH or 2-nqoH
POPOP	1,4-di[2-(5-phenyloxazolyl)]-benzene
py	pyridine
Ref.	reference(s)
t.l.c.	thin layer chromatography

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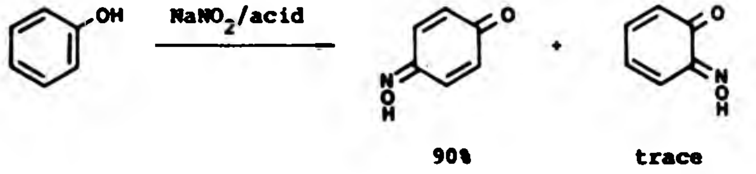
CHAPTER ONE

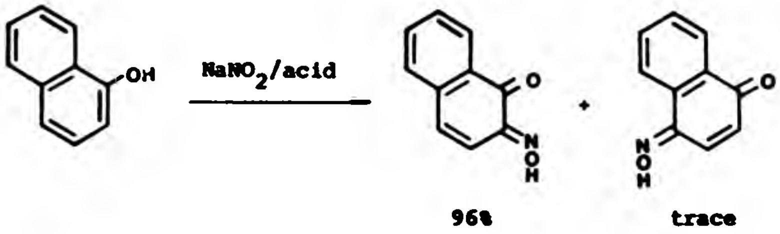
SYNTHESIS OF LITHIUM COMPLEXES DERIVED FROM THE MONO-OXIMES OF 1,2-NAPHTHOQUINONE

1.1 1,2-Quinone mono-oximes

The principal method used for the preparation of quinone mono-oximes involves the treatment of a phenol with sodium nitrite and dilute aqueous acid. This route leads mainly to the 4-substituted isomer (e.g. Reaction 1.1).[1] In the case of naphthols the 2-isomer is the main product (e.g. Reaction 1.2).[2]

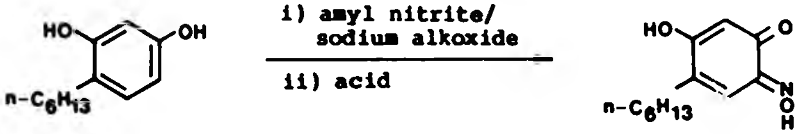


Reaction 1.1



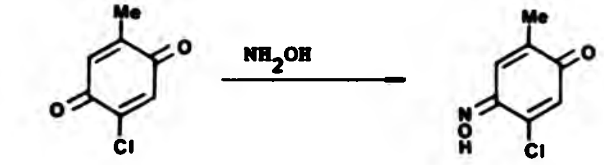
Reaction 1.2

Another method used for the preparation of quinone mono-oximes, is the reaction of a phenol with amyl nitrite and an alkali metal hydroxide or alkoxide (sodium or potassium) in ethanol. This method has been mainly used for the preparation of 5-hydroxy 1,2-benzoquinone mono-oximes (e.g. Reaction 1.3).[3]



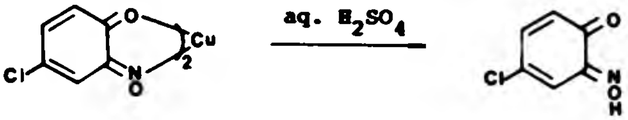
Reaction 1.3

A number of other methods have also been used for the preparation of certain quinone mono-oximes. These include (i) the action of hydroxylamine on a quinone (e.g. Reaction 1.4),[4] (ii) the action of sodium hydroxide on certain nitro-aromatic compounds (e.g. Reaction 1.5)[5] and (iii) the acidification of metal complexes of the 1,2-quinone-2-oximes (e.g. Reaction 1.6).[6] The latter method has not been fully substantiated and reports dealing with it lack in experimental detail and analytical data.



Reaction 1.4

Reaction 1.5



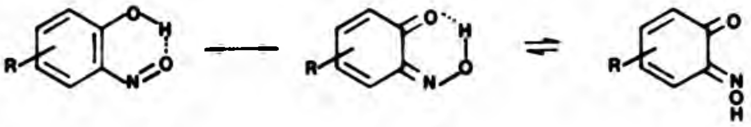
Reaction 1.6

1,2-Quinone mono-oximes are isomeric with 2-nitrosophenols.[7-10] Studies on the tautomeric behaviour of the system 1,2-quinone mono-oxime/ 2-nitrosophenol had involved mainly the 5-alkoxy-2-nitrosophenols. Henrick and Eisenach prepared 5-methoxy-2-nitrosophenol and found that it crystallised in green and yellowish/brown crystals from benzene and ethanol respectively.[11] They also noted that at 128-130 °C the green form changed to the red which subsequently melted at 154 °C. They suggested that the green form was the nitrosophenolic tautomer and the red form was the quinoneoximic one.

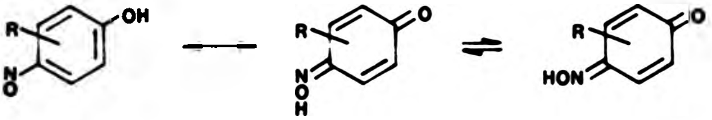
Subsequent crystal structure studies on the red form of 5-methoxy-2-nitrosophenol,[12] the green form of 5-n-propoxy-1-quinone-2-oxime[13] and the red form of 5-(2'-chloroethoxy)-1-quinone-2-oxime[14] have shown that all three compounds exist predominantly in the quinoneoximic form. However, the two red forms have the OH of the NOH group *anti* to the CO and the green form has the OH of the NOH group *syn* to the CO group. Recent crystallographic studies on substituted 1,2-naphthoquinone mono-oximes,[15-18] have also demonstrated the predominance of the oximic form.

The tautomeric behaviour of the 4-substituted isomers has also attracted attention.[19-26] Hodgson and Moore claimed to have obtained the individual tautomers of 3-chloro-4-nitrosophenol.[27] Subsequent crystallographic studies on 5-chloro and 5-bromo-1,4-benzoquinone 4-oximes showed the predominance of the quinoneoximic tautomer.[28]

On the basis of the X-ray crystallographic results outlined above the 2- or 4-nitrosophenol/quinoneoxime systems can be best described as indicated in Schemes 1.1 and 1.2. In this thesis the compounds will be referred to as quinoneoximes and the abbreviation qoH will be used. This however, does not necessarily imply that the particular compound exists in the oximic form entirely.



Scheme 1.1



(R ≠ H)

Scheme 1.2

1.2 Metal complexes of 1,2-quinone mono-oximes

Replacement of the acidic hydrogen in the tautomeric system described in Scheme 1.1, by a metal results in complex formation.

Generally first and second-row transition metals form five membered ring chelates with the anions of 1,2-quinone mono-oximes. X-ray crystallographic studies of these chelates (Fig. 1.1),[29-34] have shown that the ligands are essentially quinoneoximic in character and the bonding of the metal to the ligand, involves the ring oxygen and the nitrogen atom of the NO group. Chelation involving the ring oxygen and the oxygen atom of the NO group has also been suggested for some complexes but so far no examples of this type have been characterised crystallographically.[35,36]

Fig. 1.1

Recently in complexes containing heavier metals, e.g. the uranyl complexes $UO_2(1\text{-nqo})_2(Ph_3PO).H_2O$ and $UO_2(2\text{-nqo})_2(H_2O)_2.2CHCl_3$, another type of ligand attachment has been identified (Fig. 1.2).[37] This involves only the NO group in bonding to the metal.

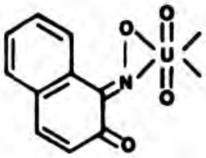
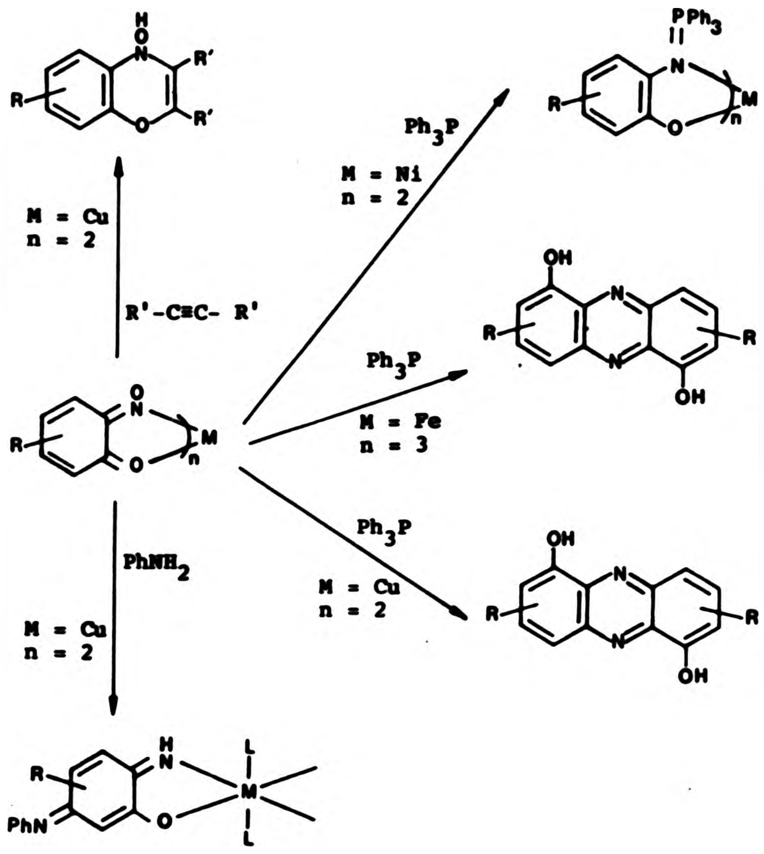


Fig. 1.2

In addition to the above complexes which involve the 1,2-quinoneoximato anion as ligand, compounds involving the neutral quinone oxime[38] e.g. $(1\text{-nqoH})_2FeCl_2$ or the protonated quinone oxime[39] e.g. $[qoH_2]_2[CuCl_4]$ (qoH = 4-chloro-1,2-benzoquinone 2-oxime) have been described.

The structure of the metal complexes of 1,2-quinone mono-oximes suggests diene, dienophile and heterodiene character and indicates the presence of reactive NO and CO groups. This multifunctional character and ready availability of 1,2-quinoneoximic complexes makes them most promising substrates for the synthesis of a variety of useful or novel types of compound (Scheme 1.3).[40-44] The metal complexes of 1,2-quinone mono-oximes have also been used industrially as dyes[45-47] and in the filtration of tobacco smoke.[48]



R' = $MeCO_2$

R = e.g. 5-MeO, 4-Me, 4-Cl,

5,6-(CH=CHCH=CH)

L = $PhNH_2$

Scheme 1.3

Most of the quinoneoximic complexes prepared, involve transition metals. Some of these complexes are illustrated in Table 1.1. The preparation of non-transition metal complexes has received considerably less attention, as Table 1.2 which summarises all the reported non-transition metal complexes indicates. Furthermore, the properties of a large number of transition metal quinoneoximic complexes have been systematically examined and the structures of several of these established crystallographically. In contrast, the characterisation, properties and structure of non-transition metal quinoneoximic complexes received only superficial attention.

In view of the limited studies on lithium quinoneoximic complexes, a systematic examination of such complexes has been undertaken and is presented in the following sections of this Chapter. The present studies were also prompted by the desirability for organo soluble lithium complexes for use in neutron liquid scintillation counters. The specific aims were (i) to establish synthetic routes to the lithium complexes and (ii) to investigate their properties and structure.

Table 1.1 Transition metal complexes derived from 1,2-quinone mono-oximes

Complex	Reported Data	Ref.
$Cu(4\text{-}Clqo)_2$	EA, MA, IR, MS, MM, M_r, ES	39, 49
$Ni(4\text{-}Clqo)_2.2py$	EA, MA, IR, MS, TA, MM, M_r, ES	50
$K[Ni(4\text{-}Clqo)_3].Me_2CO$	EA, MA, IR, MM, ES, X-ray	29
$Cu(4\text{-}Meqo)_2.py$	EA, MA, IR, MS, TA, MM, M_r, ES, X-ray	49, 33
$Fe(5\text{-}MeOqo)_3$	EA, MA, IR, MS, MM, M_r, ES, C	51
$Na[Co(qo)_2(NO_2)]$	EA, MA, M_r, C	52
$Ni(4\text{-}Me\text{-}5OHqo)_2.4H_2O$	EA, MA, IR, MS, TA, MM, ES	53
$Ni(1\text{-}nqo)_2$	EA, MA, IR, MS, MM, M_r, ES, C	54
$Co(1\text{-}nqo)_3$	EA, MA, IR, MS, MM, M_r, ES, C	52
$Rh(1\text{-}nqo)_3$	EA, MA, IR	55
$[pyH][Ir(1\text{-}nqo)(py)Cl_3]$	X-ray	55
$Ru(1\text{-}nqo)_2(py)_2$	EA, MA, IR, TA, X-ray	56
$UO_2(1\text{-}nqo)_2(Ph_3PO).H_2O$	X-ray	37
$UO_2(2\text{-}nqo)_2(H_2O)_2.2CHCl_3$	X-ray	37

Table 1.1 (continued)

Complex	Reported Data	Ref.
$Cu(2\text{-}nqo)_2 \cdot H_2O$	EA, MA, IR, MS, TA, MM, M_r, ES, C, X-ray	39, 32

EA = elemental analysis

MA = metal analysis

IR = infra-red

MS = mass spectrum

TA = thermal analysis

MM = magnetic measurements

M_r = relative molecular mass

ES = electronic spectrum

C = conductivity

Table 1.2 Non-transition metal complexes derived from 1,2-quinone mono-oximes

Complex	Reported Data	Ref.
Li(1-nqo)	EA, IR, C	57
Na(1-nqo)	EA, MA, IR, C	57
K(1-nqo)	EA, MA, IR, C	57
K(1-nqo)(1-nqoH)	EA, MA, IR, C	57
K(7-S-1-nqo).H_2O	M_r, X-ray	17
Rb(1-nqo)	EA, MA, IR, C	57
Rb(1-nqo)(1-nqoH)	EA, MA, IR, C	57
Cs(1-nqo)	EA, MA, IR, C	57
Cs(1-nqo)(1-nqoH)	EA, MA, IR, C	57
Tl(1-nqo)	MA, IR, MM, ES, C	58
$Sc(1\text{-nqo})_3$	MA, IR, MM, ES, C	58
$Bi(1\text{-nqo})_3$	MA, IR, MM, ES, C	58
$[(Me)_2Sn(1\text{-nqo})]_2O$	EA, MA, MP, IR	59
$[(Et)_2Sn(1\text{-nqo})]_2O$	EA, MA, MP, IR	59
Li(2-nqo)(2-nqoH)	EA, IR, C	60
Na(2-nqo)	IR	60
Na(2-nqo)(2-nqoH)	EA, MA, IR	60
Na(5-S-2-nqo)	X-ray	61
K(2-nqo)	IR	60
K(2-nqo)(2-nqoH)	EA, MA, IR	60
K(8-S-2-nqo).$2H_2O$	X-ray	62
K[Na(5-S-2-nqo).$3H_2O$	X-ray	63

Table 1.2 (continued)

Complex	**Reported Data**	**Ref.**
Rb(2-nqo)	IR	60
Rb(2-nqo)(2-nqoH)	EA, MA, IR	60
Cs(2-nqo)	IR	60
Cs(2-nqo)(2-nqoH)	EA, MA, IR	60
Cs(2-nqo).2(2-nqoH)	EA, MA, IR	60

7-S-1-nqoH = 1,2-naphthoquinone 1-oxime 7-sulphonic acid

5-S-2-nqoH = 1,2-naphthoquinone 2-oxime 5-sulphonic acid

8-S-2-nqoH = 1,2-naphthoquinone 2-oxime 8-sulphonic acid

EA = elemental analysis
MA = metal analysis
MP = melting point
IR = infra-red
MM = magnetic measurements
ES = electronic spectrum
M_r = relative molecular mass
C = conductivity

1.3 Lithium complexes of 1,2-naphthoquinone mono-oximes

1.3.1 Introduction

The ability of lithium to form compounds with bidentate ligands such as salicylaldehyde, nitrophenols and β-diketones or their anions, has been known for long time.[64,65]

However, it was only in the late sixties that the coordination chemistry of lithium and of other alkali metals received systematic attention. Various types of lithium complexes involving one ligand or two different ligands e.g. glycine and 8-hydroxyquinoline,[66] 2,6-dinitrophenol and 1,10-phenanthroline,[67-70] in bonding to the metal have been prepared and some of them are presented in Table 1.3.[57,60,64,65] Although some of these compounds were previously considered as salts, the covalent contribution to their bonding is now widely accepted. It must be stressed, however that the accepted covalent character is not based on any X-ray crystallographic structural determinations.

In this study a systematic investigation of the synthesis and reactions of lithium complexes derived from the mono-oximes of 1,2- naphthoquinone and the assessment of their bonding features was undertaken.

Table 1.3 Complexes of lithium

Complex	Reported Data	Ref.
Li(sal)(salH)	MA	65
Li(bzac).$2H_2O$	MA	64
Li(ox)(oxH)	EA, MP, C	57
Li(2-nqo_2)	EA, MP(dec), C	57
Li(1-nqo)	EA, C	57
Li(acetph)	EA, MP(dec), C	57
Li(2-nqo)(2-nqoH)	EA, MP, C	60

salH = salicylaldehyde
bzacH = benzoylacetone
oxH = 8-hydroxyquinoline
2-nqo_2H = 2-nitrophenol
acetphH = isonitrosoacetophenone

MA = metal analysis
EA = elemental analysis
MP = melting point
C = conductivity
dec = decomposition

1.3.2 Synthesis of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone

Complexes of the type Li(1-nqo) and Li(2-nqo)(2-nqoH) have previously been reported.[57,60] The former resulted from a 1:1 reaction of 1,2-naphthoquinone 1-oxime with a saturated solution of lithium hydroxide in hot ethanol. The complex Li(2-nqo)(2-nqoH) was also obtained in ethanol but no details of the molar ratio of the reactants have been reported. The formulation of these complexes was based on carbon, hydrogen and nitrogen analysis. For the Li(1-nqo) complex, conductance measurements were also reported. The conductivity value obtained was low, compared to values expected for electrolytes, and on this basis it was suggested that the complex has covalent character.

In this study the reactions of 1,2-naphthoquinone 1-oxime with lithium hydroxide monohydrate in 1:1 and 2:1 molar ratios were investigated in ethanol under reflux. From the 1:1 reaction a green crystalline solid of formulation Li(1-nqo).1/2 EtOH was obtained. This formulation is supported by full elemental analysis. The presence of ethanol is indicated by bands in the region 3440-3040 cm^{-1} in the i.r. spectrum. Thermal gravimetric analysis and macro-scale pyrolysis indicate that on heating half mol of ethanol is lost per mol of complex (Tables 1.4 and 1.5). The solid residue remaining from the macro-scale

Table 1.4 Thermal gravimetric analysis of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone

Complex	**Wt. of sample(mg)**	**Temp.(°C)[a]**	**Wt. loss(mg)(calc)**
Li(1-nqo).1/2 EtOH	184	90-100	25(21)[b]
Li(1-nqo)(1-nqoH).EtOH	135	70-110	17(16)[c]
Li(2-nqo).1/2 EtOH	195	90-100	22(24)[b]
Li(2-nqo)(2-nqoH).EtOH	206	80-130	19(24)[c]

[a] Temperature of loss of ethanol

[b] Calculated for loss of ethanol (0.5 mol) per mol of complex

[c] Calculated for loss of ethanol (1.0 mol) per mol of complex.

Table 1.5 Macro-scale pyrolysis of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone

Complex	Wt. of sample(g)	Temp. of rx.(^{o}C/1.0 mm)	Wt. loss(g)(calc.)
Li(1-nqo).1/2 EtOH	4.081	110-120	0.521(0.465)[a]
Li(1-nqo)(1-nqoH).EtOH	4.993	90-95	0.591(0.577)[b]
Li(2-nqo).1/2 EtOH	6.144	90-95	0.759(0.700)[a]
Li(2-nqo)(2-nqoH).EtOH	6.345	90-95	0.766(0.733)[b]

[a] Calculated for loss of ethanol (0.5 mol) per mol of complex

[b] Calculated for loss of ethanol (1.0 mol) per mol of complex

pyrolysis was formulated as Li(1-nqo) on the basis of elemental analysis and its i.r. spectrum which shows no bands due to ethanol.

Ethanol was also present in the crystalline product obtained from the 2:1 reaction. The reaction was carried out using two alternative synthetic routes. One involved addition of excess of 1,2-naphthoquinone 1-oxime in the solid state, to a solution of the lithium hydroxide and the other, addition of lithium hydroxide solution to a solution of the oxime. In both cases Li(1-nqo)(1-nqoH).EtOH was isolated as shown by full elemental analysis. Bands at 3480-2800 cm^{-1} in the i.r. spectrum of Li(1-nqo)(1-nqoH).EtOH indicate the presence of the neutral ligand 1,2-naphthoquinone 1-oxime and/or ethanol. Thermal gravimetric analysis and macro-scale pyrolysis show loss of one mol of ethanol per mol of complex (Tables 1.4 and 1.5).

Analogous reactions involving 1,2-naphthoquinone 2-oxime gave the complexes Li(2-nqo).1/2 EtOH and Li(2-nqo)(2-nqoH).EtOH which on pyrolysis gave Li(2-nqo) and Li(2-nqo)(2-nqoH) (Tables 1.4 and 1.5).

All the lithium complexes studied are highly coloured, involatile, stable in the solid form and in solution in various solvents (e.g. acetone, pyridine, ethanol). They are unaffected by water but are decomposed by aqueous acids. Their solubility behaviour in organic solvents, which is presented in Chapter 4 indicates covalent character. This is supported by conductivity measurements in ethanol (Table 1.6). In all cases the molar conductivity values obtained are very low compared to results expected for electrolytes, e.g. a value of 35-45 x 10^{-4} S m^2 mol^{-1} for 1:1 and 70-90 x 10^{-4} S m^2 mol^{-1} for 2:1 electrolytes.[71]

Table 1.6 Molar conductivities of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone in ethanol at 25 °C

Complex	C(mol m^{-3})	Λ_m(S mol^{-1} m^2)
Li(1-nqo).1/2 EtOH	10.100	5.24 x 10^{-4}
Li(1-nqo)	11.400	5.25 x 10^{-4}
Li(1-nqo)(1-nqoH).EtOH	10.000	5.84 x 10^{-4}
Li(1-nqo)(1-nqoH)	10.010	5.95 x 10^{-4}
Li(2-nqo).1/2 EtOH	10.100	9.61 x 10^{-4}
Li(2-nqo)	11.400	10.20 x 10^{-4}
Li(2-nqo)(2-nqoH).EtOH	9.948	8.65 x 10^{-4}
Li(2-nqo)(2-nqoH)	10.010	8.84 x 10^{-4}

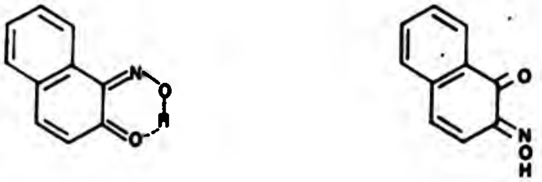
C = concentration

Λ_m = molar conductivity

The ^1H n.m.r. spectra of the mono-oximes of 1,2-naphthoquinone and their lithium complexes were recorded in dimethylsulphoxide. The ^1H n.m.r. spectra of 1-nqoH and 2-nqoH exhibit multiplets at 6.38-8.91 ppm and 7.07-8.09 ppm respectively due to the aromatic protons. A broad singlet at 14.27 ppm for 1-nqoH and at 13.57 ppm for 2-nqoH is also present due to the -OH proton, as indicated by deuterium hydrogen exchange. In the lithium complexes the aromatic protons appear as multiplets at 6.58-8.76 ppm in Li(1-nqo), 6.50-8.91 ppm in Li(1-nqo)(1-nqoH) and at 6.34-8.42 ppm in Li(2-nqo) and 6.55-8.28 ppm in Li(2-nqo)(2-nqoH). In the lithium complexes Li(1-nqo)(1-nqoH) and Li(2-nqo)(2-nqoH) the -OH proton resonates at a much higher field (8.82 and 5.62 ppm respectively) than that of the free ligands 1-nqoH and 2-nqoH. This is probably due to the involvement of this proton in an inter-ligand hydrogen bonding.

Some information regarding the structure of the lithium complexes and the mode of bonding of the ligands has been obtained from comparison of their i.r. spectra with those of the free ligands and related compounds (Table 1.7, Figs. 1.4 and 1.5).

On the basis of i.r. studies a *syn* structure has been suggested for 1-nqoH and an *anti* structure for 2-nqoH (Fig. 1.3).[24] The proposed structure for the former was subsequently confirmed by X-ray crystallographic studies.[16] In the case of 1-nqoH the absorption due to νCO is observed at 1618 cm^{-1} whereas in the 2-isomer the corresponding absorption appears at 1668 cm^{-1}. This difference clearly reflects the presence of intramolecular hydrogen bonding in the former.



1-nqoH 2-nqoH

Fig. 1.3

Generally, in complexes containing chelating 1-nqo⁻ ligands the absorption due to νCO shifts slightly (*ca.* 10 cm^{-1}) to lower frequency relative to the νCO of the protonated ligand (Table 1.7, Fig. 1.4). In contrast, in complexes containing 2-nqo⁻ chelating ligands the corresponding shift is more pronounced (*ca.* 40 cm^{-1}) (Table 1.7, Fig. 1.5). This trend can again be correlated with the hydrogen bonding characteristics of the protonated ligands. In the case of the lithium complexes Li(2-nqo) and Li(2-nqo).1/2 EtOH the shift in νCO is comparable to that observed in other complexes containing the 2-nqo⁻ ligand. However, in the case of the complexes Li(1-nqo) and Li(1-nqo).1/2 EtOH the band due to νCO appears at ca. 1620 cm^{-1} i.e. slightly higher than the corresponding band in the protonated ligand.

Table 1.7 νCO absorption of 1,2-naphthoquinone monooximes and their complexes

Compound	νCO (cm^{-1})	Ref.
1-nqoH	1618	24
2-nqoH	1668	24
$Cu(1\text{-nqo})_2$	1610	72
$Fe(1\text{-nqo})_3$	1610	72, 51
$Cr(1\text{-nqo})_3$	1608	73
Li(1-nqo).1/2 EtOH	1618	*
Li(1-nqo)	1620	*
Li(1-nqo)(1-nqoH).EtOH	1660, 1620	*
Li(1-nqo)(1-nqoH)	1665, 1618	*
$Cu(2\text{-nqo})_2$	1618	72
$Fe(2\text{-nqo})_3$	1620	72
$Cr(2\text{-nqo})_3$	1620	72
Li(2-nqo).1/2 EtOH	1618	*
Li(2-nqo)	1620	*
Li(2-nqo)(2-nqoH).EtOH	1668, 1620	*
Li(2-nqo)(2-nqoH)	1670, 1618	*

* = this work

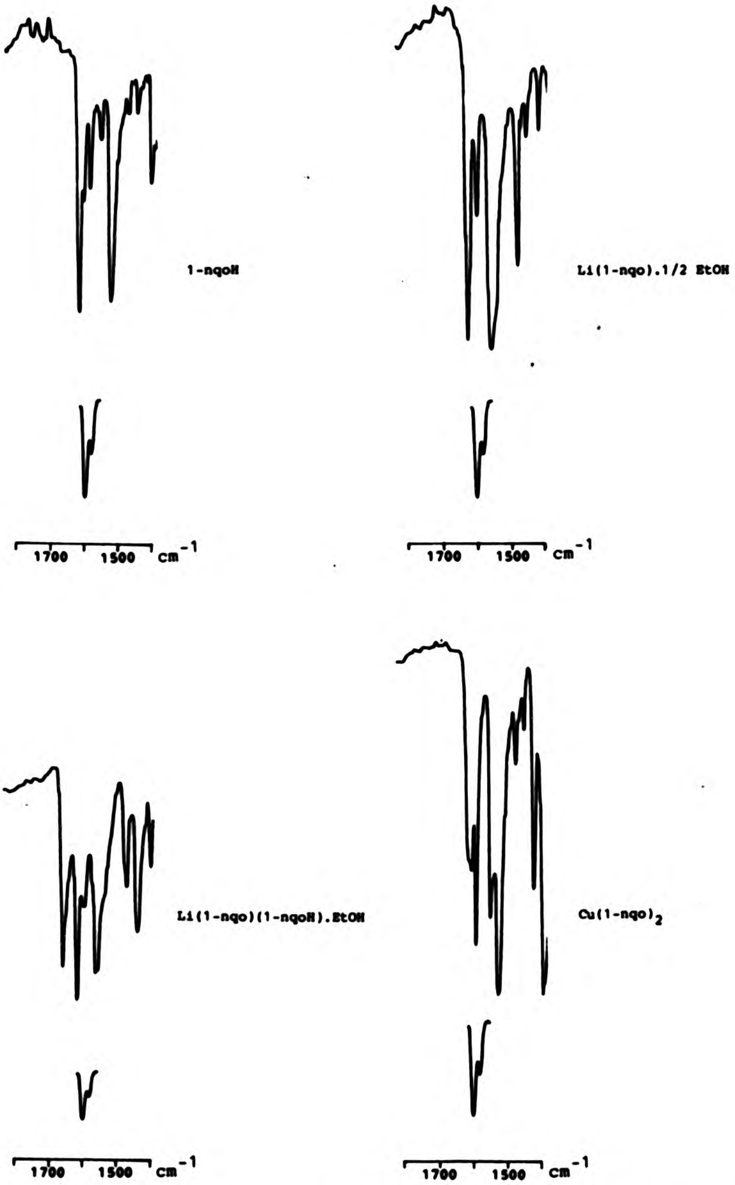


Fig. 1.4 CO stretching vibration bands in the i.r. spectra of 1,2-naphthoquinone 1-oxime and its metal complexes

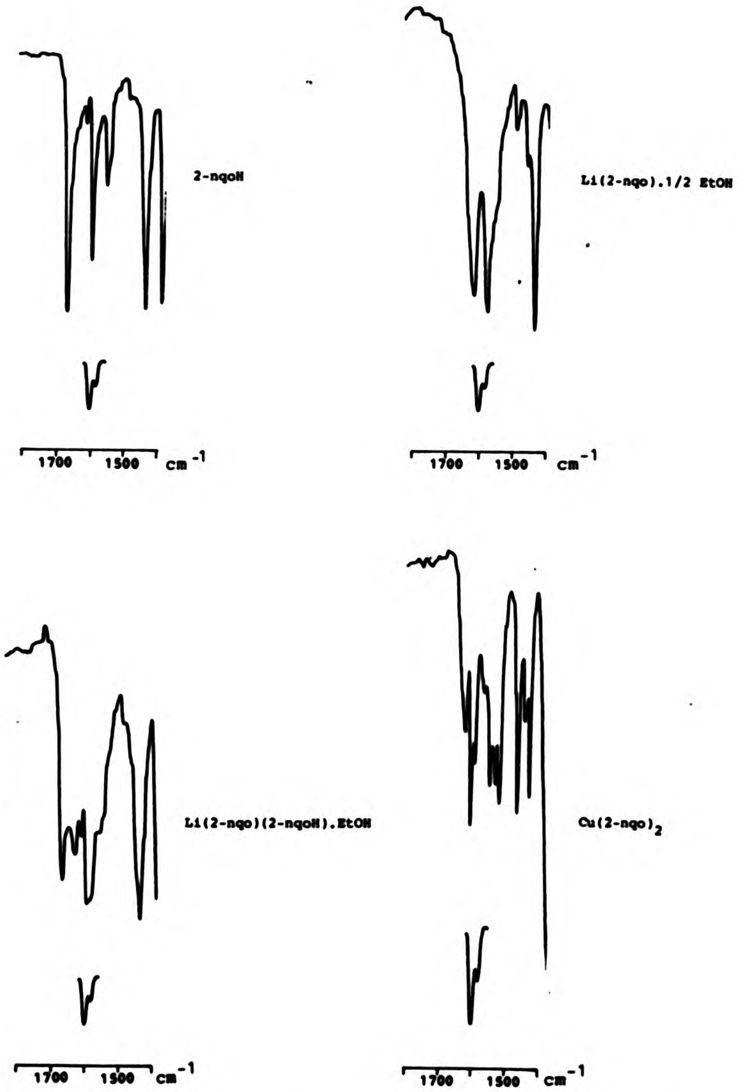


Fig. 1.5 CO stretching vibration bands in the i.r. spectra of 1,2-naphthoquinone 2-oxime and its metal complexes

In the spectra of each of the complexes Li(1-nqo)(1-nqoH), Li(1-nqo)(1-nqoH).EtOH, Li(2-nqo)(2-nqoH) and Li(2-nqo)(2-nqoH).EtOH there are two bands due to νCO, one assignable to the CO group of the neutral and the other to the CO group of the anionic ligand (Table 1.7). In the complexes derived from 1-nqoH these bands appear at *ca.* 1620 and 1665 cm^{-1} and in the complexes derived from 2-nqoH at *ca.* 1620 and 1668 cm^{-1}. The band at lower frequency, most probably corresponds to the absorption due to the CO group of the anionic ligand as indicated by comparison with the spectra of the respective complexes containing only anionic ligands. In the case of the complex Li(1-nqo)(1-nqoH).EtOH this proposal is supported by an X-ray crystallographic study. This indicates that the C-O bond of the anionic ligand (1.26 Å) is slightly lengthened relative to the C-O bond length of the protonated ligand (1.25 Å), while that of the neutral is slightly shortened (1.24 Å) (see also Chapter 2).

As noted earlier, quinoneoximato metal complexes are useful synthetically. This property reflects their multifunctional character which allows them to react with a variety of reagents (Scheme 1.3). The studies of the reactivity of quinoneoximato complexes reported so far have involved almost exclusively transition metals. These have indicated that the nature of the metal has a pronounced effect on the reactions and the type of products formed. For example, the quinone-oximato complexes of nickel undergo deoxygenation by triphenylphosphine to give an iminophosphorane complex, whereas the respective copper complexes undergo an internal redox reaction to give a copper(I) compound and organic products.[41]

Having successfully achieved the synthesis and characterisation of the lithium quinoneoximato complexes it was decided to investigate their reactions. The primary aim was to assess how this non-transition metal affects the course of the reactions and contrast the behaviour of the lithium complexes with those of transition metals.

The lithium complexes Li(1-nqo).1/2 EtOH and Li(2-nqo).1/2 EtOH reacted readily with triphenylphosphine, like the transition metal complexes of 1,2-quinone mono-oximes,[41,43,74,75] but in both cases very complex mixtures resulted which were not investigated further. The lithium complexes reacted also readily with dimethylacetylene dicarboxylate and their behaviour was both novel and interesting. This type of reactions are presented and discussed in Chapter 3.

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CHAPTER TWO

X-RAY CRYSTAL STRUCTURE OF (1,2-NAPHTHOQUINONE 1-OXIME) (1,2-NAPHTHOQUINONE 1-OXIMATO)LITHIUM(I), ETHANOL

2.1 Crystal preparation

(1,2-Naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I), ethanol, [Li(1-nqo)(1-nqoH).EtOH], precipitated as green rhombic like crystals, from ethanol from the reaction of 1,2-naphthoquinone 1-oxime with lithium hydroxide in 2:1 molar ratio. The crystal selected for the study had dimensions of 0.32 x 0.12 x 0.12 mm and it was mounted on a Philips PW1100 diffractometer with a graphite monochromator, employing Mo-K_a radiation.

2.2 Determination of the structure

The crystal's unit cell dimensions were found by least squares refinement of 25 reflections in the range $9^{o} \leqslant \theta \leqslant 12^{o}$. The dimensions were $a = 18.839(3)$ $b = 14.170(3)$, $c = 7.390(2)$ with $\alpha = \beta = \gamma = 90\ ^{o}$. From the above unit cell dimensions and from the characteristic intensity relationships $I_{hkl} \equiv I_{\bar{h}kl} \equiv I_{h\bar{k}l} \equiv I_{hk\bar{l}} \equiv I_{\bar{h}\bar{k}\bar{l}} \equiv I_{h\bar{k}\bar{l}} \equiv I_{\bar{h}k\bar{l}} \equiv I_{\bar{h}\bar{k}l}$ the crystal was found to be orthorhombic. Systematic absences h00, $h = 2n+1$; 0k0, $k = 2n+1$, 00l, $l = 2n+1$ indicated a space group $P2_12_12_1$. The molecular formula was found to be

$C_{22}H_{19}LiN_2O_5$, relative molecular mass equal to 398.35, $D_{z=4}$=1.34 g cm^{-3}. The number of reflections measured were 1998 out of which 716 had $I > 3\sigma(I)$. Corrections were made only for Lorentz polarisation factors but not for absorption.

The structure was solved, by direct methods and all non-hydrogen atoms were located. All the hydrogen atoms were located in subsequent difference Fourier maps. The hydrogen atoms were included in structure factor calculations with isotropic thermal parameters of 0.08 $Å^2$ but were not refined. The nitrogen and oxygen atoms were assigned anisotropic thermal parameters in the refinement of the structure by full matrix least squares procedure which converged to R = 0.056, ($R = \Sigma|F_o-F_c|/\Sigma|F_o|$, R_w = 0.053, ($R_w = \Sigma|F_o-F_c|w^{1/2}/\Sigma|F_o|w^{1/2}$), with weight of $w = 1/\sigma^2(F_o)$, applied to individual reflections. A final difference Fourier showed max.height of 0.18 $eÅ^{-3}$.

All the atomic coordinates, temperature factors, bond lengths, intra bond angles, inter and intra-molecular distances, are given in Tables 1-7 in Appendix 2.

2.3 Results and discussion

The lithium atom is penta-coordinated in a distorted square pyramidal environment with one neutral, and one anionic chelating ligands at the base and an ethanol molecule at the apex. This square pyramidal unit is monomeric, with the closest approach of a second donor atom from another molecule at a distance 4.09 Å (Fig. 2.1).

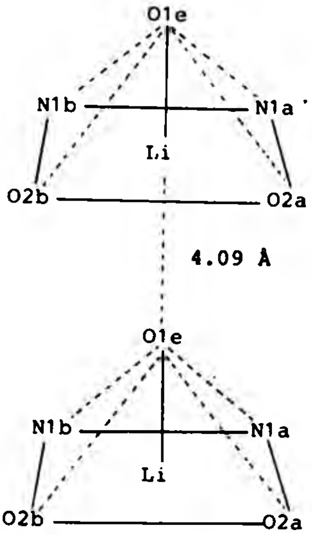

Fig. 2.1

The N1aN1bO2aO2b atoms are planar to within 0.01 Å with the lithium above the plane of best fit through the atoms at 0.53 Å towards the O1e atom of the ethanol molecule which is at 2.45 Å from this plane.

A view of the molecule with the atomic numbering scheme is shown in Fig. 2.2. Selected bond lengths and bond angles are given in Figs. 2.3 & 2.4. In the discussion

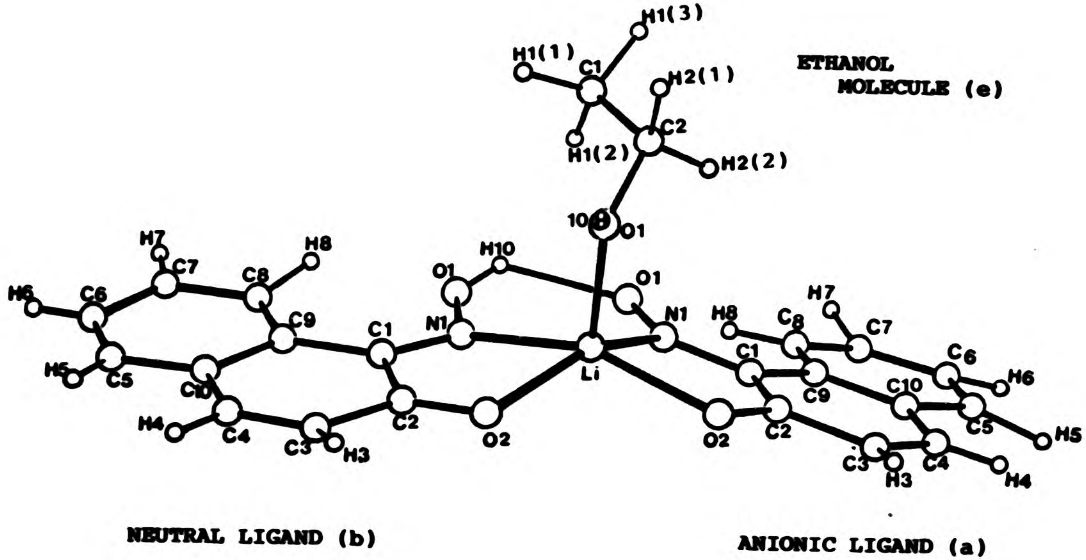

Fig. 2.2 A view of Li(1-nqo)(1-nqoH).EtOH with the atomic numbering scheme

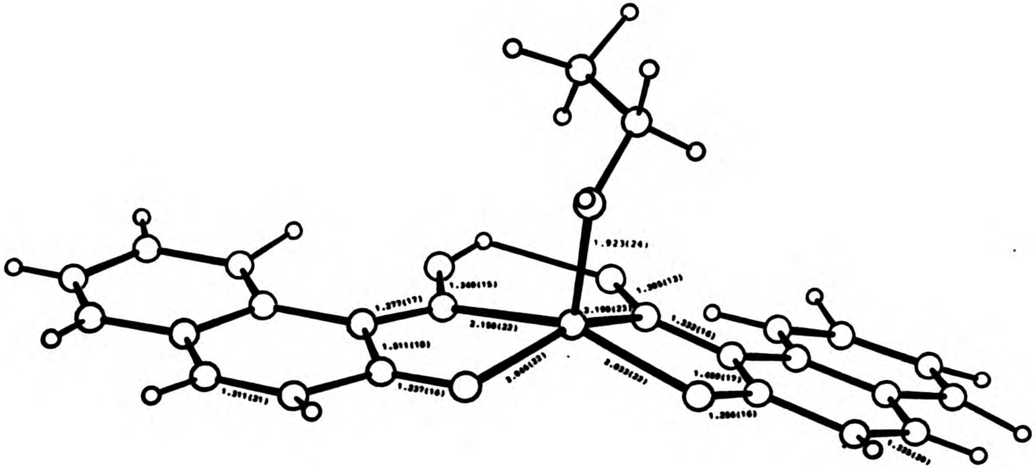

Fig. 2.3 Selected bond lengths (Å) in Li(1-nqo)(1-nqoH).EtOH

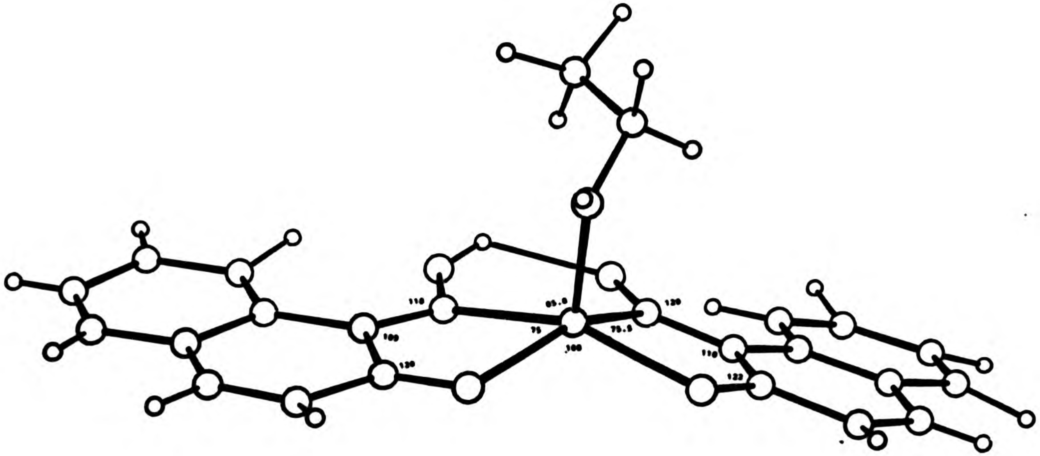

Fig. 2.4 Selected bond angles (^{o}) in Li(1-nqo)(1-nqoH).EtOH

the bond lengths are given to two significant figures to allow comparison with other reported data.

The non-hydrogen atoms of the anionic ligand are planar to within 0.10 Å and those of the neutral ligand to within 0.02 Å. The angle between the least squares planes of the anionic and neutral ligands is 159.7°. The best fit planes of the anionic and neutral ligands are bent down (away from the oxygen atom of the ethanol molecule) from the N1aN1bO2aO2b plane by angles of 6.5° and 13.8° respectively.

The bond contacts around lithium fall in the range 1.92-2.20 Å (Fig. 2.3) and are similar to those reported for other penta-coordinated lithium complexes (1.94-2.24 Å), which also involve oxygen and nitrogen donor atoms.[1-4]

The features of this crystal structure which are noteworthy are:

i) the character and arrangement of the anionic and neutral quinoneoximic ligands in the complex;

ii) the hydrogen bond between the oxygens of the NO group of the anionic and neutral quinoneoximic ligands;

iii) the metal to solvent coordination.

i) The character and arrangement of the anionic and neutral quinoneoximic ligands

As noted earlier, previous studies have shown that 1,2-naphthoquinone 1-oxime has essentially a quinoneoximic structure involving intramolecular hydrogen bonding. The quinoneoximic structure is revealed by the short CN (1.31 Å), CO (1.25 Å), C3-C4 (1.33 Å) bond lengths and the long NO (1.36 Å), C1-C2 (1.48 Å) bond lengths (Fig. 2.5).[5] The CN and NO bond distances, compare well with those found in oximes,[6] e.g. acetoxime (C=N, 1.29 Å; N-O, 1.36 Å) and the CO bond distance with that found in quinones,[7,8] e.g. 1,4-benzoquinone (C=O, 1.22 Å). In 1,2-naphthoquinone 1-oxime the CO and CN bond lengths are longer than the corresponding bonds in 1,2-quinone mono-oximes which do not exhibit intramolecular hydrogen bonding. For example in 1,2-naphthoquinone 2-oxime 5-sulphonic acid monohydrate the CO and CN bond distances are 1.24 Å and 1.30 Å respectively (Fig. 2.6).[9]

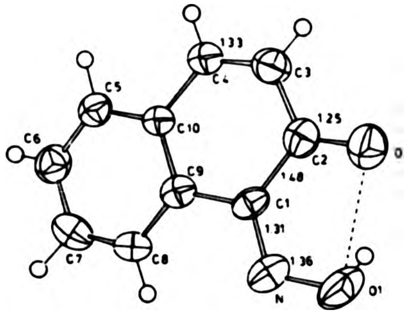

Fig. 2.5 Crystal structure of 1,2-naphthoquinone 1-oxime with the atomic numbering and selected bond lengths (Å)

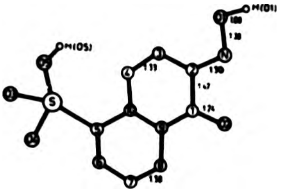

Fig. 2.6 Crystal structure of 1,2-naphthoquinone 2-oxime 5-sulphonic acid monohydrate and selected bond lengths (Å)

Two types of complexes derived from 1,2-naphthoquinone 1-oxime have been characterised crystallographically. Both types involve the anion of the ligand which either chelates to the metal or bonds to the metal via the NO group only. In both cases the ligand is essentially quinoneoximic in character. This is indicated for example, by the bond lengths of the C1-C2 and the C3-C4 bonds which have single and double bond character respectively, as shown in Figs. 2.7 and 2.8.

Chelation has been established crystallographically in four 1,2-naphthoquinone 1-oximato complexes,[10-13] $Cu(1\text{-nqo})_2.2Me_2CO$, $Cu(1\text{-nqo})(Ph_3P)_2$, $Ru(1\text{-nqo})_2(py)_2$ (Fig. 2.7) and $[pyH][Ir(1\text{-nqo})(py)Cl_3]$. This type of bonding has also been established in several other complexes derived from other 1,2-quinoneoximic ligands.[14-22]

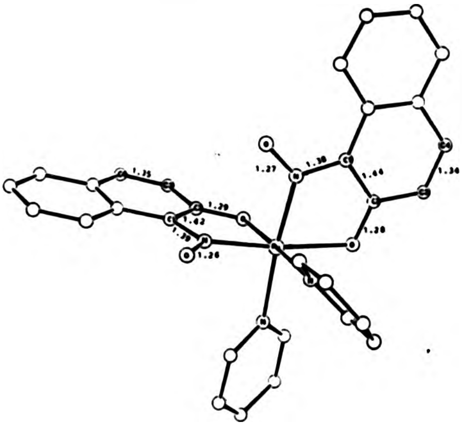

Fig. 2.7 Crystal structure of $Ru(1\text{-}nqo)_2(py)_2$ and selected bond lengths (Å)

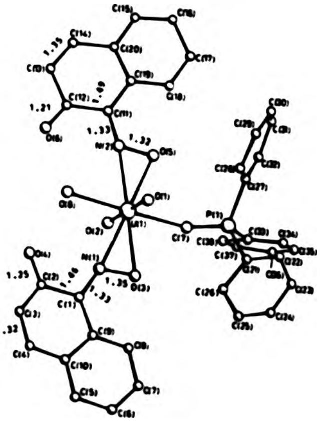

Fig. 2.8 Crystal structure of $UO_2(1\text{-}nqo)_2(Ph_3PO).H_2O$ and selected bond lengths (Å)

Bonding through both the nitrogen and oxygen atoms of the NO group has recently been identified in the complex $UO_2(1\text{-nqo})_2(Ph_3PO).H_2O$ (Fig. 2.8).[23] In this complex the CO group is not involved in bonding. Bonding involving only the NO group has also been observed in platinum complexes derived from 4-isonitroso-3(R)-isoxazol-5-one.[24] However, in these platinum complexes, bonding to the metal is only through the nitrogen atom of the NO group.

In the complexes involving the anionic chelated 1-nqo^- ligand, the CO and CN bonds are longer than in the free ligand (Table 2.1). This is in accord with the shift to lower frequency of the νCO absorption in their i.r. spectra noted earlier in Chapter 1. In contrast, the NO bond length in the complexes is shorter than in the free ligand. This is due, at least in part, to the disruption of the hydrogen bonding present in the free ligand.

In the $UO_2(1\text{-nqo})_2(Ph_3PO).H_2O$ complex the CN bond is longer than the respective bond in the free ligand. In contrast, the CO bond, which does not participate in bonding to the metal, is slightly shorter than the CO bond in the free ligand (Table 2.1, Fig. 2.8).

Table 2.1 Selected bond lengths (Å) of 1,2-naphthoquinone 1-oxime and its metal complexes

Compound	**C-O**	**C-N**	**N-O**	**Ref.**
1-nqoH	1.25	1.31	1.36	5
Cu(1-nqo)2.2Me$_2$CO	1.29	1.35	1.26	10
Cu(1-nqo).(Ph$_3$P)$_2$	1.26	1.37	1.29	11
Ru(1-nqo)$_2$(py)$_2$	1.28	1.38	1.27	
	1.29	1.39	1.26	12
[pyH][Ir(1-nqo)(py)Cl$_3$]	1.30	1.35	1.27	13
UO$_2$(1-nqo)$_2$(Ph$_3$PO).H$_2$O	1.25	1.33	1.35	
	1.21	1.33	1.32	23
Li(1-nqo)(1-nqoH).EtOH	1.26	1.33	1.30	
	1.24	1.28	1.34	*

* = This work

In the complex Li(1-nqo)(1-nqoH).EtOH both the anionic 1-nqo$^-$ and neutral 1-nqoH ligands are quinoneoximic in character and are chelated to the metal. The quinoneoximic character of these ligands is indicated by the long C1-C2 (1.49 ± 0.03 Å) and the short C3-C4 (1.32 ± 0.01 Å) average bond distances (Fig. 2.3). The NO groups of the two ligands are in a *cis* arrangement. This contrasts the *trans* arrangement which is shown by other chelated quinoneoximato complexes, e.g. Ru(1-nqo)$_2$(py)$_2$ (Fig. 2.7).

The CO (1.26 Å) and CN (1.33 Å) bond lengths of the anionic ligand are i) slightly longer than the respective bonds in the free ligand and ii) shorter than the corresponding bond lengths in the respective copper, ruthenium and iridium complexes (Table 2.1). These observations suggest that the bonding of the 1-nqo$^-$ ligand to the metal is weaker in the lithium complex than in complexes of other metals. This is also apparent in the i.r. spectrum of the lithium complex in which, as discussed in Chapter 1, the νCO absorption does not shift to lower frequency relative to the protonated free ligand.

Both the CO (1.24 Å) and CN (1.28 Å) bond lengths in the neutral 1-nqoH ligand of Li(1-nqo)(1-nqoH).EtOH are shorter than the corresponding bonds in the free ligand and its copper, ruthenium and iridium complexes (Table 2.1). This implies that the 1-nqoH ligand in Li(1-nqo)(1-nqoH).EtOH is also weakly bound to lithium.

The NO bond length in both the anionic and neutral chelated ligands of the lithium complex Li(1-nqo)(1-nqoH).EtOH is longer than the corresponding bond length in the copper, ruthenium and iridium complexes. This is probably due to the presence of hydrogen bonding between the ligands in the lithium complex.

ii) Hydrogen bond between the oxygens of the NO group of the anionic and neutral ligands

The crystal data indicate that an asymmetrical hydrogen bridge exists between the neutral and anionic ligands in Li(1-nqo)(1-nqoH).EtOH. The hydrogen atom is positioned at 0.84 Å from the oxygen of the neutral ligand and at 1.90 Å from the oxygen of the anionic ligand. Such an asymmetrical hydrogen bridge at 0.72 Å from the NO oxygen and at 1.88 Å from the carbonyl oxygen is also found in the protonated free ligand.

Similar hydrogen bridges have also been observed in bis(dimethylglyoximato)nickel(II) and bis(salicylaldoximato)nickel(II) complexes (e.g. Fig. 2.9).[25-27] In the former the hydrogen bridge is believed to be symmetrical, while in the latter is asymmetrical.

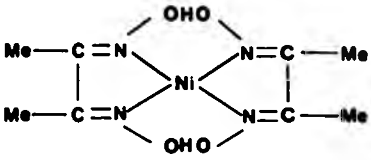

Fig. 2.9 Bis(dimethylglyoximato)nickel(II)

iii) Metal to solvent coordination

In the complex Li(1-nqo)(1-nqoH).EtOH lithium attains a coordination number of 5 and a distorted square pyramidal geometry through the attachment of an ethanol molecule. Penta-coordinated lithium has been found in several other complexes mainly those of crown ethers,[1-3,28,29] as for example in the complex derived from lithium picrate and dibenzo-36-crown-12 ether, [2Li(pic)DB36C12.2H_2O] (Fig. 2.10).

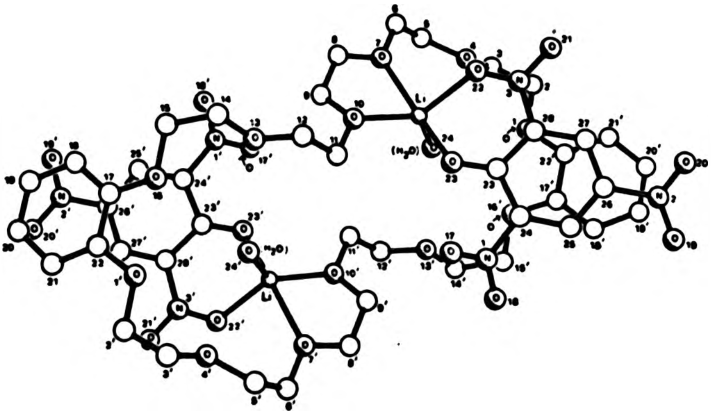

Fig. 2.10 Crystal structure of [2Li(pic)DB36C12.2H_2O

In Li(1-nqo)(1-nqoH).EtOH, the metal is at a distance of 1.92 Å from the oxygen atom of the ethanol molecule. Other lithium solvated complexes (mainly those of crown ethers[3,30,31] and diorganophosphides[32]) have also been studied by X-ray crystallographic techniques. In these complexes the distance of the lithium from the oxygen atom of the solvent molecule (water, tetrahydrofuran or diethyl ether) is close to that found between the lithium and the ethanol molecule in Li(1-nqo)(1-nqoH).EtOH (Table 2.2).

Table 2.2 Metal-solvent bond lengths in solvated lithium complexes (Å)

Complex	Li-O(solvent)	Ref.
Li(1-nqo)(1-nqoH).EtOH	1.92	*
$[\{Li(Et_2O)Ph_2P\}]$	1.92	32
$[\{Li(THF)_2Ph_2P\}]$	1.94	32
$[\{Li(THF)P(C_6H_{11})_2\}]$	1.94	32
$2Li(pic)DB36C12.2H_2O$	1.93	3
$[Li(C_6N_3O_7H_2).2H_2O][C_{14}H_{20}O_5]$	1.86	30
$LiClO_4.(CH_2CH_2O)_6.2H_2O$	1.91	31
$(LiSCN)_2(CH_2CH_2O)_6.2H_2O$	1.93	31
$[Li(CH_2(OH)CO_2].H_2O$	2.03	4

* = This work

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CHAPTER THREE

REACTION OF COPPER AND LITHIUM COMPLEXES DERIVED FROM 1,2-QUINONE MONO-OXIMES WITH DIMETHYLACETYLENE DICARBOXYLATE (DMAD)

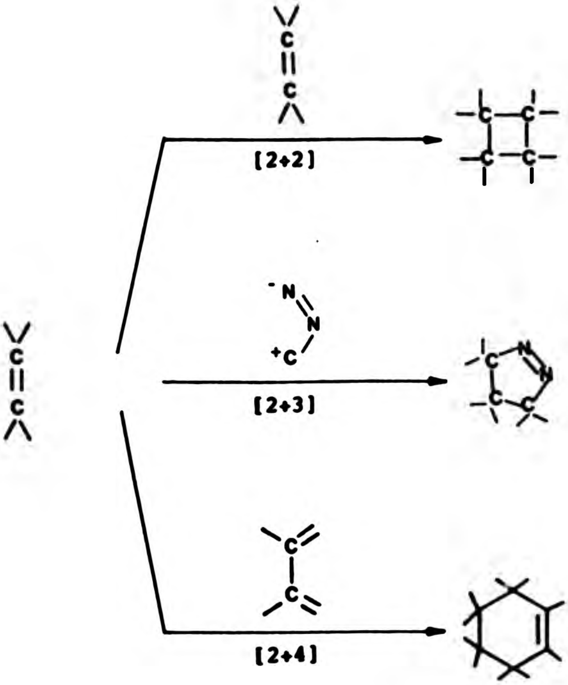
3.1 Cycloaddition and nucleophilic addition reactions

Cycloaddition reactions provide excellent pathways to the formation of a wide range of ring systems.[1,2,3] Some of these reactions, described as [2+2], [2+3] and [4+2] cycloadditions, are illustrated in Scheme 3.1.

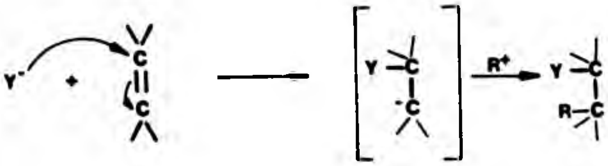
The [2+2] cycloaddition is a photochemically initiated reaction between two olefins leading to four membered rings. The [2+3] cycloaddition involves addition of 1,3-dipolar compounds to olefinic substrates leading to five membered rings. The [4+2] cycloaddition which is commonly known as the Diels-Alder reaction, involves the reaction of a diene or a heterodiene with a dienophile to give six membered rings. In the Diels-Alder reaction olefins (eg. maleic anhydride) or acetylenes (e.g. dimethylacetylene dicarboxylate) with electron withdrawing groups serve as good dienophiles.

Nucleophilic additions, involve the addition of a nucleophile known as the donor, to an olefin or acetylene known as the acceptor[2,4,5] (Scheme 3.2). This type of reaction is generally promoted by bases e.g. alkali metal alkoxides.

Electron withdrawing groups on the acceptor, also facilitate the reaction. When the nucleophile attacking the substituted olefin or acetylene is a carbanion, the process is referred to as Michael reaction. All other nucleophilic additions that follow Michael's reaction mechanism are called Michael-type reactions.



Scheme 3.1



R = H, alkyl

Y^- = nucleophile

Scheme 3.2

Quinoneoximato complexes have diene and heterodiene character and in principle are expected to undergo Diels-Alder reactions or nucleophilic addition reactions. Diels-Alder adducts involving the heterodiene part of the complexes have been isolated from the reaction of quinoneoximato complexes with dimethylacetylene dicarboxylate.[6,7] The complexes can also act as dienophiles but such behaviour has not so far been established.

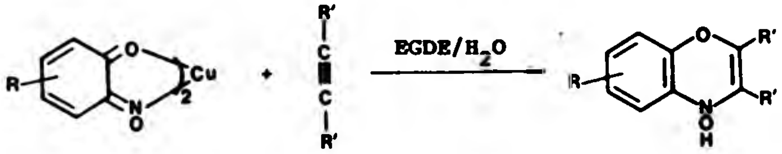
During this work, the reactivity of the lithium complexes derived from the mono-oximes of 1,2-naphthoquinone towards dimethylacetylene dicarboxylate has been undertaken. In addition, analogous reactions of copper(II) complexes derived from 1,2-quinone mono-oximes have been re-examined.

3.2 Reaction of metal complexes derived from 1,2-quinone mono-oximes and related compounds with dimethylacetylene dicarboxylate

The first study of the reaction of metal complexes derived from 1,2-quinone mono-oximes with dimethylacetylene dicarboxylate was reported in 1976.[6] This study showed that the copper(II) quinoneoximato complexes react readily with the dienophile in ethylene glycol dimethyl ether in the presence of water. The reaction involves the heterodiene part of the complex and leads to a 1,4-oxazine (Scheme 3.3). In contrast, no reaction was observed with the cobalt(III) complex of 1,2-benzoquinone 2-oxime, the free quinone mono-oximes, or their methyl ethers.

These observations, were accounted for in terms of i) the coordinative unsaturation of copper, ii) the polarising ability of the metal and iii) the ability of the metal to participate in π-bonding with the triple bond of the dienophile.

Subsequently, other workers[7] reinvestigated the reaction of bis(4-chloro-1,2-benzoquinone 2-oximato) copper(II) with dimethylacetylene dicarboxylate in a mixture of ethylene glycol dimethyl ether and water, and confirmed the earlier findings. They also reported, that the analogous reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), dipyridyl, whose octahedral structure has been established by X-ray crystallography,[8] also leads to the 1,4-oxazine. This observation showed that, contrary to earlier suggestion, coordinative unsaturation of the metal is not a requirement for the reaction.

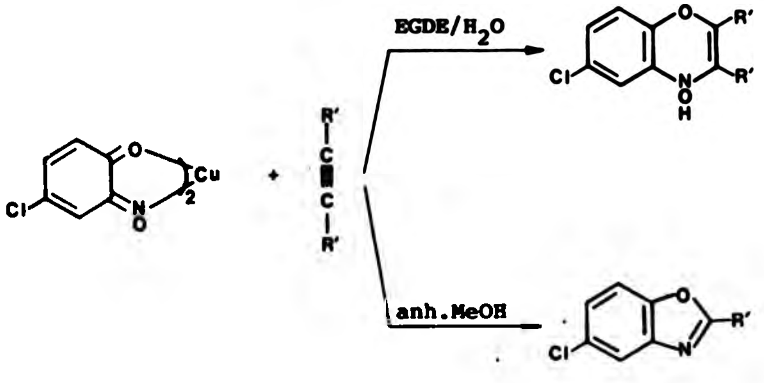


R' = $MeCO_2$

R = 4-Me, 4-Cl, 4-Br, 5-MeO, 5-Me_2N,
3,4-(CH=CHCH=CH), 5,6-(CH=CHCH=CH),
3,4 and 5,6-(CH=CHCH=CH)

Scheme 3.3

The second group of workers also reported that when the reaction of bis(4-chloro-1,2-benzoquinone 2-oximato) copper(II) with the dienophile is carried out in anhydrous methanol, a 1,3-oxazole rather than a 1,4-oxazine results (Scheme 3.4), together with an unidentified Cu(I) product.[7] The formation of the oxazole was accounted in terms of reduction of copper(II) to copper(I). Furthermore, it was suggested that the reaction proceeds via a deoxygenation route analogous to that proposed for the $Cu(qo)_2/Ph_3P$ system.[9] However, no mechanistic details were given.



R' = $MeCO_2$

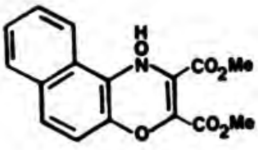
Scheme 3.4

When the reaction of the (1,2-naphthoquinone 1-oximato) lithium(I) with dimethylacetylene dicarboxylate in aqueous ethylene glycol dimethyl ether was examined during the present study, it was found that neither a 1,4-oxazine nor a 1,3-oxazole is obtained. The product was shown by mass spectrometry to be a species isomeric with the 1,4-oxazine. Analogous studies of the Li(2-nqo)/DMAD system showed that in this case the reaction does lead to the respective 1,4-oxazine, as well as, to its isomer.

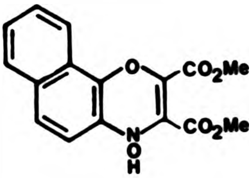
The above clearly indicate that the metal and the reaction conditions have a pronounced effect on the nature of the organic products arising from the reaction of quinoneoximato complexes with dimethylacetylene dicarboxylate. As a consequence, in parallel to the study of the reaction of lithium quinoneoximato complexes with dimethylacetylene dicarboxylate, the reactions of the copper naphthoquinoneoximato complexes with this dienophile were reinvestigated in depth.

3.3 Reinvestigation of the reaction of $Cu(1\text{-nqo})_2$ and $Cu(2\text{-nqo})_2$ with DMAD

When the reaction of bis(1,2-naphthoquinone 1-oximato) copper(II) with dimethylacetylene dicarboxylate in aqueous ethylene glycol dimethyl ether was carried out, the previously described 1,4-oxazine (1) resulted in comparable yield (77%) to that reported earlier (91%). The $Cu(2\text{-nqo})_2$/DMAD system also gave a 1,4-oxazine (2). In this case however, the yield (32%) was considerably lower than previously reported (72%). Both oxazines were fully characterised by elemental analysis, spectroscopic methods (i.r., ^1H n.m.r., m.s.) and comparative melting point determinations.



1



2

The 1,4-oxazine **1** showed absorptions at 3350, 1760, and 1700 cm^{-1} due to hydroxy and ester carbonyl groups. Its ^{1}H n.m.r. spectrum exhibited two singlets at 3.94 and 3.97 ppm due to the six carbomethoxy protons, a singlet at 5.23 ppm due to the proton of the hydroxy group and a multiplet at 7.11-8.70 ppm due to the six aromatic protons.

The i.r. spectrum of the 1,4-oxazine **2** indicated again the presence of hydroxy and ester carbonyl groups. In its ^{1}H n.m.r. spectrum the six methyl protons of the ester group appeared at 3.98 and 3.99 ppm as two singlets, the proton of the hydroxy group at 5.30 ppm as a singlet and the six aromatic protons at 7.27-8.24 ppm as a multiplet.

The mass spectra of both compounds showed fairly intense molecular ion peaks at 315 and exhibited fragmentation patterns supporting the formulations.

In addition to the oxazine, a metal-containing product was also isolated from each of the reaction systems $Cu(1\text{-nqo})_2$/DMAD and $Cu(2\text{-nqo})_2$/DMAD. The i.r. spectra of these products were fairly simple, well defined and almost identical. The latter observation suggested that these reactions lead to the same metal-containing product. The spectra included absorptions at 3440, 1680-1620 and 1430 cm^{-1} indicating the presence of hydroxy and carboxylate groups, and resembled the i.r. spectrum of acetylenedicarboxylic acid.

For both products, elemental analysis suggested the presence of four carbon atoms per copper. Both samples also contained a low percentage of nitrogen impurities. Attempts to purify the solids by further washing with methanol were unsuccessful. However, it was possible to conclude from the analytical and spectroscopic results that the products are crude hydrated copper complexes of the carboxylate dianion 3. Both solids were found to be paramagnetic.

Support for the suggested formulation, was obtained by the direct synthesis of the copper(II) complex of 3. Thus reaction of copper hydroxide with dimethylacetylene dicarboxylate afforded a solid which had an identical i.r. spectrum to that of the copper-containing products obtained from the reaction of DMAD with Cu(1-nqo)$_2$ or Cu(2-nqo)$_2$.

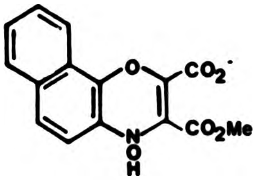
$^{-}O_2C{-}C{\equiv}C{-}CO_2^{-}$

3

The 1,4-oxazines 1 and 2 were also obtained from the reaction of the copper complexes Cu(1-nqo)$_2$ and

$Cu(2\text{-}nqo)_2$ with dimethylacetylene dicarboxylate in anhydrous methanol. Each of these reactions again afforded a paramagnetic metal-containing product.

Elemental analysis suggested that the metal-containing product obtained from the $Cu(2\text{-}nqo)_2$/DMAD system was the hydrated copper complex of the partially hydrolysed oxazine anion **4**. This was supported by the i.r. spectrum. In contrast to the spectrum of the solid obtained from the reaction of the complex $Cu(2\text{-}nqo)_2$ with DMAD in aqueous ethylene glycol dimethyl ether, this was fairly complex with rich absorptions in the aromatic fingerprint region. The i.r. spectrum also included bands at 3400, 1735 and 1610 cm^{-1}. The magnetic moment of this copper carboxylate was found to be subnormal (μ_{eff} = 0.55 BM). Such low magnetic moments are not uncommon for copper(II) carboxylates.[10]

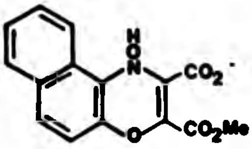


4

Further support for the proposed formulation of the copper-containing product was obtained by acidifying it and extracting the organic moiety with diethyl ether.

This procedure afforded a small quantity of an organic compound. The i.r. spectrum of this compound showed absorptions at 3600-3400, 1740 and 1655 cm^{-1}, due to hydroxy, ester carbonyl and carboxylate groups. More significantly, the ^1H n.m.r. spectrum gave resonances for aromatic (7.27-8.24 ppm), carbomethoxy protons (3.94 ppm) in a ratio of 2:1, and for the proton of the hydroxy group attached to the oxazine ring (5.35 ppm).

Elemental analysis of the copper-containing solid obtained from the reaction of the $Cu(1\text{-nqo})_2$ complex with dimethyl acetylene dicarboxylate indicated that it was a mixture of the copper derivatives of the hydrolysed oxazine mono- and di-anions **5** and **6**. Its i.r. spectrum included peaks due to carbonyl and aromatic groups. The solid was again found to be paramagnetic. Acidification of this solid followed by extraction with diethyl ether, afforded a small amount of an organic species whose i.r. spectrum had absorptions due to hydroxy, ester carbonyl and aromatic groups. The ^1H n.m.r. spectrum showed resonances due to the proton of the hydroxy group attached to the oxazine ring (5.35 ppm) and due to aromatic (7.22-8.20 ppm) and carbomethoxy protons (3.91 ppm) in the approximate ratio of 5:1, which is in accord with the presence of a mixture of the protonated anions **5** and **6**.



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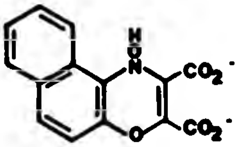

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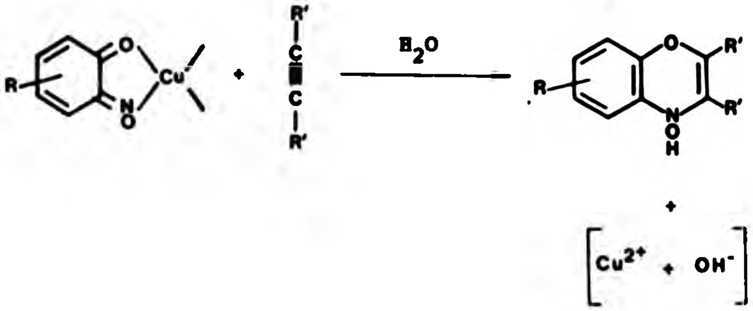
The characterisation of the copper-containing compounds obtained from the reaction of the naphthoquinoneoximato copper complexes with the acetylene dicarboxylate gives a clear understanding of the reaction behaviour. As indicated in the Scheme 3.5, water is not merely part of the solvent system but a reactant. Thus, the formation of the oxazine requires not only the ligand i.e. the diene and the dienophile but also a proton, which arises from the water. Concurrently with the formation of the oxazine, Cu^{2+} and OH^{-} ions are formed. The latter cause subsequent hydrolysis of the carbomethoxy groups of either the acetylene dicarboxylate or the oxazine to carboxylated anions which react with the metal ions to give the metal-containing products.

The hydrolytic reactions involving the oxazine, clearly affect the yield of this product. As a consequence, it was thought that by using acetic acid as the proton donor instead of water, the hydrolytic effects could be suppressed and thus the yield of the oxazine will increase. However, when the reaction between bis(1,2-naphthoquinone 2-oximato)copper(II) and dimethylacetylene dicarboxylate was carried out in ethylene glycol dimethyl ether in the presence of acetic acid, the yield of the 1,4-oxazine did not increase.

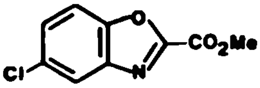


R' = $MeCO_2$
R = 3,4-(CH=CHCH=CH), 5,6-(CH=CHCH=CH)

Scheme 3.5

The isolation of the 1,4-oxazine derivatives from the reaction of the copper complexes $Cu(1\text{-nqo})_2$ and $Cu(2\text{-nqo})_2$ with dimethylacetylene dicarboxylate in anhydrous methanol, contrasts with a previous report indicating that under these conditions bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) reacts with the acetylene dicarboxylate to give the 1,3-benzoxazole 7. When the reaction of the $Cu(4\text{-Clqo})_2$ complex with the dienophile was re-examined in anhydrous methanol, the product obtained, was the 1,4-benzoxazine 8, and not the 1,3-benzoxazole. As a consequence, it was thought that the formation of the benzoxazole in the earlier study, must have been due to some other factor. Transition metal complexes are known to be very effective catalysts for the aerobic oxidation of a variety of organic substrates.[11-22] Therefore it is likely that the oxazole arises from the oxazine via an oxidation process catalysed by the initial $Cu(qo)_2$ complex.

In order to check this hypothesis, the oxazine **8** was heated under reflux together with the copper complex $Cu(4\text{-}Clqo)_2$ in methanol. As predicted the reaction did afford the oxazole **7** which had the same m.p. and ^1H n.m.r. spectrum to that reported earlier.[7] In its mass spectrum the parent ion at *m/z* 211 had the expected isotopic pattern and corresponded to the base peak. Peaks arising from loss of $MeO^{\bullet}$, $MeCO_2^{\bullet}$, and $[MeCO_2^{\bullet} + CO]$ from the parent ion were also present.



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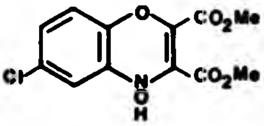
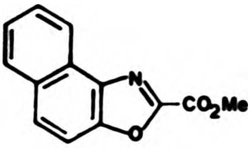


8

Subsequently, samples of the oxazine **1** were also heated under reflux in methanol in the presence of air and i) catalytic amounts of bis(1,2-naphthoquinone 1-oximato) copper(II), or ii) 1,2-naphthoquinone 1-oxime, or iii) without any other additive. From the latter two reactions the oxazine was recovered unchanged. In contrast, the reaction involving the copper complex afforded the oxazole **9** in high yield (63%), thus supporting further the validity of the oxidation proposal.



9

The 1,3-oxazole **9** has not been reported previously. This compound was characterised by elemental analysis, i.r., ^{1}H n.m.r., and m.s. Its ^{1}H n.m.r. spectrum (Fig. 3.1) gave a singlet at 4.14 ppm due to the three methyl protons of the ester group and a multiplet at 7.59-8.71 ppm due to the six aromatic protons. The i.r. spectrum (Fig. 3.2) included peaks due to ester carbonyl, carbomethoxy and aromatic groups. In the mass spectrum the parent peak at *m/z* 227 was also the base peak (Fig. 3.3). Peaks due to loss of MeO$^\bullet$, $MeCO_2^\bullet$ and [$MeCO_2^\bullet$ + CO] from the parent ion were also present.

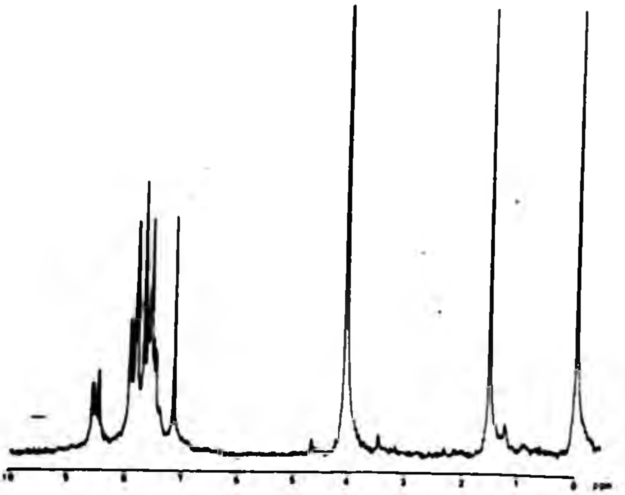


Fig. 3.1 ^{1}H n.m.r. spectrum of 9, Bruker WP 80 MHz

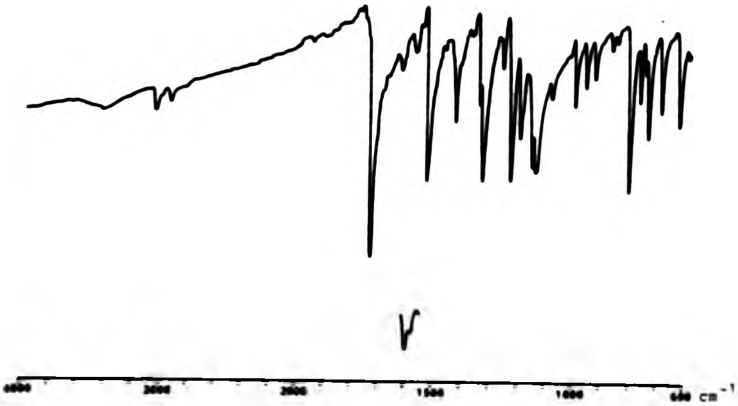


Fig. 3.2 Infra-red spectrum of 9

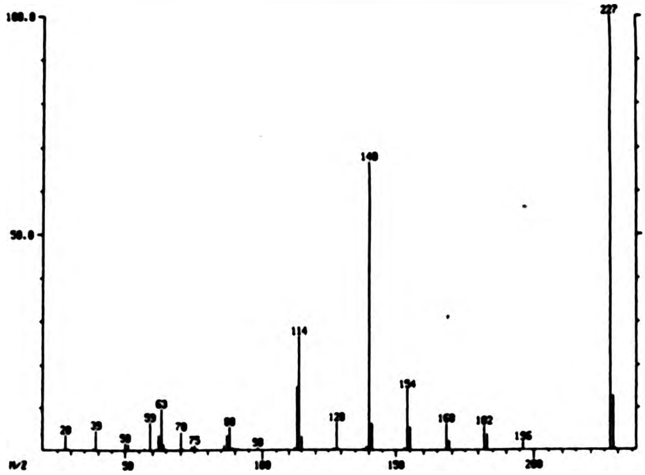


Fig. 3.3 Mass spectrum of 9

3.4 Reactions of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone with dimethylacetylene dicarboxylate

3.4.1 Lithium complexes of 1,2-naphthoquinone 1-oxime

The reactions between the lithium complexes derived from 1,2-naphthoquinone 1-oxime with dimethylacetylene dicarboxylate, were investigated in different molar ratios and at various temperatures using aqueous ethylene glycol dimethyl ether as the solvent system (Table 3.1). In general, the reactions were relatively fast and for example at *ca.* 20 °C they were complete within 1 h. The molar ratios of the reactants and

Table 3.1 Reaction of the lithium complexes of 1,2-naphthoquinone 1-oxime with dimethylacetylene dicarboxylate (DMAD)

Complex	**Molar ratio of complex:DMAD**	**Temp. of reaction(^{o}C)**	**Yield of addition product (13/14)(%)**
Li(1-nqo).1/2 EtOH	1:2	20	41
Li(1-nqo).1/2 EtOH	1:2	0	44
Li(1-nqo).1/2 EtOH	1:2	50	30
Li(1-nqo).1/2 EtOH	1:4	20	51
Li(1-nqo)	1:4	20	53
Li(1-nqo)(1-nqoH)	1:4	20	51

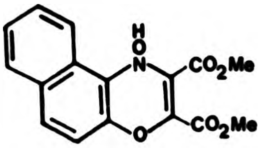
the temperature had no effect on the nature of the products. However, the yield of the organic product was higher at lower reaction temperature and when a 1:4 molar ratio of the complex to the dienophile was used.

In all cases, the reaction led to a small amount of an insoluble inorganic lithium-containing product. This was isolated by filtration and identified as lithium hydroxide in view of the alkalinity of its aqueous solution and its lithium content. Extraction of the residue obtained by drying the filtrate, afforded an organic product and a metal-containing product.

Purification and characterisation of the organic product

Recrystallisation of the organic product afforded a yellow solid S in pure form. Elemental analysis suggested the formula $C_{16}H_{13}NO_6$ which corresponds to that required by the Diels-Alder adduct **10** whose formula is presented again below for the convenience of the reader. However, the m.p. and the i.r. and ^1H n.m.r. spectra of the product were fundamentally different from that of the cycloaddition product **10**. The mass spectrum showed a molecular ion peak at 315 indicating that solid S is isomeric to **10**.

Various structural formulae are possible for this isomer, e.g. **11**, **12**, and **13**.



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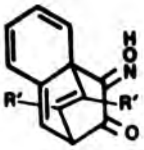

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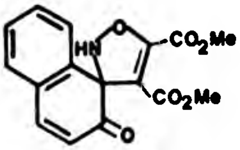

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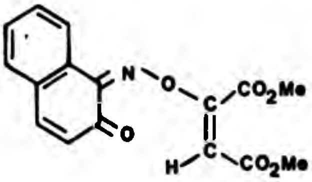


13

R' = $MeCO_2$

Initially, it was thought that the product was either the adduct **11** arising from a [4+2] cycloaddition involving the diene moiety of the 1-nqo$^-$ ligand and the dienophile, or the adduct **12** arising from an 1,3-dipolar addition of the 1,3-dipole of the ligand to the acetylene dicarboxylate.

However, the i.r. spectrum of the yellow solid S (Fig. 3.4) showed no absorption in the region 3600-3200 cm^{-1} where absorptions due to νOH or νNH are expected for **11** and **12** respectively. In the ^{1}H n.m.r. spectrum (Fig. 3.5) no resonances due to -OH or -NH protons could be detected. Furthermore, the ^{1}H n.m.r.

spectrum showed four singlets in the region where the methyl protons of the ester groups normally resonate (3-4 ppm) rather than a maximum of two expected for either structure **11** or **12**. Clearly, the above spectroscopic features precluded these structures.

In the case of structure **11** this conclusion is also supported by the lack of reaction between the product S and cobalt(II) or nickel(II) sulphate.

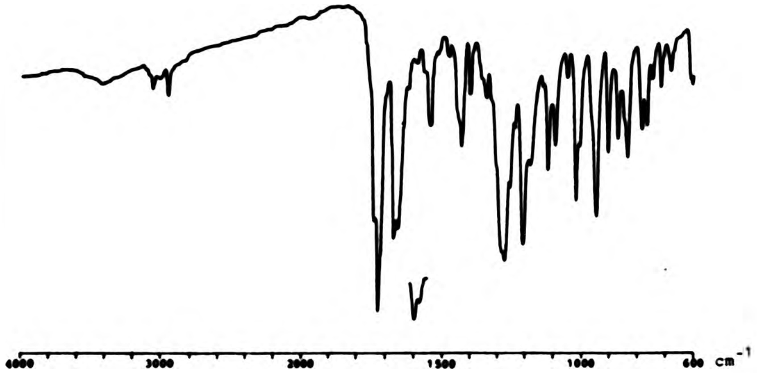


Fig. 3.4 Infra-red spectrum of product S (**13**/**14**)

Having ruled out the formulation of the product as a cycloadduct, structure **13** was considered. This corresponds to the product arising from the nucleophilic addition of the heterodiene moiety of the ligand to the acetylene dicarboxylate.

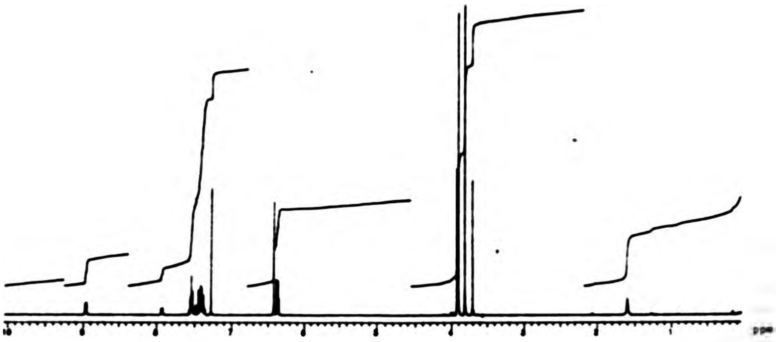


Fig. 3.5 ^{1}H n.m.r. spectrum of product S, (13/14)
Varian XVR-400 MHz ($CDCl_3$ as reference)

The i.r. and mass spectral features of the isolated product were as expected for this formulation. Thus, in the i.r. spectrum (Fig. 3.4) there were no bands in the region 3600-3200 cm^{-1}, and there were intense absorptions at 1730 and at 1680, 1660 cm^{-1} due to the νCO of the ester and quinone groups respectively. In the mass spectrum (Fig. 3.6) there was a prominent parent ion peak at 315 and fragments arising by the loss of MeO$^\bullet$, and $MeCO_2^\bullet$ from the parent ion. Most significantly, there was also a prominent peak at 156 due to $[nqo - O]^+$ ion and ions of lower mass analogous to those found in the spectrum of 1,2-naphthoquinone 1-oxime, were also present.[23]

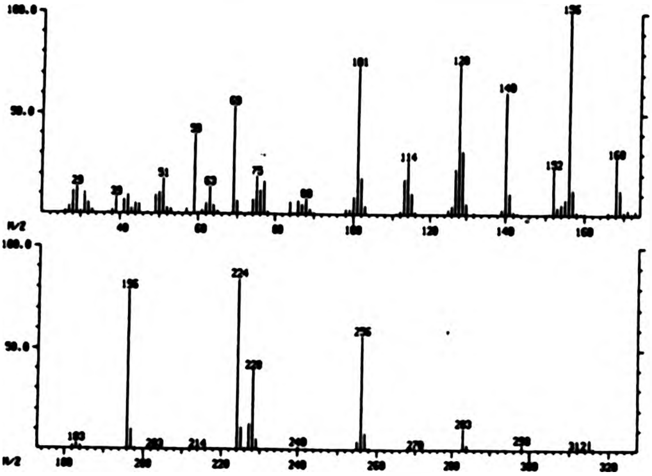
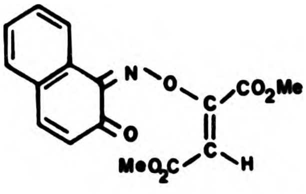


Fig. 3.6 Mass spectrum of product S (13/14)

The ^{1}H n.m.r. spectrum (Fig. 3.5) showed the expected resonances at 3.71, 3.82, 3.91, and 3.93 ppm (singlets) due to the six carbomethoxy protons and at 6.36-8.98 ppm (multiplet) due to the vinylic and aromatic protons.

The presence of four singlets due to the methyl protons of the ester groups could not be accounted for, in terms of structure **13** alone. However, they can be explained, if the product S is a mixture of 13 and its *trans*-isomer **14**.

This was verified by investigating the product further. Qualitative H.P.L.C. indicated the presence of two components, which were successfully separated using this technique.



14

Using an ethyl acetate/light petrol solvent mixture as eluent two isomers A (m.p. 99-100 °C) and B (m.p. 103-104 °C) were isolated. Both showed a molecular ion peak at 315 and had very similar fragmentation patterns. Their i.r. spectra (Figs. 3.7 and 3.9) showed absorptions due to ester carbonyl and quinone groups at 1740, 1720, 1658 cm^{-1} for component A and at 1740, 1730, 1678, 1660 cm^{-1} for component B respectively. In their ^{1}H n.m.r. spectra (Figs. 3.8 and 3.10), the six carbomethoxy protons resonate at 4.52 and 4.74 ppm for A and at 4.63 and 4.72 ppm for B, while the vinylic/aromatic protons resonate at 7.16-8.75 ppm and at 7.16-9.78 ppm for isomers A and B respectively.

In both cases, the spectra are in accord with the proposed formulation but do not allow to unambiguously establish which is the *cis* or *trans* isomer.

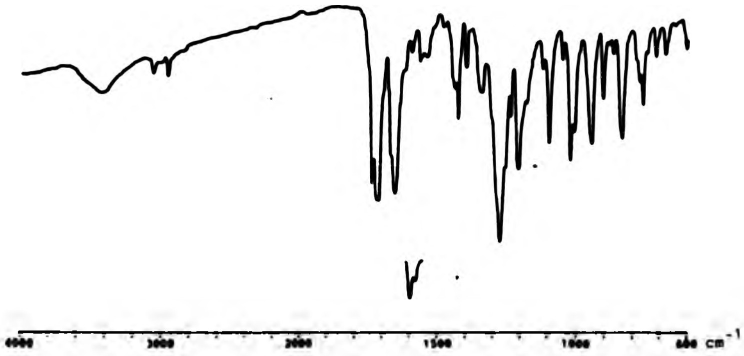


Fig. 3.7 Infra-red spectrum of isomer A

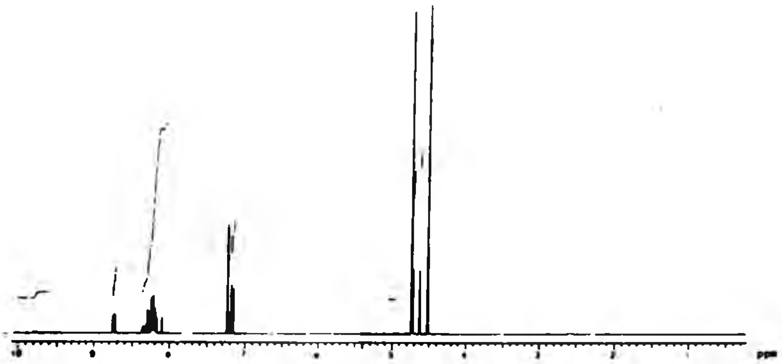


Fig. 3.8 ^{1}H n.m.r. spectrum of isomer A, Varian XVR-400 MHz ($CDCl_3$ as reference)

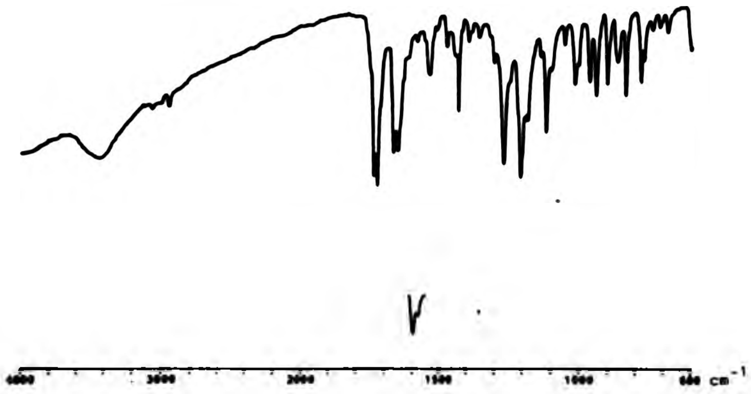


Fig. 3.9 Infra-red spectrum of isomer B

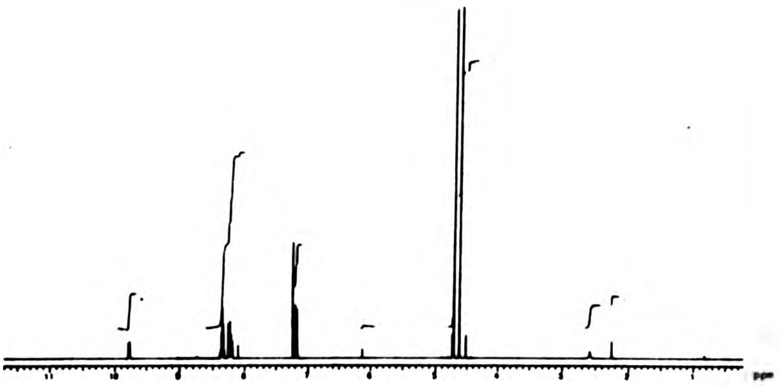
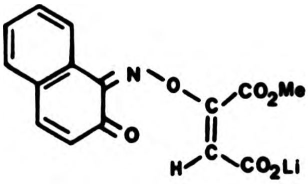


Fig. 3.10 ^{1}H n.m.r. spectrum of isomer B, Varian XVR-400 MHz ($CDCl_3$ as reference)

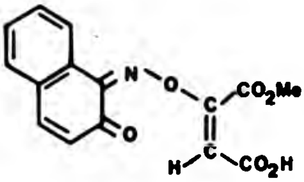
Characterisation of the metal-containing product

The i.r. spectrum of the metal-containing product obtained from the reaction of the lithium complexes derived from 1,2-naphthoquinone 1-oxime with dimethylacetylene dicarboxylate showed bands in the region 3600-3200 cm^{-1} and at 1730-1720, 1680-1640 cm^{-1} due to hydroxy, ester carbonyl and quinone groups respectively. Its ^1H n.m.r. spectrum in D_2O, showed two major peaks at 3.78 and 3.80 ppm in accord with presence of methyl protons attached to ester group and peaks not well resolved at 6.66-7.91 ppm in a ratio of *ca.* 1:2. The above observations, together with the metal analysis and the C:H:N ratio suggested that the metal-containing product was a slightly impure mixture of the hydrated lithium salt **15** and its isomer, which were formed by hydrolysis of the adducts **13** and **14**.



15

Support for the above formulation was obtained by treating the mixture with aqueous hydrochloric acid and extracting the resultant organic species with diethyl ether. By this procedure, a small quantity of compound **16** was obtained. The ^1H n.m.r. spectrum of this compound showed signals at δ 3.78, 3.85 and at δ 6.40-8.75 in a ratio of *ca.* 1:2 as expected.



16

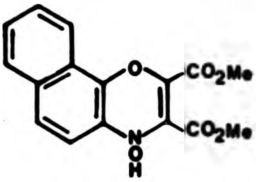
Conclusive evidence for the formulation of **15** was obtained by investigating the reaction of lithium hydroxide with i) the nucleophilic addition product S (**13**/**14**) ii) the cycloaddition product **10** and iii) the dimethylacetylene dicarboxylate. The first reaction afforded a compound identical to the metal-containing product obtained from the Li(1-nqo)/DMAD systems. This was established by full elemental analysis, and comparison of the i.r. and ^{1}H n.m.r. spectra. Reaction ii) gave the dilithium salt of the partially hydrolysed 1,4-oxazine and reaction iii) the lithium methylacetylene dicarboxylate, whose i.r. and ^{1}H n.m.r. spectra were different from those of the Li(1-nqo)/DMAD systems.

3.4.2 Lithium complex of 1,2-naphthoquinone 2-oxime

In contrast to the Li(1-nqo)/DMAD system, the reaction between the lithium complex derived from

1,2-naphthoquinone 2-oxime and the acetylene dicarboxylate afforded a complex mixture from which both the cycloadduct **17** and the nucleophilic addition product **18** were isolated using chromatographic and preparative t.l.c. techniques.

The cycloadduct **17** was characterised by comparison of its m.p. and its spectra (i.r., ^{1}H n.m.r., and m.s.) with those of an authentic sample. The nucleophilic addition product **18** was characterised by using an analogous procedure to that used for the characterisation of **13/14**. This compound can also exhibit *cis/trans* isomerism, but no attempt was made to separate them.



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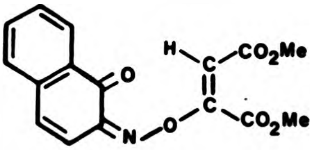


18

The isolation of both the cycloadduct **17** and the nucleophilic addition product **18**, indicate that the 2-nqo$^-$ system shows a more complex behaviour than the 1-nqo$^-$ system. Similar tendency of the 2-nqo$^-$ system i.e. formation of several products, has also been noted by other workers in reactions of its transition metal complexes towards Lewis bases, e.g.

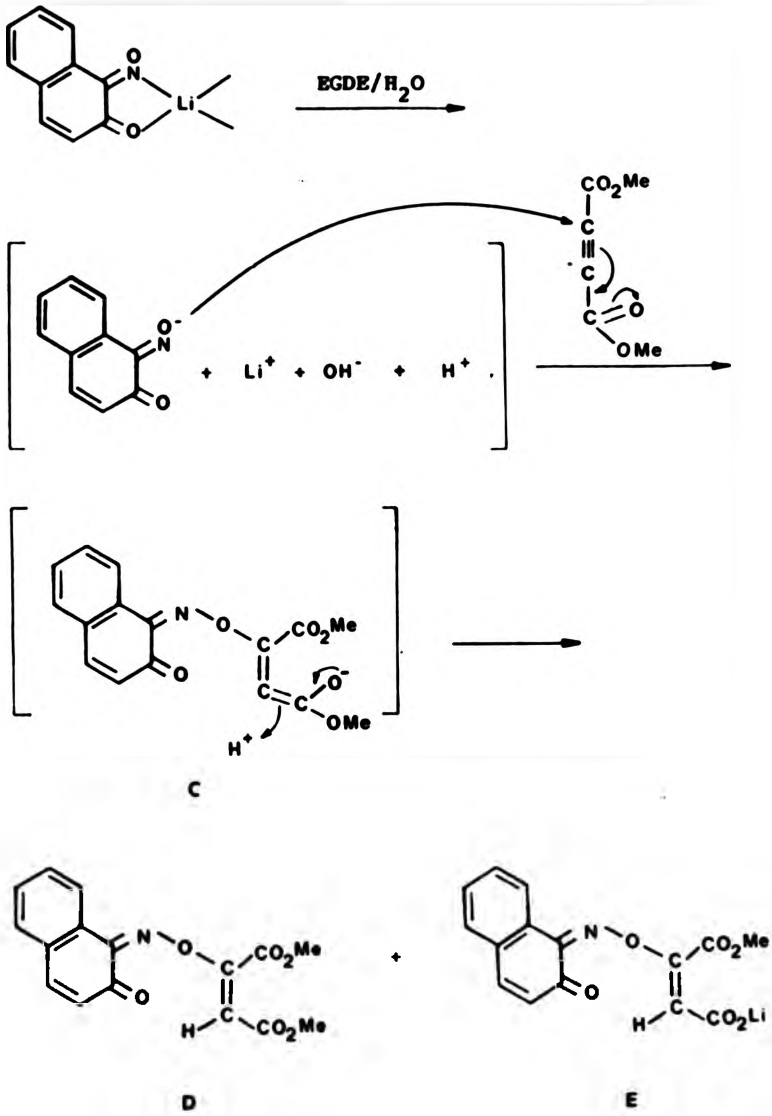
triphenylphosphine, pyridine.[24,25]

3.5 Mechanistic appraisal of the reactions

The results obtained from the study of the Li(nqo)/DMAD systems, demonstrate that the nature of the metal has a pronounced effect on the reaction behaviour of naphthoquinoneoximato complexes. The results also show that the coordination environment of the metal is not an important factor and the reaction proceeds irrespective to whether the metal is coordinatively saturated or not.

As in the reaction between the copper quinoneoximato complexes and dimethylacetylene dicarboxylate, the presence of water is an important prerequisite for the reaction systems Li(nqo)/DMAD. The formation of Michael's type addition products from the reaction of the lithium naphthoquinoneoximato complexes with the acetylene dicarboxylate can be best rationalised as outlined in Scheme 3.6.

Lithium being a highly electropositive metal, polarises the ligand. The ligand thus attacks the electrophilic site of the acetylene dicarboxylate to give the intermediate C. This intermediate reacts further with a proton, originating from the water present in the reaction system, to give the corresponding neutral



Scheme 3.6

species D and its *trans* isomer. This process is accompanied by the formation of lithium hydroxide. Subsequent hydrolytic action of the hydroxide on D, gives rise to the metal-containing product E and its respective *trans* isomer.

Products arising from Michael's addition processes have also been observed in reactions of oximes with Michael's acceptors[26,27] and in the reaction of copper complexes of substituted 2-quinone monophenylhydrazones with dimethylacetylene dicarboxylate.[28]

In the case of the Li(2-nqo)/DMAD system the [4+2] cycloadduct 17, is also isolated, together with the nucleophilic addition product 18. The different behaviour between Li(1-nqo)/DMAD and Li(2-nqo)/DMAD systems could reflect differences in orbital allignment between the heterodiene system and the dienophile.

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CHAPTER FOUR

SOLUBILITY STUDIES OF LITHIUM AND OTHER METAL COMPLEXES

4.1 Introduction

The understanding of the solubility behaviour of elements and compounds is of considerable importance in their purification, analysis and use. The importance of solubility is apparent in a variety of diverse fields, such as drug administration, cosmetic and semiconductor industries, extraction of metals and pollution control.[1-9] The solubility of a compound in a solvent is primarily affected by its nature and the properties of the solvent which control the type of interaction between the compound and the solvent, generally referred to as solute-solvent interaction.[10-14]

The possible types of interaction between solute and solvent molecules are:

i) London dispersion forces. These are the forces of attraction between non-polar molecules and mainly depend on the number and 'looseness' of the valence electrons.

ii) Dipole-dipole interactions i.e. forces between permanent dipoles dependent upon their relative orientation.

iii) Hydrogen bonding

The selection of a solvent for a particular solute was achieved earlier by using an empirical approach rather than by a theoretically based understanding of the solubility process. A major step forward in the prediction of solvency of non polar systems was made by Hildebrand with the introduction of the 'solubility parameter'.[10,15,16] The solubility parameter, δ, $(\text{cal cm}^{-3})^{1/2}$ is the square root of the ratio of the vaporization energy ΔE (cal) of the compound and its molar volume (V) (cm^3) (Equation 4.1).

$$\delta = \sqrt{\Delta E/V}$$

Equation 4.1

For single component systems, the vaporization energy can be determined by using the empirical Equation 4.2; where T_b is the boiling point of the compound in degrees Kelvin.

$$\Delta E = -3540 + 23.7T_b + 0.02T_b^2$$

Equation 4.2

According to Hildebrand's theoretical model, a solute has a greater solubility in a solvent, when the value of its solubility parameter (δ) is close to that of the solvent.

If a mixture of solvents is used, the δ value is given by Equation 4.3 where Φ_a, Φ_b are the volume fractions of solvents a and b in the mixture.

$$\delta_{ab} = \delta_a\Phi_a + \delta_b\Phi_b$$

Equation 4.3

Hildebrand's theory is based on the premise that the interaction between solvent and solute is due mainly to London dispersion forces. As a consequence, the theory is less accurate for polar compounds e.g. methanol, water and solutes where dipole or hydrogen bonding interactions could take place. In order to account for the dipole-dipole and hydrogen bonding interactions between solvent and solute molecules, Hildebrand's theory was expanded further and the idea of partial solubility parameters was introduced.[16]

The partial solubility parameters arise from the specific interactions due to London dispersion forces (δ_d), dipole orientations (δ_o) and hydrogen bonding (δ_h). Use of partial δ values for the prediction of solubility of various polymers in different solvents, has shown that maximum solubility occurs when the partial δ values of solvent and solute are matched.[16] However, this expanded approach of Hildebrand's solubility parameter theory towards more polar systems, has also its drawbacks. For example, it requires the partial δ values for solutes as well as for solvents, and the former are not readily available; it results in complex equations for solubility thus discouraging their use in practice.

Despite all the limitations of the original and expanded Hildebrand's theory, they still represent the best approach towards a rationalisation of solvency. Furthermore, they have proved useful in various solubility problems encountered in industry, such as in the pharmaceutical, cosmetics, and petroleum areas.[1,3,5]

In this work, the solubilities of some lithium carboxylato and metal quinoneoximato complexes in several organic solvents were investigated. The aims were:

i) to study the solubility behaviour of these types of complex and select promising lithium complexes and solvents for subsequent application in scintillation counting;

ii) to assess the applicability of Hildebrand's theoretical model to such systems and thus determine the solubility parameters range of the compounds studied.

4.2 Results

4.2.1 Procedure and solvents employed

During this study the solute/solvent mixture under study, was magnetically agitated at 25.0 ± 0.2 °C in a thermostatically controlled water bath, thus minimising errors due to agitation and thermal losses.

In each case, the time required for equilibrium to be reached between the solvent and the solute was determined in a preliminary study. Thus, the amount of solute dissolved in the supernatant liquid was monitored hourly till a constant value was obtained. In general equilibrium was reached in *ca*. seven hours. The solubility measurements were subsequently carried out on fresh solute/solvent mixtures in triplicate, and from the results obtained the standard deviation was also calculated.

The range of solvents employed in the solubility studies of all the metal complexes, spread over a wide spectrum of solubility parameters (7.30-12.70). The solvents tried, together with their solubility parameters[10,15] and dipole moments[17] (debye) (used in the discussion in later sections) are shown in Table 4.1.

Table 4.1 Solvents used in solubility studies and selected physical data

Solvent	δ $(\mathrm{cal\ cm^{-3}})^{1/2}$	Dipole Moment (debye)
Hexane	7.30	0.08
Cyclohexane	8.20	0.00
Toluene	8.90	0.36
Acetone	9.70	2.89
Dichloromethane	9.70	1.60
Pyridine	10.70	2.19
Ethanol	12.70	1.69

1 cal = 4.184 Joules
1 debye = 3.338×10^{-30} C m

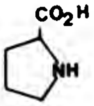
4.2.2 Lithium complexes of carboxylic acids

In general, solubility studies on metal complexes are limited and are mainly qualitative.[17-22] For lithium complexes of carboxylic acids, no solubility data have been reported previously, except in the case of lithium complexes of straight chain carboxylic acids.[17]

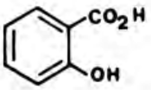
The carboxylic acids used for the synthesis of the lithium carboxylato complexes had various structures and the number of carbon atoms ranged from two to ten. The acids employed were glycolic (I) (glycoH), L-proline (II) (prolH), salicylic (III) (salH) and decanoic, and complexes of type LiL or LiL.LH (LH = carboxylic acid and L = its anion) were obtained.

$HOCH_2CO_2H$

I



II



III

The solubility results in hexane, toluene, acetone, pyridine, and ethanol, expressed in g/100 cm^3 solvent, are presented in Table 4.2 and illustrated in Graphs 4.1 and 4.2. In Table 4.2 the solubilities are also expressed in terms of the molar ratios of solute/solvent i.e. in terms of the mols of solute dissolved per mol of solvent.

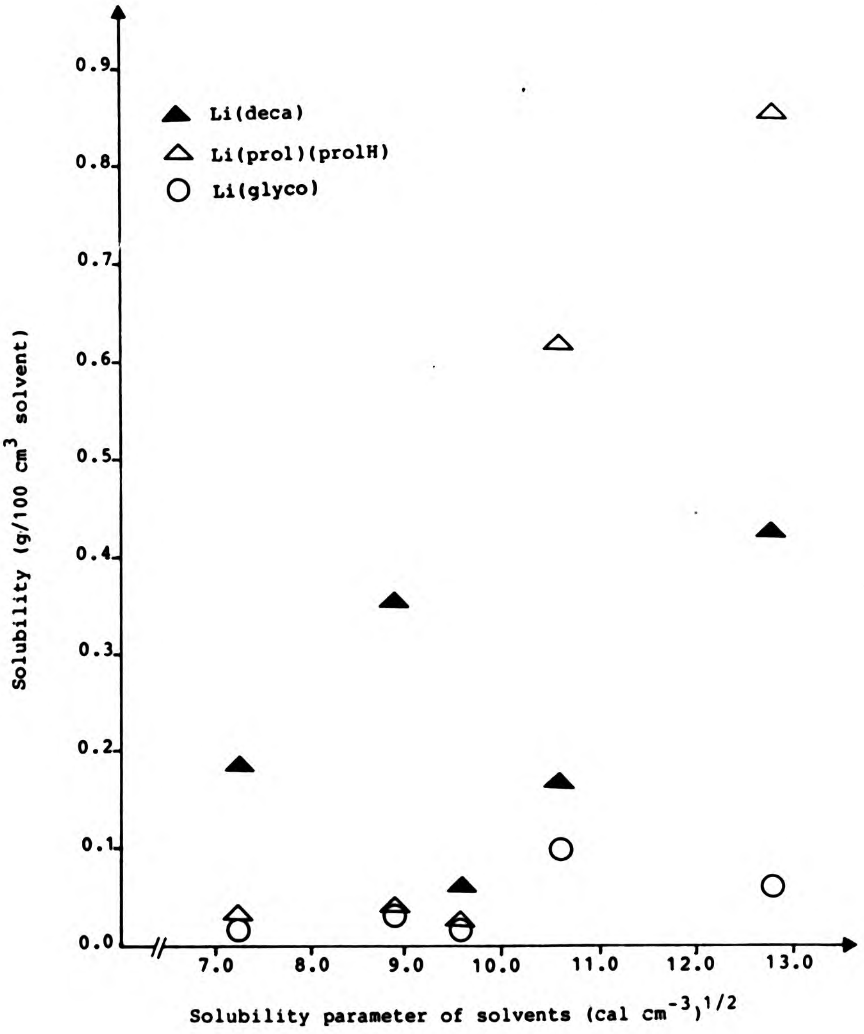
In general, most of the lithium carboxylato complexes, show increased solubility in pyridine and ethanol, thus suggesting that the solubility parameters of these compounds lie within the range 10.70-12.70. However, Li(sal)(salH) in comparison to the other carboxylato complexes shows extremely high solubility in pyridine and also in acetone and ethanol. This behaviour, in terms of the Hildebrand theoretical model on solubility, would suggest that the solubility parameter of this complex falls within the range 9.70-

Table 4.2 Solubility of lithium complexes derived from carboxylic acids at 25.0 ± 0.2 °C

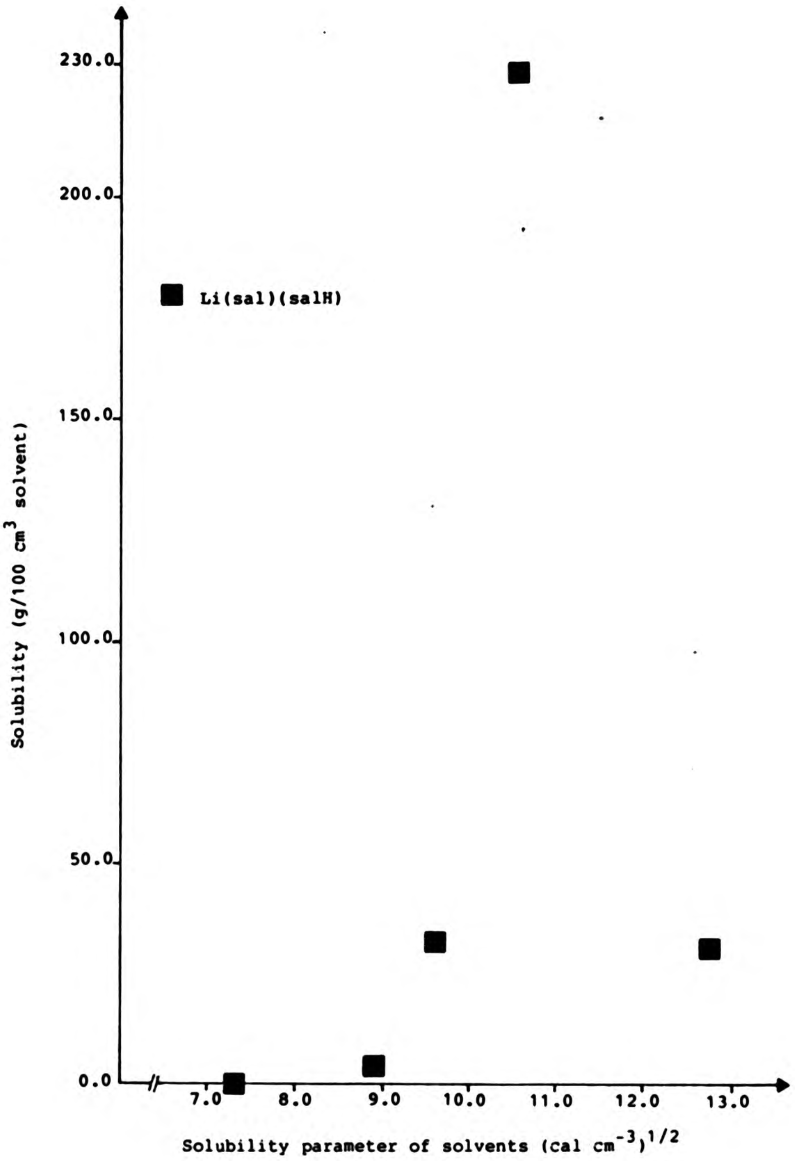
Complex	Solvent				
	Hexane	Toluene	Acetone	Pyridine	Ethanol
			Solubility (g/100 cm^3 solvent)		
Li(glyco)	0.0152 ± 0.0010	0.0286 ± 0.0023	0.0142 ± 0.0003	0.1007 ± 0.0013	0.0639 ± 0.0003
Li(prol)(prolH)	0.0290 ± 0.0004	0.0364 ± 0.0032	0.0213 ± 0.0017	0.6190 ± 0.0053	0.8565 ± 0.0016
Li(deca)	0.1885 ± 0.0019	0.3563 ± 0.0015	0.0656 ± 0.0023	0.1839 ± 0.0002	0.4310 ± 0.0035
Li(sal)(salH)	0.0521 ± 0.0004	0.4725 ± 0.0005	32.4619 ± 1.1200	228.9693 ± 4.2300	31.5334 ± 1.1000
			Molar ratios (mols of dissolved solute/mol of solvent)		
Li(glyco)	0.00025	0.00037	0.00013	0.00099	0.00046
Li(prol)(prolH)	0.00016	0.00017	0.00007	0.00222	0.00222
Li(deca)	0.00143	0.00213	0.00027	0.00083	0.00142
Li(sal)(salH)	0.00025	0.00178	0.08486	0.65917	0.06587

glycoH = glycolic acid
prolH = L-proline
decaH = decanoic acid
salH = salicylic acid

Graph 4.1 Solubility of lithium complexes derived from carboxylic acids at 25.0 ± 0.2 °C



Graph 4.2 Solubility of Li(sal)(salH) at 25.0 ± 0.2 °C



12.70 but is rather closer to that of pyridine (δ = 10.70).

In order to check whether the appreciably higher solubility of Li(sal)(salH) in pyridine, acetone and ethanol, with respect to the other lithium carboxylato complexes, is due to dissociation rather than due to similar solubility parameters between the solvent and Li(sal)(salH), the conductivity of this complex in pyridine, acetone and ethanol was measured (Table 4.3).

Table 4.3 Molar conductivity of Li(sal)(salH) at 25 °C

Solvent	C(mol m^{-3})	Λ_m(S mol^{-1} m^2)
Pyridine	12.896	0.79×10^{-4}
Acetone	12.752	10.64×10^{-4}
Ethanol	12.980	28.58×10^{-4}

C = concentration

Λ_m = molar conductivity

Λ_m = $100\text{-}140 \times 10^{-4}$ S mol^{-1} m^2 (1:1 electrolytes)
$160\text{-}200 \times 10^{-4}$ S mol^{-1} m^2 (2:1 electrolytes)
in acetone[23]

Λ_m = $35\text{-}45 \times 10^{-4}$ S mol^{-1} m^2 (1:1 electrolytes)
$70\text{-}90 \times 10^{-4}$ S mol^{-1} m^2 (2:1 electrolytes)
in ethanol[23]

The molar conductivities indicate that Li(sal)(salH) is partly dissociated in ethanol but its dissociation in acetone and also in pyridine is inappreciable. These observations show that the high solubility of the complex in acetone and pyridine in not due to dissociation. Another feature shown by this complex and also by Li(deca) is their higher solubility in toluene in comparison to the other lithium carboxylato complexes.

4.2.3 Metal complexes of 1,2-quinone mono-oximes

Lithium complexes of 1,2-naphthoquinone mono-oximes

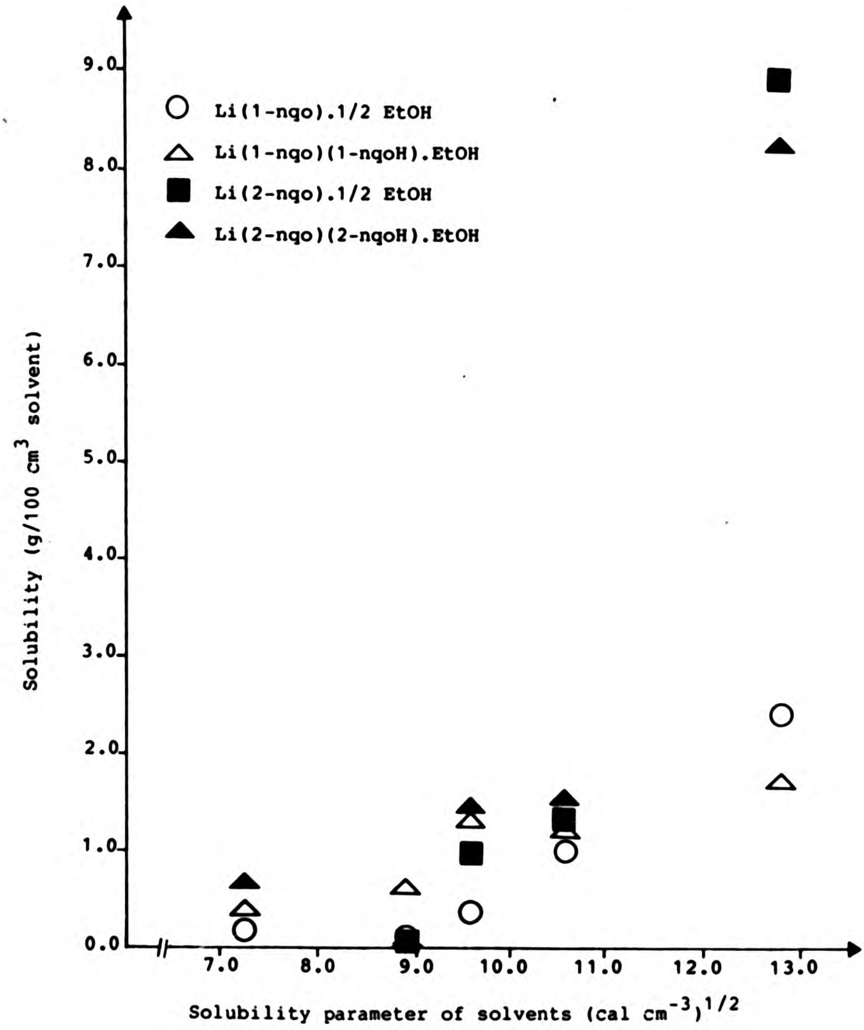
The solubility characteristics of the lithium complexes Li(1-nqo).1/2 EtOH, Li(1-nqo)(1-nqoH).EtOH, Li(2-nqo).1/2 EtOH, and Li(2-nqo)(2-nqoH).EtOH in hexane, toluene, acetone, pyridine and ethanol were also investigated. The results are presented in Table 4.4 and illustrated in Graph 4.3.

The results indicate that the solubilities of these lithium complexes are in general, appreciably higher in ethanol than in the other solvents. High solubility is also observed in pyridine and acetone. It was thought that the solubility behaviour of these complexes in ethanol is due to its higher dielectric constant (ε = 24.3) [*cf.* pyridine (ε = 12.3) or acetone (ε = 20.7)][13] which could lead to dissociation. This hypothesis,

Table 4.4 Solubility of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone at 25.0 ± 0.2 °C

Complex	Solvent				
	Hexane	Toluene	Acetone	Pyridine	Ethanol
			Solubility (g/100 cm^3 solvent)		
Li(1-nqo).1/2 EtOH	0.1900 ± 0.0001	0.0663 ± 0.0003	0.2909 ± 0.0024	1.0460 ± 0.0002	2.3931 ± 0.0180
Li(1-nqo)(1-nqoH).EtOH	0.3882 ± 0.0002	0.5645 ± 0.0005	1.2821 ± 0.0003	1.1672 ± 0.0005	1.7150 ± 0.0010
Li(2-nqo).1/2 EtOH	0.2936 ± 0.0016	0.0232 ± 0.0001	0.9269 ± 0.0002	1.3044 ± 0.0015	8.9326 ± 0.0088
Li(2-nqo)(2-nqoH).EtOH	0.6398 ± 0.0005	0.0116 ± 0.0002	1.4609 ± 0.0017	1.5150 ± 0.0015	8.2658 ± 0.0071
			Molar ratios (mols of dissolved solute/mol of solvent)		
Li(1-nqo).1/2 EtOH	0.00123	0.00035	0.00106	0.00419	0.00695
Li(1-nqo)(1-nqoH).EtOH	0.00127	0.00151	0.00236	0.00237	0.00253
Li(2-nqo).1/2 EtOH	0.00190	0.00012	0.00337	0.00522	0.02596
Li(2-nqo)(2-nqoH).EtOH	0.00210	0.00003	0.00269	0.00307	0.01219

Graph 4.3 Solubility of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone at 25.0 ± 0.2 °C



however, was not borne out by conductivity measurements, which showed that dissociation was inappreciable (Table 4.5).

The above observations would suggest that the solubility parameter of these complexes falls within the region 9.70-12.70 and is rather closer to that of ethanol (δ = 12.70).

Table 4.5 Molar conductivities of lithium complexes derived from the mono-oximes of 1,2-naphthoquinone in ethanol at 25 °C

Complex	C(mol m^{-3})	Λ_m(S mol^{-1} m^2)
Li(1-nqo).1/2 EtOH	10.100	5.24×10^{-4}
Li(1-nqo)(nqoH).EtOH	10.000	5.84×10^{-4}
Li(2-nqo).1/2 EtOH	10.100	9.61×10^{-4}
Li(2-nqo)(2-nqoH).EtOH	9.948	8.65×10^{-4}

C = concentration

Λ_m = molar conductivity

Λ_m(1:1 electrolytes) = $35\text{-}45 \times 10^{-4}$ S mol^{-1} m^2

Λ_m(2:1 electrolytes) = $70\text{-}90 \times 10^{-4}$ S mol^{-1} m^2

Furthermore, it is also noted that: i) the

Li(nqo).1/2 EtOH complexes show greater solubility in ethanol, than the Li(nqo)(nqoH).EtOH complexes; ii) the solubility of the lithium naphthoquinoneoximato complexes in hexane is significantly higher than in toluene. Li(1-nqo)(1-nqoH).EtOH is anomalous in this respect, and shows smaller change in solubility with variation of solvent.

Alkali metal complexes of 5-hydroxy-1,2-benzoquinone-2-oximes and transition metal complexes of 1,2-quinone mono-oximes

As noted earlier, the lithium naphthoquinoneoximato complexes showed in general, higher solubility in ethanol and pyridine, rather than in acetone, toluene and hexane.

Recently, solubility studies on alkali and transition metal complexes of 1,2-quinone mono-oximes have been conducted by other workers, in these laboratories, using the technique developed during this work. It was of interest to see how these types of complex behave with respect to the Hildebrand solubility parameter theory, thus observing whether the solubility parameter range 9.70-12.70 (*vide supra*) shown by the lithium naphthoquinoneoximato complexes, applies to the benzoquinoneoximato complexes also.

The studies have been concerned with the solubility characteristics of alkali metal complexes of 5-hydroxy-1,2-benzoquinone 2-oxime (5-OHqoH) and 3-methyl-5-hydroxy-1,2-benzoquinone 2-oxime (3-Me-5-OHqoH) in pyridine and ethanol. In addition, the solubility of some transition metal complexes of substituted 1,2-quinone mono-oximes (qoH) and 1,2-naphthoquinone 1-oxime (1-nqoH) in various solvents was measured.

The alkali metal complexes derived from 5-OHqoH and 3-Me-5-OHqoH (Table 4.6) show appreciably higher solubility in ethanol than in pyridine, as was also observed for the lithium naphthoquinoneoximato complexes (Table 4.4), and have similar solubility parameters. The molar conductivities exhibited by these complexes in ethanol (Table 4.7) are higher than those of the naphthoquinoneoximato complexes but are still low enough for the Hildebrand solubility parameter theory to be applicable.

Another trend also observed is that the complexes Li(5-OHqo) and Li(3-Me-5-OHqo) show appreciably higher solubility in both ethanol and pyridine, than the respective sodium and potassium complexes.

The solubility behaviour of transition metal complexes $Ni(4\text{-}Meqo)_2.(py)_2$, $Ni(4\text{-}Brqo)_2.(py)_2$ and $Co(1\text{-}nqo)_3$ was examined in hexane, acetone, dichloromethane and ethanol (Table 4.8). All these complexes show in general, higher solubility in acetone, dichloro-

Table 4.6 Solubility of alkali metal complexes derived from 5-hydroxy 1,2-benzoquinone 2-oxime (5-OHqoH) and 3-methyl-5-hydroxy 1,2-benzoquinone 2-oxime (3-Me-5-OHqoH) at 25.0 ± 0.2 °C

Complex	Solvent	
	Pyridine	Ethanol
	Solubility (g/100 cm^3 solvent)	
Li(5-OHqo)*	1.4120 ± 0.4869	7.0860 ± 0.1483
Li(3-Me-5-OHqo)*	2.1231 ± 0.2401	22.1695 ± 1.1346
Na(5-OHqo)*	0.0906 ± 0.0029	0.3121 ± 0.0089
Na(3-Me-5-OHqo)*	0.1810 ± 0.0028	3.4170 ± 0.0594
K(5-OHqo)*	0.1597 ± 0.0047	0.9551 ± 0.0598
	Molar ratios (mols of dissolved solute/mol of solvent)	
Li(5-OHqo)	0.00788	0.02869
Li(3-Me-5-OHqo)	0.01080	0.08186
Na(5-OHqo)	0.00045	0.00114
Na(3-Me-5-OHqo)	0.00084	0.01146
K(5-OHqo)	0.00073	0.00316

* Data provided by E. Spyrou under my supervision

methane, and ethanol, than in hexane, suggesting that their solubility parameters do lie within the range 9.70-12.70.

The solubility trend shown by Ni(4-Meqo)$_2$.(py)$_2$, (dichloromethane › acetone › ethanol › hexane), and the maximum solubility in acetone exhibited by Ni(4-Brqo)$_2$.(py)$_2$ and Co(1-nqo)$_3$ suggest, that their solubility parameters are closer to that of acetone/dichloromethane (9.70).

Table 4.7 Molar conductivities of alkali metal complexes of 5-hydroxy-1,2-benzoquinone 2-oximes in ethanol at 25 °C

Complex	C(mol m^{-3})	Λ_m(S mol^{-1} m^2)
Li(5-OHqo)	9.980	20.65×10^{-4}
Li(3-Me-5-OHqo)	9.940	21.62×10^{-4}
Na(5-OHqo)	10.890	21.90×10^{-4}
Na(3-Me-5-OHqo)	11.360	22.79×10^{-4}
K(5-OHqo)	11.050	22.45×10^{-4}

C = concentration

Λ_m = molar conductivity

Λ_m(1:1 electrolytes)[23] = $35\text{-}45 \times 10^{-4}$ S mol^{-1} m^2

Λ_m(2:1 electrolytes)[23] = $70\text{-}90 \times 10^{-4}$ S mol^{-1} m^2

Table 4.8 Solubility of transition metal complexes derived from 1,2-quinone mono-oximes at 25.0 ± 0.2 °C

Complex	**Solvent**			
	Hexane	Acetone	Dichloromethane	Ethanol
	Solubility(g/100 cm^3 solvent)			
Ni(4-Meqo)$_2$.(py)$_2$*	0.0501 ± 0.0036	1.1759 ± 0.0490	2.1659 ± 0.0410	0.8225 ± 0.0260
Ni(4-Brqo)$_2$.(py)$_2$*	0.1006 ± 0.0004	3.7687 ± 0.0004	2.0326 ± 0.0005	2.3424 ± 0.0003
Co(1-nqo)$_3$*	0.1321 ± 0.0013	3.4282 ± 0.0009	1.7319 ± 0.0012	1.8844 ± 0.0003
	Molar ratios (mols of dissolved solute/mol of solvent)			
Ni(4-Meqo)$_2$.(py)$_2$	0.00013	0.00176	0.00284	0.00099
Ni(4-Brqo)$_2$.(py)$_2$	0.00027	0.00583	0.00274	0.00289
Co(1-nqo)$_3$	0.00030	0.00437	0.00193	0.00192

4-MeqoH = 4-Methyl 1,2-benzoquinone 2-oxime

4-BrqoH = 4-Bromo 1,2-benzoquinone 2-oxime

* Data provided by J. Swami/M. Al-Bahrani under my supervision

Finally, the solubility behaviour of the transition metal complexes derived from 5-N-acetylamino-1,2-benzoquinone 2-oxime (5-NHqoH) in cyclohexane, acetone and ethanol was also investigated (Table 4.9). These complexes show maximum solubility in ethanol and increased solubility in acetone. This observation indicates once more, that their solubility parameters lie within the range 9.70-12.70.

4.3 Relationship of the dipole moment, the solubility parameter of solvents and solubility

Hildebrand's original theoretical model on solubility does not take into account the dipole-dipole interactions between the solvent and the solute. Some consideration to these interactions has been given on this study.

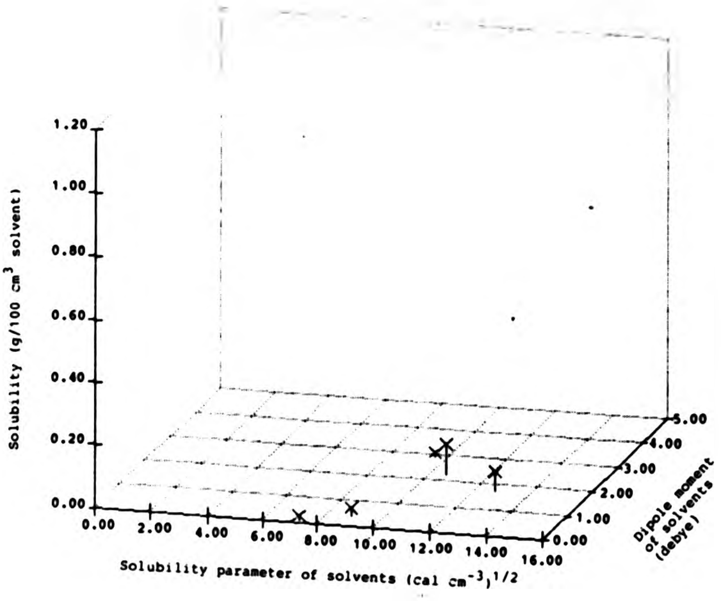
The relationship between the dipole moment, the solubility parameter of solvents and solubility was examined using a three dimensional representation, which involved plotting the solubility data versus the dipole moments, and the solubility parameters of the solvents. Typical graphs are shown in Graphs 4.5-4.12. This representation has indicated that there is no direct relationship between solubility and dipole moment/solubility parameter. However, it has allowed to identify the dipole moment range in which high

Table 4.9 Solubility of transition metal complexes derived from 5-N-acetylamino 1,2-benzoquinone 2-oxime (5-NHqoH) at 25.0 ± 0.2 °C

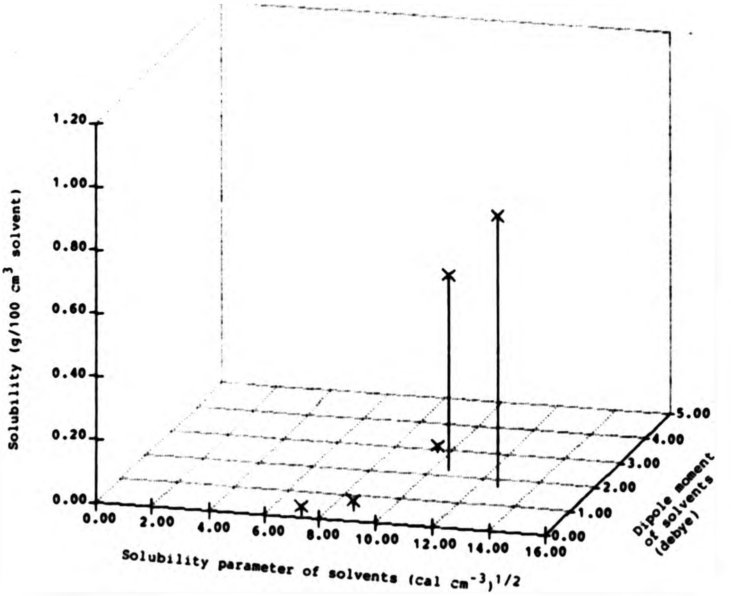
Complex	**Solvent**		
	Cyclohexane	Acetone	Ethanol
	Solubility (g/100 cm^3 solvent)		
Ni(5-NHqo)$_2$*	0.0131 ± 0.0008	0.1502 ± 0.0002	0.5211 ± 0.0010
Cu(5-NHqo)$_2$*	0.0114 ± 0.0001	0.1014 ± 0.0010	0.2122 ± 0.0002
Cu(5-NHqo)$_2$.(py)*	0.0312 ± 0.0019	0.1916 ± 0.0001	0.4231 ± 0.0011
	Molar ratios (mols of dissolved solute/mol of solvent)		
Ni(5-NHqo)$_2$	0.00003	0.00026	0.00073
Cu(5-NHqo)$_2$	0.00003	0.00018	0.00029
Cu(5-NHqo)$_2$.(py)	0.00007	0.00028	0.00049

* Data provided by S. Ashraf under my supevision

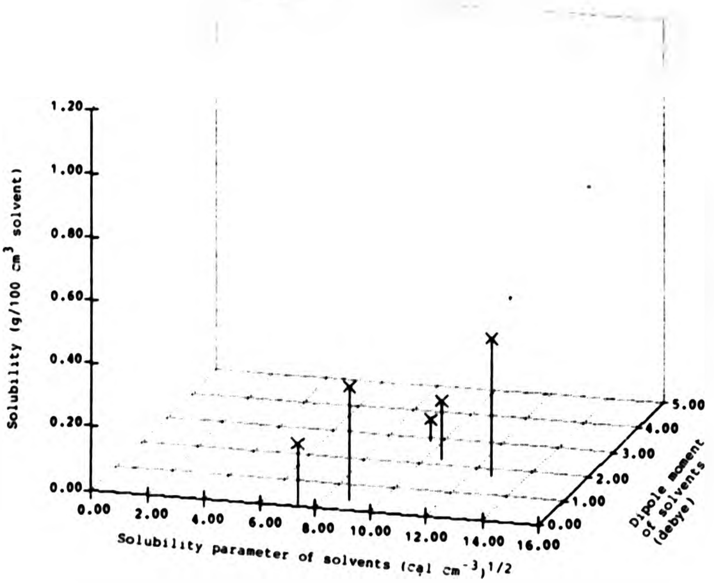
Graph 4.5 Three dimensional graph of Li(glyco)



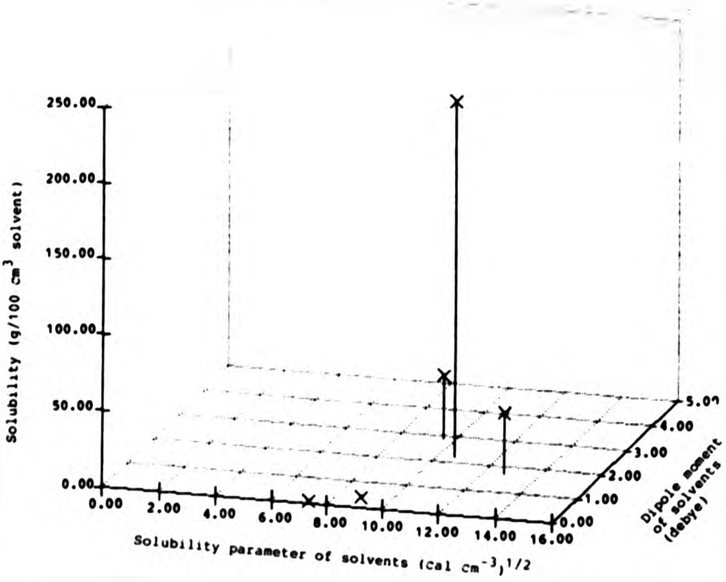
Graph 4.6 Three dimensional graph of Li(prol)(prolH)



Graph 4.7 Three dimensional graph of Li(deca)

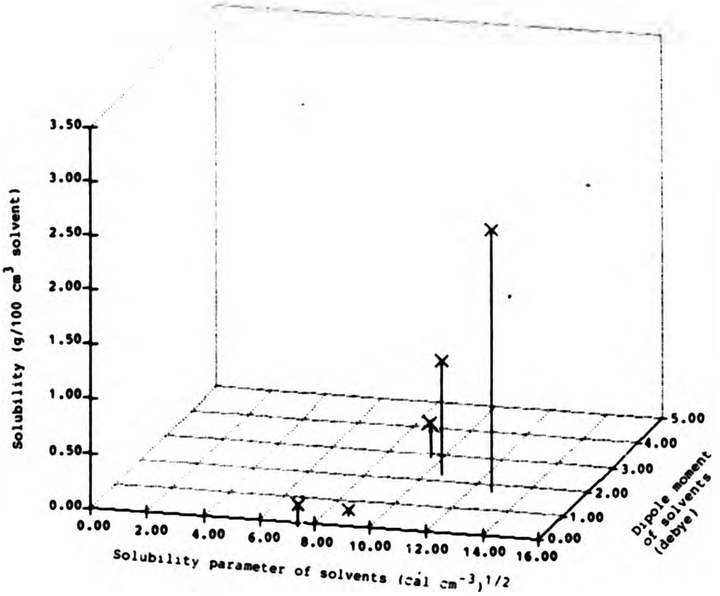


Graph 4.8 Three dimensional graph of Li(sal)(salH)



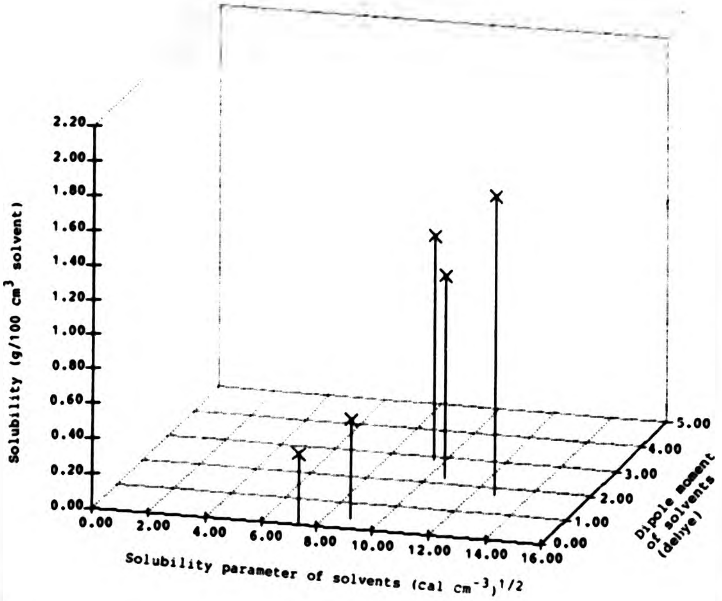
Graph 4.9 Three dimensional graph of

Li(1-nqo).1/2 EtOH



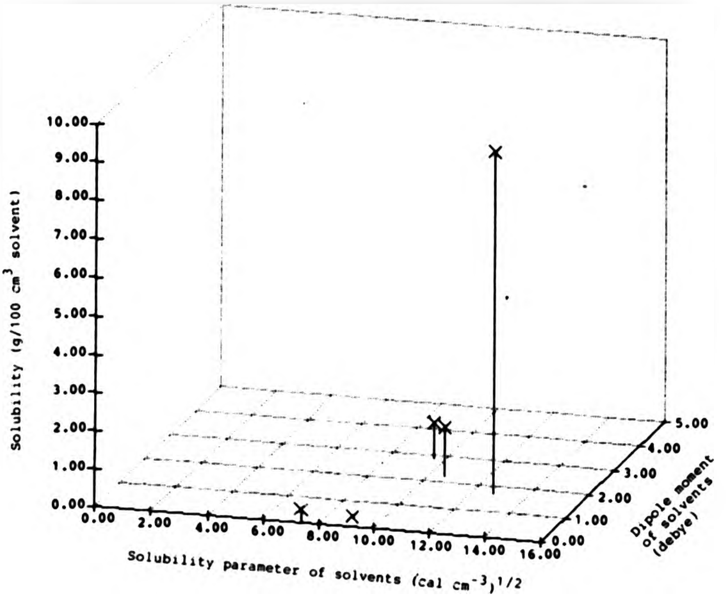
Graph 4.10 Three dimensional graph of

Li(1-nqo)(1-nqoH).EtOH



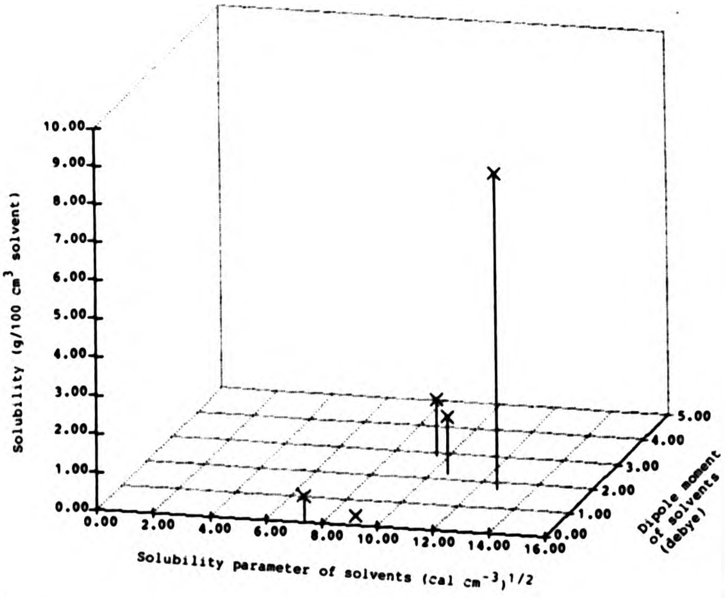
Graph 4.11 Three dimensional graph of

Li(2-nqo).1/2 EtOH



Graph 4.12 Three dimensional graph of

Li(2-nqo)(2-nqoH).EtOH



solubility is observed for a given solute. A consequence of this is that by considering both the solubility parameter range and the dipole moment range, more suitable solvents can be selected.

For the majority of the complexes examined, the most appropriate solvent systems should have a solubility parameter in the range of 9.70-12.70 and dipole moment in the range of 1.60-2.90.

4.4 Conclusions

During this study, it has been found, that Hildebrand's theoretical model on solubility, can be applied to the lithium carboxylato and metal quinoneoximato complexes. These complexes are in general more soluble in solvents whose solubility parameters are within the range 9.70-12.70. In addition, the introduction of the dipole moments of the solvents, as a means of developing further Hildebrand's approach towards solvency, suggests greater solubility in solvents with dipole moments within 1.60 and 2.90.

Finally the appreciably high solubility of Li(sal)(salH) in pyridine and of Li(nqo).1/2 EtOH, Li(nqo)(nqoH).EtOH complexes in pyridine and ethanol, indicate that these types of compound are promising for application in scintillation counting (see Chapter 5).

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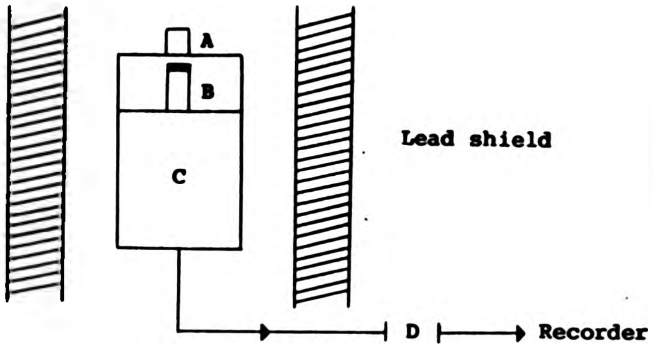
CHAPTER FIVE

DEVELOPMENT OF A LITHIUM LOADED LIQUID SCINTILLATOR FOR NEUTRON COUNTING

5.1 Introduction

Liquid scintillation counting is a technique for the detection and measurement of radioactivity.[1-6] It employs a radioactive source, a liquid scintillator and a photomultiplier (Fig. 5.1).



A = Radioactive source

B = Vial with liquid scintillator

C = Photomultiplier box

D = Amplifiers

Fig. 5.1

The source is necessary for providing the energy needed for the excitation of the liquid scintillator components.

The liquid scintillator, plays the role of an energy transducer, transforming energy from nuclear decay into light photons; the efficiency of the liquid scintillator depends on its power to convert incident radiation into light photons. The light photons, are then sensed by the photomultiplier and converted to electrical pulses; their size is proportional to the amount of light photons produced, and only pulses greater than the set discriminator level are accepted. The pulses are subsequently amplified by means of amplifiers and then recorded as counts or count rate (Fig. 5.1).

The liquid scintillator is a solution of one or more solutes in a solvent.

The role of the solvent is to facilitate energy conversion and energy transmission. Detailed studies[7-12] have shown that the best scintillation solvents are aromatic hydrocarbons e.g. toluene, xylene. This feature is due to the presence of π-electrons that can be readily excited.

The function of the solute, is to trap the excitation energy of the solvent molecules and then release part of this energy in the form of light photons. In some liquid scintillators, more than one solute can be used.

The solute which gives a higher yield of light photons is called the primary solute and any others are called secondary.[7,13-16]

Primary solutes are usually polyaryl compounds e.g. p-terphenyl (TP), 2,5-diphenyloxazole (PPO).

Secondary solutes such as 1,4-di[2-(5-phenyloxazolyl)]-benzene, (POPOP), and 1,4-di[2-(4-methyl-5-phenyloxazolyl)]-benzene, (dimethylPOPOP), are also called wavelength shifters. This is because they are used to shift the emission spectrum of the photons to longer wavelengths, so as to match the spectral response of the photomultiplier.[2,7]

Although liquid scintillators have found wide application for detecting charged particles, attempts to modify them for detecting neutrons have been less successful.[17,18] Thus, liquid scintillators loaded with different materials (e.g. boron, heavy metal compounds) have been investigated for many years for the detection of neutrons.[17-29]

The initial aim of this work was to develop a lithium loaded liquid scintillator for neutron counting. Lithium was chosen as the loading material because of i) its high cross section for slow neutrons, ii) its high energy output and iii) its low cross section for γ-ray interaction. It was essential that the scintillator should have a high percentage of lithium in solution. Thus, it was necessary to prepare lithium compounds with high lithium content and high solubility in organic solvents.

To achieve these objectives, the following steps have been undertaken:

i) Preparation of a range of known and new lithium compounds.

ii) Assessment of the solubility of these compounds in various solvents ranging from non-polar (e.g. hexane) to polar (e.g. ethanol).

iii) Evaluation of the scintillation efficiency of the solvents in which the lithium compounds showed high solubility, in a range of scintillator mixtures.

iv) Evaluation of the scintillation efficiency of those lithium compounds which showed high solubility.

5.2 Lithium complexes derived from miscellaneous ligands and their solubility characteristics in a range of solvents

Lithium complexes derived from carboxylic, dithiocarbamic and 1,2-quinoneoximic ligands have been prepared and characterised, as described in Chapter 1 and Appendix 3.

Lithium dithiocarbamato complexes imposed synthetic difficulties but a successful and interesting method was developed. This involved the reaction of lithium chloride with carbon disulphide and the amine in carbon tetrachloride. This type of reaction had been previously utilised for the preparation of dithiocarbamato complexes of metal halides which are essentially covalent in character, e.g. $AsCl_3$.[30] Lithium complexes derived from benzylamine and morpholine dithiocarbamic acids were prepared.

The solubility of all the lithium compounds was examined qualitatively in various solvents, i.e. hexane, toluene, acetone, ethanol, pyridine, dimethylsulphoxide, dioxane and diglyme (Table 5.1).

The solubility of some of the complexes was examined in greater depth as described in Chapter 4 and summarised in Tables 4.2 and 4.3.

The lithium salicylato, dithiocarbamato and quinoneoximato complexes showed high solubility in dimethylsulphoxide, pyridine and ethanol. The solubility trend was dimethylsulphoxide > pyridine > ethanol. All the other lithium carboxylato complexes showed very low solubility in practically all solvents (Table 5.1).

On the basis of the above, it was considered that dimethylsulphoxide, pyridine and ethanol were the most

Table 5.1 Solubilities of lithium compounds derived from miscellaneous ligands

Compound	**Solvent**							
	H	T	A	E	P	D	DO	DG
Li(glyco)	I	I	I	P	P	-	-	-
Li(prol)(prolH)	I	I	I	P	P	-	-	-
Li(deca)	P	P	P	P	P	-	-	-
Li(sal)(salH)	P	P	S	S	S	S	P	P
Li(5-Cl-sal)	I	I	S	S	S	S	P	P
Li(5-Me-sal)	I	I	S	S	S	S	P	P
Li(bdtc)(bdtcH)	I	I	P	P	S	S	P	P
Li(mdtc)(mdtcH)	I	I	P	P	P	S	P	P
Li(1-nqo).1/2 EtOH	P	I	P	S	S	S	P	P
Li(1-nqo)(1-nqoH).EtOH	P	P	S	S	S	S	P	P
Li(2-nqo).1/2 EtOH	P	I	S	S	S	S	S	P
Li(2-nqo)(2-nqoH).EtOH	P	I	S	S	S	S	S	P

Table 5.1 (continued)

H = Hexane
T = Toluene
A = Acetone
E = Ethanol

P = Pyridine
D = Dimethylsulphoxide
DO = Dioxane
DG = Diglyme

I = Insoluble
P = Partially soluble
S = Soluble

glycoH = glycolic acid
prolH = L-proline
decaH = decanoic acid
salH = salicylic acid
5-Cl-salH = 5-chloro-salicylic acid
5-Me-salH = 5-methyl-salicylic acid
bdtcH = benzylamine dithiocarbamic acid
mdtcH = morpholine dithiocarbamic acid

promising solvents with regard to the amount of solubilised lithium present.

5.3 Scintillation behaviour of organic solvents in different scintillator mixtures

Solvents, in which the lithium salicylato, dithiocarbamato and quinoneoximato complexes showed maximum solubility, were investigated. Their scintillation efficiency was examined in commercially available scintillator mixtures and in scintillator mixtures formulated and made during this study. Their behaviour is indicated by the number of counts recorded per half minute, over the discriminator lever range 0.0-10.0, at 0.8 level intervals. ^{137}Cs was employed as the radioactive source (γ-ray emitter) and measurements were carried out in duplicate. From the results the standard deviation was also determined. The efficiency of the solvents under test was compared with that of toluene or xylene, which as noted earlier (section 5.1) are the best scintillation solvents.

The initial studies were carried out using scintillation systems consisting of the solvent under examination and the commercially available scintillator mixtures Unisolve 100 and Unisolve 1, both incorporating the primary and secondary solutes. Unisolve 100 is a pseudocumene based emulsifying scintillator and Unisolve 1 is a general purpose emulsifying scintillator, composed of a non-ionic surfactant blend and xylene.

A scintillator mixture free from emulsifying agents and surfactants, coded PNL 1 was also made during this study by mixing p-terphenyl (0.2500 g) and dimethylPOPOP (0.0125 g) in toluene (50 cm^3). The results obtained for the solvents under test using Unisolve 100, Unisolve 1 and PNL 1 are shown in Tables 5.2, 5.3 and 5.4 respectively.

It is evident from the data, that dimethylsulphoxide and to a greater extent pyridine and ethanol, although are very satisfactory solvents for the lithium compounds, they show very poor scintillation efficiency compared to that of toluene or xylene. This is indicated by the drastic drop in the number of counts over the discriminator level range. This behaviour is best illustrated in Graph 5.1, which compares the efficiency of toluene, xylene and dimethylsulphoxide in Unisolve 100.

With regard to the liquid scintillator mixtures employed, the results obtained in Unisolve 100 (Table 5.2) are in general better than those obtained in Unisolve 1 (Table 5.3). Even more satisfactory results were obtained by using PNL 1, (Table 5.4), as is best shown by the behaviour of xylene in this

Table 5.2 **Scintillation efficiency of selected solvents in Unisolve 100**

DL	NO. OF COUNTS				
	Toluene	Xylene	DMSO	Pyridine	Ethanol
0.2	180 ± 13	205 ± 14	256 ± 16	150 ± 12	291 ± 17
1.0	94 ± 9	78 ± 8	67 ± 8	0 ± 0	56 ± 7
1.8	58 ± 7	76 ± 8	2 ± 1	1 ± 1	1 ± 1
2.6	85 ± 9	69 ± 8	3 ± 2	0 ± 0	0 ± 0
3.4	54 ± 7	52 ± 7	0 ± 0		
4.2	16 ± 4	22 ± 4	0 ± 0		
5.0	4 ± 2	3 ± 1			
5.8	0 ± 0				

DL = Discriminator level

Graph 5.1 Scinitillation efficiency of various solvents in Unisolve 100

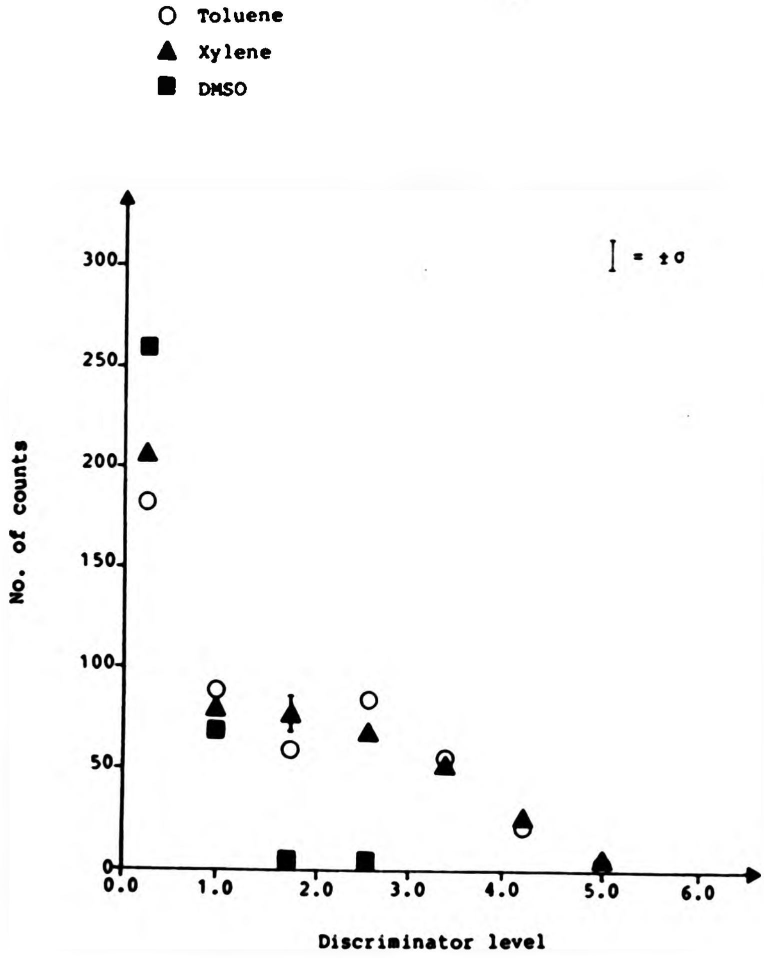


Table 5.3 Scintillation efficiency of selected solvents in Unisolve 1

DL	NO. OF COUNTS	
	Toluene	DMSO
0.2	225 ± 15	310 ± 17
1.0	132 ± 11	15 ± 4
1.8	92 ± 9	2 ± 1
2.6	39 ± 6	0 ± 0
3.4	2 ± 1	
4.2	0 ± 0	

Table 5.4 Scintillation efficiency of selected solvents in PNL 1

DL	NO. OF COUNTS	
	Xylene	DMSO
0.2	202 ± 14	318 ± 17
1.0	85 ± 19	5 ± 2
1.8	57 ± 7	0 ± 0
2.6	68 ± 8	
3.4	52 ± 7	
4.2	47 ± 7	
5.0	28 ± 5	
5.8	0 ± 0	

DL = Discriminator level

scintillator mixture in relation to that shown in Unisolve 100.

Further development of the scintillator mixture PNL 1 was also tried by: i) varying the amount of the wavelength shifter dimethylPOPOP in relation to p-terphenyl and ii) altering the wavelength shifter from dimethylPOPOP to POPOP. The latter variable was examined in order to assess, whether the emission spectrum of POPOP matches better the response of the photomultiplier.

Three more scintillator mixtures were prepared and their scintillation efficiency evaluated. The scintillator mixtures were PNL 1-A (p-terphenyl 0.2540 g/dimethylPOPOP 0.0250 g/toluene 50 cm^3), PNL 1-B (p-terphenyl 0.2570 g/POPOP 0.0200 g/toluene 50 cm^3) and PNL 1-C (p-terphenyl 0.2450 g/POPOP 0.0280 g/toluene 50 cm^3). The results are presented in Table 5.5 and illustrated in Graph 5.2.

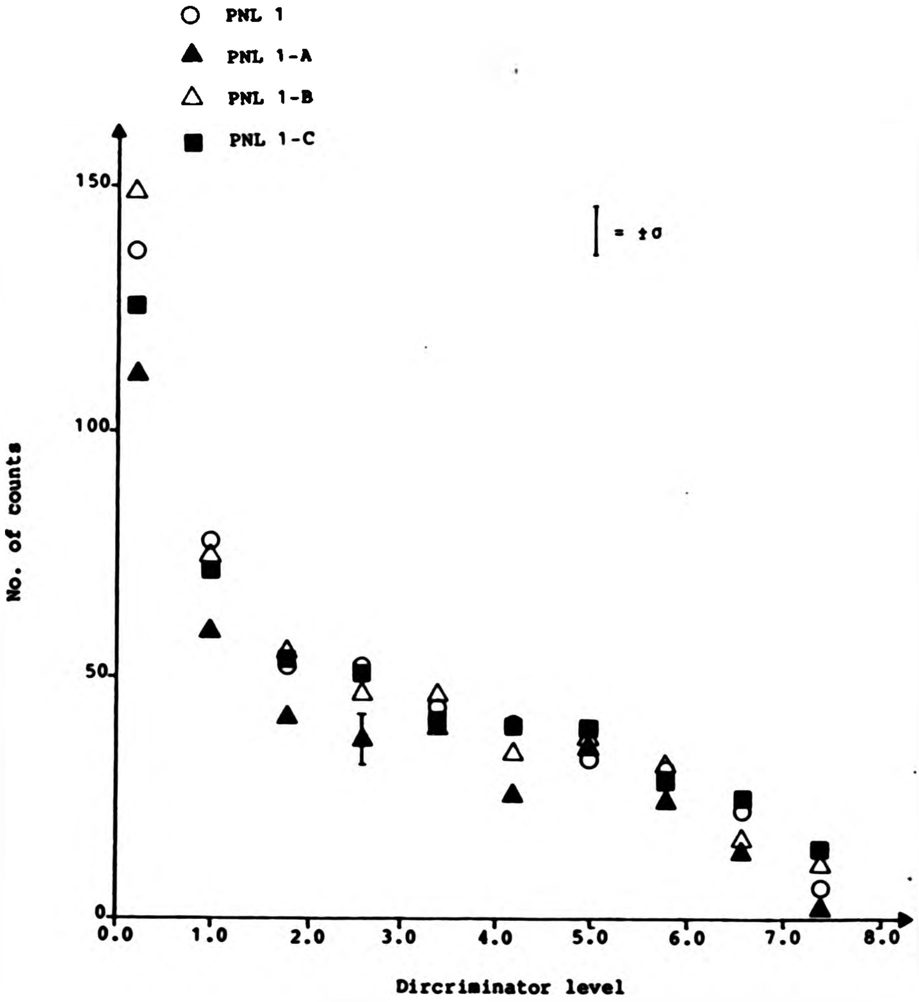
In general, the scintillation efficiency of all the scintillator mixtures tried is very good. This is adduced from the number of counts recorded, which i) extend over a wide discriminator level range and ii) do not drop drastically from one level to the other. The scintillation behaviour of PNL 1-A however, is inferior to that of PNL 1, while the scintillation efficiencies of PNL 1-B and PNL 1-C compare well.

Table 5.5 Scintillation efficiency of various scintillator mixtures

DL	NO. OF COUNTS			
	PNL 1	PNL 1-A	PNL 1-B	PNL 1-C
0.2	137 ± 12	112 ± 10	149 ± 12	127 ± 13
1.0	77 ± 3	59 ± 7	79 ± 9	71 ± 10
1.8	51 ± 6	41 ± 6	54 ± 1	52 ± 6
2.6	51 ± 8	36 ± 6	46 ± 7	50 ± 6
3.4	43 ± 5	40 ± 6	46 ± 7	41 ± 5
4.2	40 ± 3	25 ± 5	34 ± 6	40 ± 2
5.0	32 ± 6	34 ± 6	37 ± 6	38 ± 5
5.8	30 ± 5	24 ± 5	31 ± 5	28 ± 3
6.6	22 ± 6	13 ± 3	16 ± 4	24 ± 3
7.4	6 ± 2	1 ± 1	11 ± 3	14 ± 4
8.2	0 ± 0	0 ± 0	3 ± 3	6 ± 3

DL = Discriminator level

Graph 5.2 Scintillation efficiency of various scintillator mixtures



5.4 Scintillation behaviour of lithium complexes derived from miscellaneous ligands

The scintillation behaviour of lithium salicylato, dithiocarbamato and quinoneoximato complexes was determined in exactly the same way as that reported earlier for the solvents (section 5.3). Their efficiency was examined primarily in scintillator mixture PNL 1. The most promising compounds were also studied in PNL 1-C, whose efficiency was slightly better to that of PNL 1-B.

Different amounts of the lithium complexes under study, were added into the liquid scintillators PNL 1 and PNL 1-C. The amount used varied within the range of *ca.* 0.01-0.30 g. The scintillation behaviour was checked with the lithium complexes present i) as 'solid' in the scintillator mixture thus having a heterogeneous system and ii) as solutes i.e. dissolved in the liquid scintillator by the use of varying amounts of the solubiliser dimethylsulphoxide (DMSO), thus having a homogeneous system. Although DMSO was a poor scintillator as described in section 5.3, however it was used as a means of increasing the solubility of the lithium complex and thus the amount of lithium present in solution in the liquid scintillator. The results are presented in Tables 5.6-5.12 and selected compounds are illustrated in Graphs 5.3-5.7. For comparison, the number of counts of PNL 1 is also included in the above tables.

All the lithium salicylato complexes (Tables 5.6-5.8, Graphs 5.3-5.5) show a decrease in their scintillation efficiency when the amount of the solubiliser DMSO is increased. In the case of the lithium compound derived from 5-chloro-salicylic acid, [Li(5-Cl-sal), Table 5.6, Graph 5.3], (S1), the scintillation efficiency also decreases with an increase of its amount present as 'solid' in the scintillator. This observation would suggest, that the efficiency of S1 is affected by the size of the solid particles and the refractive indices of S1 and PNL 1, rather than by its amount present in the scintillator.

The lithium compounds derived from 5-methyl-salicylic acid, [Li(5-Me-sal), Table 5.7, Graph 5.4], (S2), and salicylic acid, [Li(sal)(salH), Table 5.8, Graph 5.5], (S3), when present as 'solid' in the scintillator mixture show a very promising scintillation efficiency. Their efficiency is also unaffected by an almost tenfold increase of the amount of lithium compound present. This would indicate that scattering of light photons, or self-absorption by the solid particles of the complexes is inappreciable. Their efficiency is also similar to that of the free from lithium, scintillator mixture PNL 1.

Table 5.6 **Scintillation efficiency of (5-chloro-salicylato)lithium(I) (S1) in PNL 1 ($5\ cm^3$)**

DL	NO. OF COUNTS						
	S1(0.0201 g) (as solid)	S1(0.0201 g) DMSO(5dr)	S1(0.0512 g) (as solid)	S1(0.0512 g) DMSO(7dr)	S1(0.1043 g) (as solid)	S1(0.1043 g) DMSO(8dr)	PNL 1($5\ cm^3$)
0.2	160 ± 14	152 ± 2	173 ± 4	176 ± 8	184 ± 16	190 ± 15	137 ± 12
1.0	99 ± 1	105 ± 2	90 ± 6	114 ± 7	110 ± 8	120 ± 7	77 ± 3
1.8	66 ± 10	74 ± 1	79 ± 7	82 ± 7	74 ± 3	45 ± 7	51 ± 6
2.6	64 ± 7	62 ± 1	68 ± 4	26 ± 1	8 ± 1	3 ± 1	51 ± 8
3.4	59 ± 1	36 ± 3	25 ± 5	3 ± 1			43 ± 5
4.2	48 ± 5	4 ± 1	2 ± 0				40 ± 3
5.0	14 ± 1						32 ± 6
5.8	2 ± 0						30 ± 5
6.6							22 ± 6
7.4							6 ± 2

DL = Discriminator level

dr = drops (34 dr = $1\ cm^3$)

Graph 5.3 Scintillation efficiency of (5-chlorosalicylato)lithium(I) (S1) as solid in PNL 1

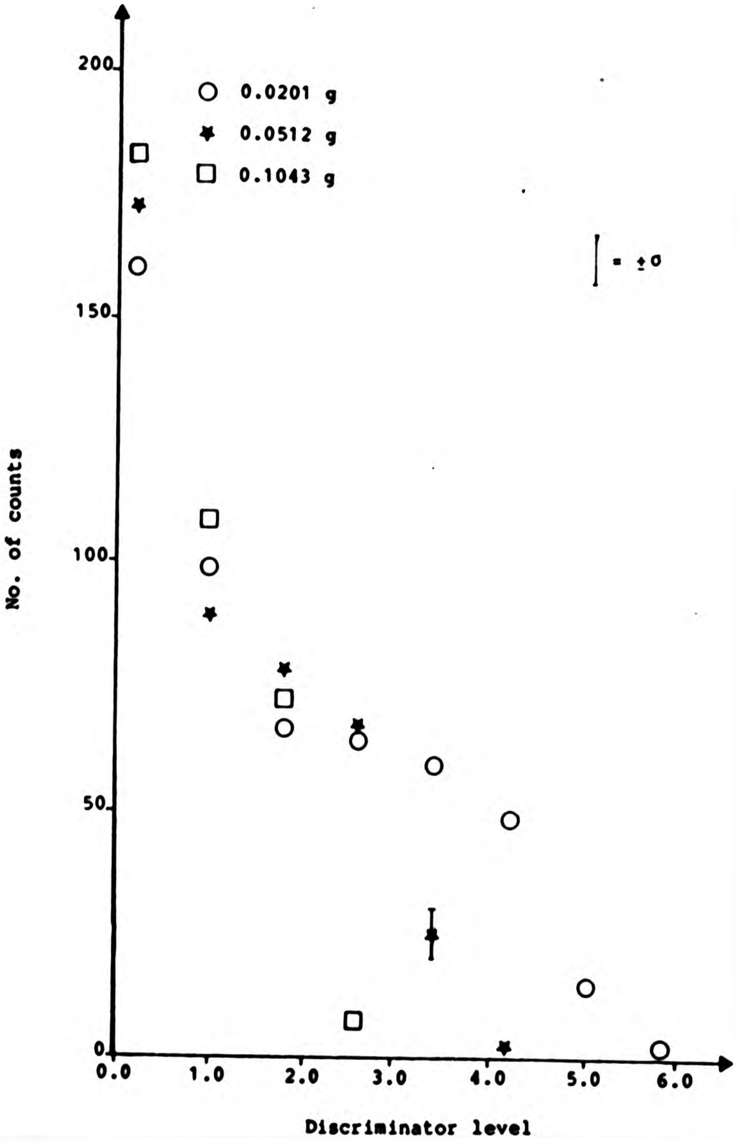


Table 5.7 Scintillation efficiency of (5-methyl-salicylato)lithium(I) (S2) in PNL 1 (5 cm^3)

DL	NO. OF COUNTS							
	S2(0.0201 g) (as solid)	S2(0.0201 g) DMSO(6dr)	S2(0.0508 g) (as solid)	S2(0.0508 g) DMSO(7dr)	S2(0.1044 g) (as solid)	S2(0.1044 g) DMSO(10dr)	S2(0.2990 g) (as solid)	PNL 1(5 cm^3)
0.2	139 ± 9	167 ± 5	139 ± 12	201 ± 10	135 ± 7	216 ± 16	137 ± 17	137 ± 12
1.0	81 ± 5	94 ± 6	78 ± 6	119 ± 5	68 ± 4	77 ± 8	67 ± 1	77 ± 3
1.8	54 ± 5	83 ± 7	54 ± 5	50 ± 7	53 ± 5	4 ± 1	61 ± 3	51 ± 6
2.6	52 ± 8	53 ± 4	46 ± 4	4 ± 1	52 ± 4		47 ± 5	51 ± 8
3.4	41 ± 1	16 ± 1	50 ± 8		36 ± 6		47 ± 3	43 ± 5
4.2	43 ± 6	1 ± 0	40 ± 3		34 ± 1		43 ± 2	40 ± 3
5.0	33 ± 3		35 ± 0		37 ± 8		30 ± 5	32 ± 6
5.8	34 ± 5		20 ± 4		19 ± 2		11 ± 0	30 ± 5
6.6	11 ± 4		4 ± 2		4 ± 2		3 ± 1	22 ± 6
7.4	5 ± 0							6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Graph 5.4 Scintillation efficiency of (5-methylsalicylato)lithium(I) (S2) as solid in PNL 1

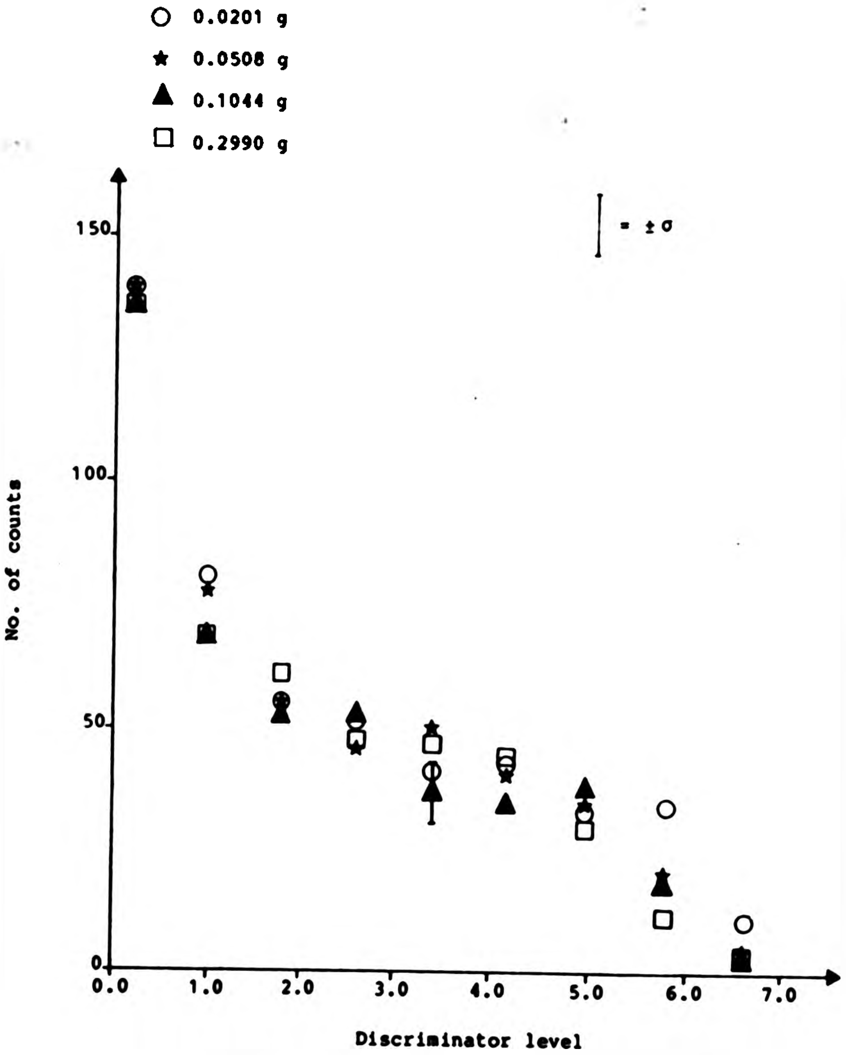


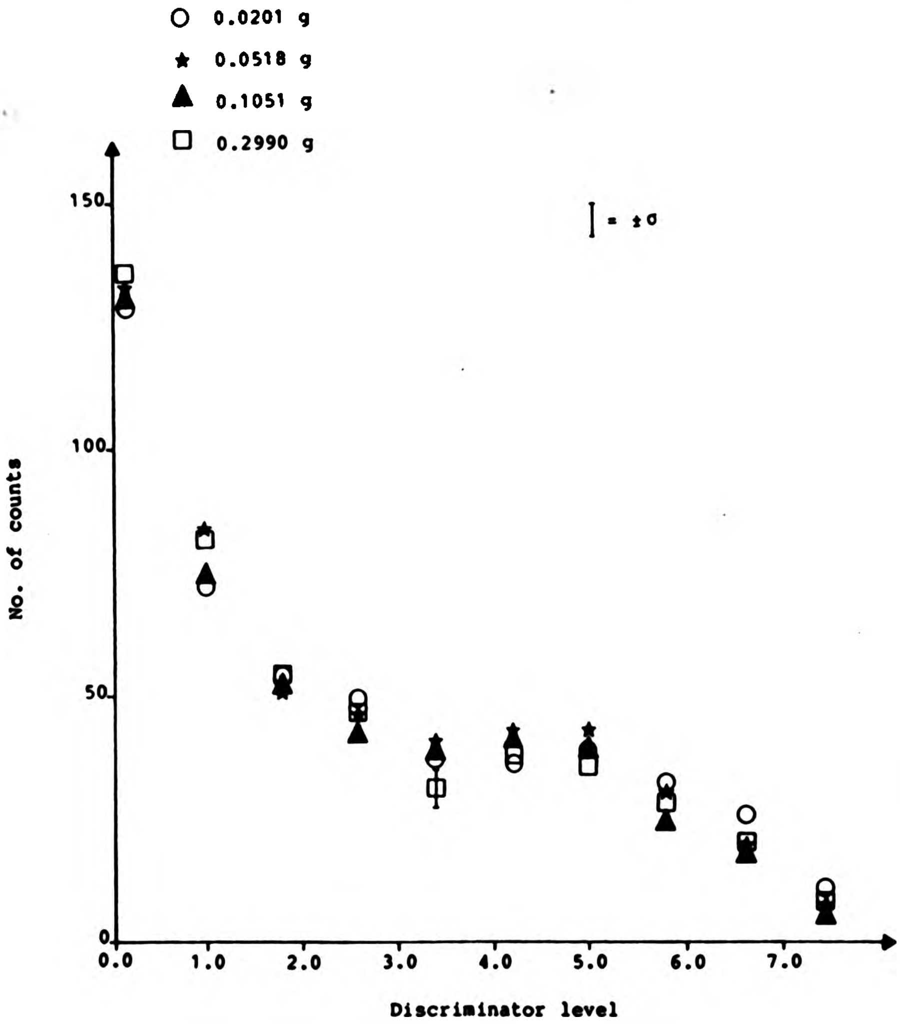
Table 5.8 Scintillation efficiency of (salicylic acid)(salicylato)lithium(I) (S3) in PNL 1 (5 cm^3)

DL	NO. OF COUNTS							
	S3(0.0201 g) (as solid)	S3(0.0201 g) DMSO(7dr)	S3(0.0518 g) (as solid)	S3(0.0518 g) DMSO(9dr)	S3(0.1051 g) (as solid)	S3(0.1051 g) DMSO(15dr)	S3(0.2990 g) (as solid)	PNL 1(5 cm^3)
0.2	129 ± 8	156 ± 2	133 ± 4	162 ± 1	132 ± 15	178 ± 15	137 ± 7	137 ± 12
1.0	72 ± 10	85 ± 2	84 ± 9	95 ± 9	75 ± 10	122 ± 10	82 ± 7	77 ± 3
1.8	54 ± 3	76 ± 10	51 ± 6	92 ± 8	52 ± 4	63 ± 4	54 ± 4	51 ± 6
2.6	50 ± 3	61 ± 8	46 ± 5	45 ± 8	41 ± 3	6 ± 1	47 ± 2	51 ± 8
3.4	37 ± 2	50 ± 3	41 ± 8	3 ± 0	39 ± 5		31 ± 4	43 ± 5
4.2	36 ± 5	14 ± 3	42 ± 3		41 ± 3		38 ± 8	40 ± 3
5.0	39 ± 6		43 ± 4		39 ± 5		36 ± 3	32 ± 6
5.8	32 ± 7		30 ± 6		24 ± 3		29 ± 8	30 ± 5
6.6	25 ± 4		19 ± 3		18 ± 3		20 ± 2	22 ± 6
7.4	11 ± 3		7 ± 0		6 ± 3		9 ± 1	6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Graph 5.5 Scintillation efficiency of (salicylic acid) (salicylato)lithium(I) (S3) as solid in PNL 1



The lithium complexes derived from benzylamine dithiocarbamic acid [Li(bdtc)(bdtcH)], (D1) and morpholine dithiocarbamic acid [Li(mdtc)(mdtcH)], (D2), show in general poor scintillation efficiency when DMSO was used as solubiliser (Tables 5.9 and 5.10). However, Li(bdtc)(bdtcH) shows a good scintillation behaviour when present as 'solid' in the scintillator mixture, and this behaviour is sustained up to about 0.10 g of its amount present (Table 5.9, Graph 5.6). The Li(mdtc)(mdtcH) complex exhibits again good scintillation efficiency when present as 'solid' in PNL 1 (Table 5.10, Graph 5.7). Its efficiency is greater than that of D1, as it can be adduced from the number of counts which extend over a wider discriminator level range for D2. This behaviour is also unaffected by a tenfold increase in the amount of D2 present in the scintillator mixture (*ca*. 0.30 g), suggesting again as in the case of complexes S2 and S3 (*vide supra*), that scattering of light photons or self-absorption by the solid is inappreciable.

The scintillation efficiency of the lithium quinoneoximato complexes Li(1-nqo).1/2 EtOH (Q1), Li(1-nqo)(1-nqoH).EtOH (Q2), Li(2-nqo).1/2 EtOH (Q3), and Li(2-nqo)(2-nqoH).EtOH (Q4) (Tables 5.11 and 5.12) was also investigated. Their scintillation behaviour is better when the complexes are present as 'solid' in the scintillator mixture, but in general is not satisfactory. This is not entirely unexpected because

Table 5.9 Scintillation efficiency of (benzylamine dithiocarbamic acid)(benzylamine dithiocarbamato)lithium(I) (D1) in PNL 1 (5 cm^3)

DL	NO. OF COUNTS							
	D1(0.0202 g) (as solid)	D1(0.0202 g) DMSO(4dr)	D1(0.0516 g) (as solid)	D1(0.0516 g) DMSO(5dr)	D1(0.1051 g) (as solid)	D1(0.1051 g) DMSO(11dr)	D1(0.2966 g) (as solid)	PNL 1(5 cm^3)
0.2	150 ± 5	156 ± 5	138 ± 8	179 ± 9	132 ± 6	215 ± 16	153 ± 20	137 ± 12
1.0	79 ± 2	88 ± 5	77 ± 5	109 ± 7	67 ± 6	74 ± 4	74 ± 10	77 ± 3
1.8	60 ± 6	2 ± 31	58 ± 5	47 ± 4	59 ± 1	2 ± 0	69 ± 1	51 ± 6
2.6	52 ± 4	41 ± 3	50 ± 5	3 ± 1	53 ± 2		55 ± 8	51 ± 8
3.4	51 ± 6	6 ± 1	46 ± 7		48 ± 4		32 ± 4	43 ± 5
4.2	39 ± 2		46 ± 8		41 ± 4		6 ± 1	40 ± 3
5.0	44 ± 1		31 ± 3		15 ± 3			32 ± 6
5.8	24 ± 4		8 ± 1		2 ± 1			30 ± 5
6.6	4 ± 2							22 ± 6
7.4								6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Graph 5.6 Scintillation efficiency of (benzylamine dithiocarbamic acid)(benzylamine dithiocarbamato)lithium(I) (D1) as solid in PNL 1

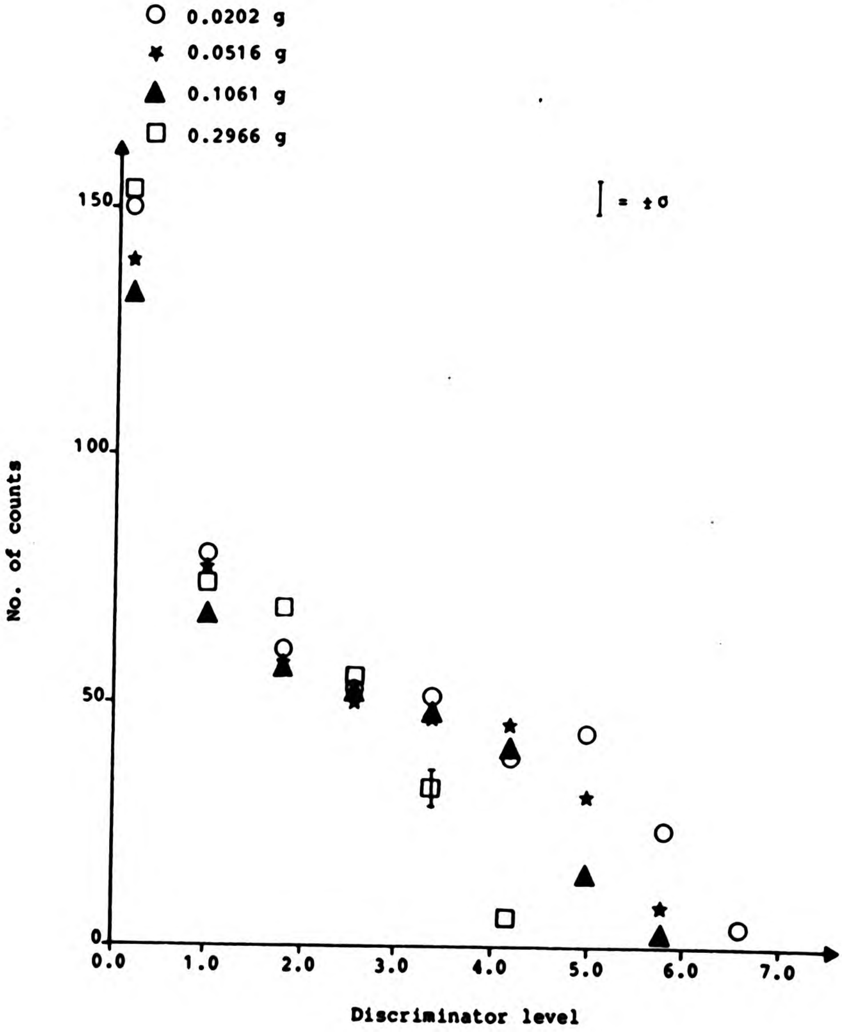


Table 5.10 **Scintillation efficiency of (morpholine dithiocarbamic acid)(morpholine dithiocarbamato)lithium(I) (D2) in PNL 1 (5 cm^3)**

DL	NO. OF COUNTS					
	D2(0.0201 g) (as solid)	D2(0.0201 g) DMSO(40dr)	D2(0.0514 g) (as solid)	D2(0.1047 g) (as solid)	D2(0.2952 g) (as solid)	PNL 1(5 cm^3)
0.2	134 ± 4	284 ± 14	131 ± 6	134 ± 13	122 ± 2	137 ± 12
1.0	77 ± 10	88 ± 15	72 ± 5	70 ± 5	70 ± 4	77 ± 3
1.8	55 ± 6	2 ± 1	52 ± 4	51 ± 3	43 ± 7	51 ± 6
2.6	47 ± 3		44 ± 5	44 ± 1	41 ± 5	51 ± 8
3.4	44 ± 7		40 ± 6	39 ± 3	41 ± 1	43 ± 5
4.2	43 ± 5		38 ± 9	37 ± 6	32 ± 4	40 ± 3
5.0	34 ± 2		35 ± 1	39 ± 1	33 ± 4	32 ± 6
5.8	33 ± 1		33 ± 5	24 ± 3	23 ± 4	30 ± 5
6.6	19 ± 2		18 ± 5	20 ± 1	13 ± 2	22 ± 6
7.4	4 ± 0		7 ± 4	2 ± 1	1 ± 0	6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Graph 5.7 Scintillation efficiency of(morpholine dithiocarbamic acid)(morpholine dithiocarbamato)lithium(I) (D2) as solid in PNL 1

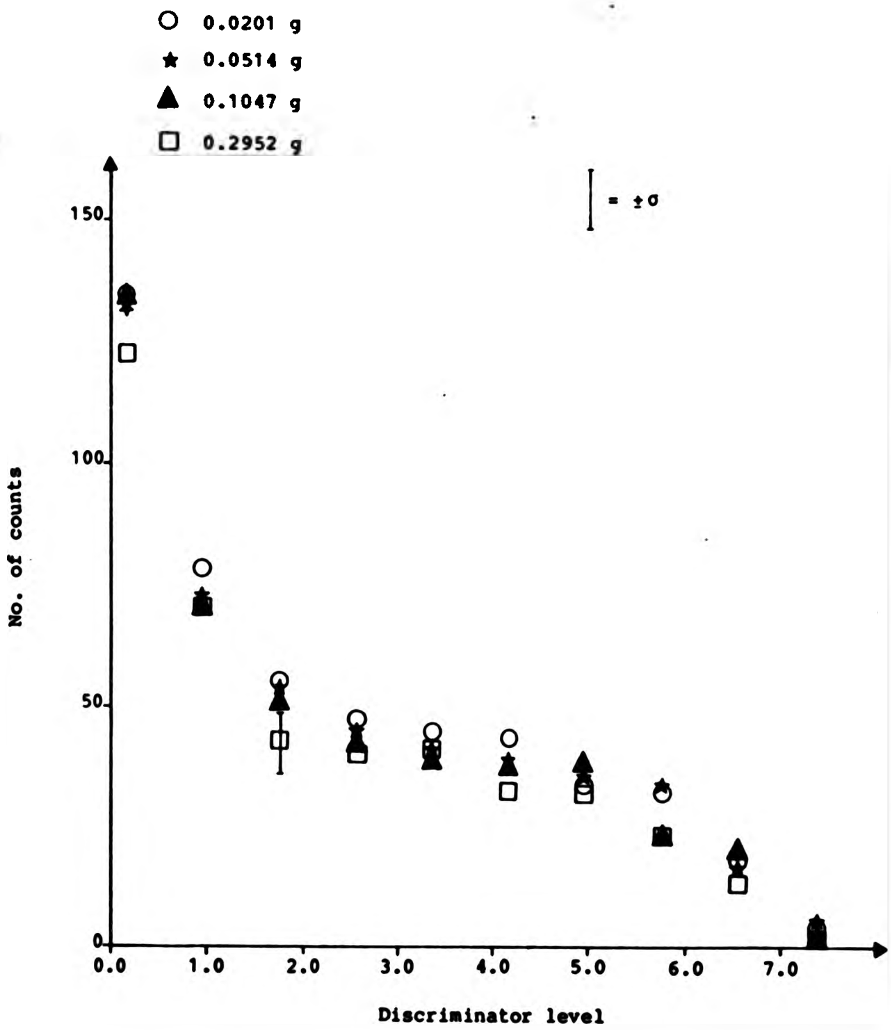


Table 5.11 Scintillation efficiency of (1,2-naphthoquinone 1-oximato)lithium(I),1/2 ethanol (Q1) and bis(1,2-naphthoquinone 1-oxime)(1,2-naphthoquinone 1-oximato)lithium(I), ethanol (Q2) in PNL 1 (5 cm^3)

DL	NO. OF COUNTS						
	Q1(0.0116 g) (as solid)	Q1(0.0116 g) DMSO(7dr)	Q1(0.0511 g) (as solid)	Q1(0.1044 g) (as solid)	Q2(0.0114 g) (as solid)	Q2(0.0514 g) (as solid)	PNL 1(5 cm^3)
0.2	162 ± 12	5 ± 1	160 ± 11	155 ± 7	201 ± 7	4 ± 1	137 ± 12
1.0	102 ± 10		93 ± 10	103 ± 4	29 ± 4		77 ± 3
1.8	78 ± 5		61 ± 6	49 ± 3	4 ± 2		51 ± 6
2.6	53 ± 5		20 ± 3	8 ± 1			51 ± 8
3.4	25 ± 2		2 ± 1				43 ± 5
4.2	4 ± 3						40 ± 3
5.0							32 ± 6
5.8							30 ± 5
6.6							22 ± 6
7.4							6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Table 5.12 Scintillation efficiency of (1,2-naphthoquinone 2-oximato)lithium(I),1/2 ethanol (Q3) and (1,2-naphthoquinone 2-oxime)(1,2-naphthoquinone 2-oximato)lithium(I), ethanol (Q4) in PNL 1 (5 cm^3)

DL	NO. OF COUNTS						
	Q3(0.0115 g) (as solid)	Q3(0.0115 g) DMSO(8dr)	Q3(0.0521 g) (as solid)	Q3(0.1051 g) (as solid)	Q4(0.0114 g) (as solid)	Q4(0.0516 g) (as solid)	PNL 1(5 cm^3)
0.2	166 ± 10	1 ± 0	185 ± 10	204 ± 14	12 ± 4	6 ± 1	137 ± 12
1.0	108 ± 8		107 ± 5	67 ± 6	3 ± 1		77 ± 3
1.8	76 ± 5		38 ± 8	8 ± 2			51 ± 6
2.6	49 ± 6		3 ± 1				51 ± 8
3.4	19 ± 2						43 ± 5
4.2	4 ± 0						40 ± 3
5.0							32 ± 6
5.8							30 ± 5
6.6							22 ± 6
7.4							6 ± 2

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

these complexes are highly coloured and therefore they will absorb rather than emit light.

The scintillation efficiency of the lithium salicylato and lithium dithiocarbamato complexes was also investigated in the scintillator mixture PNL 1-C, which incorporates POPOP as the wavelength shifter instead of dimethylPOPOP in PNL 1. The amount of the lithium complex present in the scintillator mixture varied from *ca.* 0.01-0.10 g. The number of counts per discriminator level for the lithium salicylato complexes are presented in Tables 5.13-5.15 and for the lithium dithiocarbamato complexes in Tables 5.16 and 5.17.

The scintillation behaviour of the complexes studied in PNL 1-C is again better when the complexes are present as 'solid' in the scintillator mixture, rather than in solution. The scintillation efficiency of Li(5-Me-sal), Li(sal)(salH) and Li(mdtc)(mdtcH) (Tables 5.14, 5.15 and 5.17 respectively) is greater than that of Li(5-Cl-sal) and Li(bdtc)(bdtcH) complexes (Tables 5.13 and 5.16). In addition their efficiency is very similar to that exhibited, when these complexes were present as 'solid' in PNL 1. This behaviour is also sustained when the amount of complex in PNL 1-C increases by a factor of ten. The lithium complex S1 (Table 5.13) derived from 5-chloro-salicylic acid and D1 (Table 5.16) derived from benzylamine dithiocarbamic

Table 5.13 Scintillation efficiency of (5-chloro-salicylato)lithium(I) (S1) in PNL 1-C (5 cm^3)

DL	NO. OF COUNTS						
	S1(0.0203 g) (as solid)	S1(0.0203 g) DMSO(5dr)	S1(0.0513 g) (as solid)	S1(0.0513 g) DMSO(7dr)	S1(0.1047 g) (as solid)	S1(0.1047 g) DMSO(8dr)	PNL 1-C(5 cm^3)
0.2	136 ± 8	158 ± 12	154 ± 11	161 ± 3	157 ± 11	178 ± 14	127 ± 13
1.0	72 ± 3	88 ± 7	83 ± 9	104 ± 13	102 ± 5	110 ± 5	71 ± 10
1.8	57 ± 5	76 ± 6	67 ± 6	77 ± 9	83 ± 7	66 ± 8	52 ± 6
2.6	52 ± 8	64 ± 10	68 ± 4	54 ± 4	31 ± 4	16 ± 3	50 ± 6
3.4	46 ± 3	46 ± 5	52 ± 6	16 ± 4	2 ± 0	1 ± 0	41 ± 5
4.2	43 ± 6	21 ± 6	20 ± 3	1 ± 0			40 ± 2
5.0	33 ± 4	4 ± 0	5 ± 2				38 ± 5
5.8	18 ± 3						28 ± 3
6.6	4 ± 2						24 ± 3
7.4							14 ± 4
8.2							6 ± 3

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Table 5.14 Scintillation efficiency of (5-methyl-salicylato)lithium(I) (S2) in PNL 1-C (5 cm^3)

DL	NO. OF COUNTS						
	S2(0.0205 g) (as solid)	S2(0.0205 g) DMSO(5dr)	S2(0.0511 g) (as solid)	S2(0.0511 g) DMSO(9dr)	S2(0.1047 g) (as solid)	S2(0.1047 g) DMSO(12dr)	PNL 1-C(5 cm^3)
0.2	125 ± 12	157 ± 6	119 ± 15	174 ± 14	123 ± 11	231 ± 8	127 ± 13
1.0	76 ± 2	84 ± 9	74 ± 3	115 ± 9	69 ± 7	100 ± 2	71 ± 10
1.8	54 ± 4	74 ± 3	53 ± 13	66 ± 10	54 ± 7	8 ± 2	52 ± 6
2.6	53 ± 7	66 ± 7	51 ± 8	18 ± 3	46 ± 6		50 ± 6
3.4	40 ± 5	36 ± 10	48 ± 8	1 ± 0	47 ± 7		41 ± 5
4.2	45 ± 4	4 ± 0	35 ± 2		34 ± 1		40 ± 2
5.0	40 ± 4		36 ± 3		26 ± 4		38 ± 5
5.8	32 ± 6		26 ± 4		19 ± 4		28 ± 3
6.6	21 ± 4		13 ± 3		8 ± 0		24 ± 3
7.4	8 ± 0		3 ± 0				14 ± 4
8.2							6 ± 3

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Table 5.15 Scintillation efficiency of (salicylic acid)(salicylato)lithium(I) (S3) in PNL 1-C (5 cm^3)

DL	NO. OF COUNTS						
	S3(0.0203 g) (as solid)	S3(0.0203 g) DMSO(7dr)	S3(0.0521 g) (as solid)	S3(0.0521 g) DMSO(10dr)	S3(0.1051 g) (as solid)	S3(0.1051 g) DMSO(16dr)	PNL 1-C(5 cm^3)
0.2	130 ± 3	151 ± 8	122 ± 14	160 ± 14	131 ± 4	177 ± 13	127 ± 13
1.0	74 ± 7	90 ± 5	73 ± 4	88 ± 8	80 ± 10	129 ± 8	71 ± 10
1.8	53 ± 9	78 ± 5	52 ± 6	83 ± 6	49 ± 4	82 ± 7	52 ± 6
2.6	49 ± 6	63 ± 3	47 ± 2	66 ± 7	46 ± 5	18 ± 1	50 ± 6
3.4	35 ± 4	56 ± 6	40 ± 5	24 ± 1	40 ± 5	0 ± 0	41 ± 5
4.2	37 ± 7	34 ± 2	42 ± 9	2 ± 1	38 ± 2		40 ± 2
5.0	39 ± 2	7 ± 0	41 ± 1		38 ± 4		38 ± 5
5.8	34 ± 4		33 ± 7		34 ± 7		28 ± 3
6.6	30 ± 2		24 ± 4		26 ± 8		24 ± 3
7.4	15 ± 5		17 ± 1		19 ± 3		14 ± 4
8.2	4 ± 0		4 ± 0		5 ± 0		6 ± 3

DL = Discriminator level

dr = drops(34 dr = 1 cm^3)

Table 5.16 **Scintillation efficiency of (benzylamine dithiocarbamic acid)(benzylamine dithiocarbamato)lithium(I) (D1) in PNL 1-C (5 cm^3)**

DL	NO. OF COUNTS						
	D1(0.0205 g) (as solid)	D1(0.0205 g) DMSO(4dr)	D1(0.0516 g) (as solid)	D1(0.0516 g) DMSO(6dr)	D1(0.1053 g) (as solid)	D1(0.1053 g) DMSO(12dr)	PNL 1-C(5 cm^3)
0.2	130 ± 6	154 ± 10	133 ± 6	169 ± 5	150 ± 14	203 ± 96	127 ± 13
1.0	66 ± 4	92 ± 10	66 ± 4	109 ± 6	76 ± 8	91 ± 5	71 ± 10
1.8	55 ± 2	82 ± 4	54 ± 4	64 ± 8	62 ± 5	10 ± 2	52 ± 6
2.6	37 ± 3	52 ± 4	43 ± 10	7 ± 1	45 ± 1		50 ± 6
3.4	39 ± 6	16 ± 2	44 ± 8		48 ± 3		41 ± 5
4.2	34 ± 1	1 ± 0	39 ± 1		45 ± 5		40 ± 2
5.0	41 ± 5		21 ± 2		30 ± 7		38 ± 5
5.8	33 ± 7		7 ± 1		9 ± 4		28 ± 3
6.6	15 ± 5						24 ± 3
7.4	5 ± 0						14 ± 4
8.2							6 ± 3

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

Table 5.17 Scintillation efficiency of (morpholine dithiocarbamic acid)(morpholine dithiocarbamato)lithium(I) (D2) in PNL 1-C (5 cm^3)

DL	NO. OF COUNTS				
	D2(0.0203 g) (as solid)	D2(0.0203 g) DMSO(34dr)	D2(0.0515 g) (as solid)	D2(0.1047 g) (as solid)	PNL 1-C(5 cm^3)
0.2	133 ± 3	241 ± 12	130 ± 13	126 ± 13	127 ± 13
1.0	70 ± 11	151 ± 14	74 ± 3	68 ± 6	71 ± 10
1.8	48 ± 7	22 ± 3	53 ± 1	51 ± 4	52 ± 6
2.6	48 ± 5	2 ± 1	46 ± 3	46 ± 6	50 ± 6
3.4	34 ± 2		42 ± 4	38 ± 3	41 ± 5
4.2	36 ± 2		36 ± 5	38 ± 7	40 ± 2
5.0	34 ± 5		39 ± 7	32 ± 7	38 ± 5
5.8	31 ± 6		32 ± 4	29 ± 4	28 ± 3
6.6	25 ± 2		21 ± 2	26 ± 3	24 ± 3
7.4	14 ± 3		10 ± 1	8 ± 2	14 ± 4
8.2	3 ± 2		2 ± 1		6 ± 3

DL = Discriminator level

dr = drops (34 dr = 1 cm^3)

acid behave slightly better in PNL 1-C than PNL 1. This is adduced from the number of counts which extend over a wider range of discriminator level.

5.5 Summary and conclusions

It is evident from all the data obtained so far that:
i) the scintillator mixtures PNL 1 and PNL 1-C, which were prepared during this study, have a better scintillation efficiency than the commercially available ones Unisolve 100 and Unisolve 1;
ii) the solvents DMSO, pyridine and ethanol, although very good solvents for all the lithium complexes studied, however, they show poor scintillation efficiency;
iii) the lithium complexes derived from salicylic acid and 5-methyl-salicylic acid which was developed during this study, exhibit a promising scintillation behaviour. Similar behaviour is also shown by the lithium dithiocarbamato complexes mainly that derived from morpholine dithiocarbamic acid, also developed during this study;
iv) both the lithium salicylato and lithium dithiocarbamato complexes, show a more satisfactory scintillation efficiency when present as solids in the liquid scintillator mixtures PNL 1 and PNL 1-C;
v) the incorporation of large amounts of dimethylsulphoxide as solubiliser has a detrimental

effect on the scintillation behaviour of all the lithium complexes studied.

The overall result accrued from the studies carried out during this work is that the amount of solubilised lithium in the scintillator mixture is not sufficient, in order to obtain an efficient lithium loaded liquid scintillator for neutron counting.

However, the results have also shown that the presence of the lithium complexes as 'solid' in the liquid scintillator, had little effect on the overall scintillation efficiency. This behaviour could be explored further, by developing binary or more complex melts, which will incorporate the above mentioned complexes and the primary/secondary solutes.

5.6 References

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CHAPTER SIX

EXPERIMENTAL

6.1 Reagents

All reagents used in this work were obtained commercially and used without further purification. The silica absorbent used in the chromatography columns was Merck silica gel 60 of 70-230 mesh. Thin layer chromatography was performed using commercially supplied silica coated alumina plates. The following complexes were prepared by methods described in the literature.

Complex	Ref.
Bis(1,2-naphthoquinone 1-oximato)copper(II)	1
Bis(1,2-naphthoquinone 2-oximato)copper(II)	1
Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II)	1

6.2 Solvents

The solvents used in reactions were of GPR grade. Toluene used in purifications was distilled prior to its use. Anhydrous methanol was obtained by fractional distillation followed by standing over Type 4A molecular sieve.[2]

All the solvents used for solubility studies were distilled and dried prior to use.

Pyridine was distilled after standing over sodium hydroxide pellets. Benzene was added to this fraction and the benzene/water azeotrope distilled off at 65-85 °C/760 mm before the portion boiling at 115 °C/ 760 mm was collected and kept over sodium hydroxide pellets.[2] This experiment was carried out in a well ventilated fumecupboard.

Solvents used in scintillation counting were distilled, dried and deoxygenated with nitrogen for 15 minutes prior to their use. The dimethylsulphoxide used as solubiliser was of scintillation grade.

6.3 General Techniques

6.3.1 Solubility studies

All weighings were carried out to 4 decimals and all volumetric measurements were performed using either 5.00 ± 0.01 or 2.00 ± 0.01 cm^3 graduated pipettes.

The solubility measurements of the lithium complexes were carried out using Quickfit tubes, small magnetic followers for the agitation of the solute/solvent mixture and a water bath fitted with a water pump and a thermostatically controlled water heater. The water temperature in the bath was kept at 25.0 ± 0.2 °C. A sufficient quantity of solid needed to give a saturated solution (*ca.* 0.1-15.0 g) was mixed with the solvent (*ca.* 5-10 cm^3) in the Quickfit tubes and the measurements were carried out in triplicate. The mixtures were continuously stirred and were allowed to reach saturation for *ca.* 7 h in the thermostat. The necessary time required for saturation was determined in a preliminary study of the complex under test, where the amount of solute dissolved in the supernatant liquid was determined hourly till a constant value was obtained. The mixtures were then allowed to settle at 25 °C and an accurately measured portion (*ca.* 2 cm^3) of the supernatant liquid was withdrawn and transferred to preweighed sample bottles. In order to prevent withdrawal of excess solute, glass wool acting as filter, was fitted at the tip of the pipette. The weight of the withdrawn solvent was also recorded. The solvent was subsequently removed under nitrogen and the residues were dried at 20 °C/1.0 mm to constant weight.

6.3.2 Liquid scintillation counting

Liquid scintillation counting was performed on a Packard Tri-carb liquid scintillator counter, Model 3320 using an external ^{137}Cs source(γ-ray emitter), 8% gain and 8% window. The discriminator level was increased from 0.2-8.2 at 0.8 intervals, and half minute counts were recorded in duplicate. Glass vials of *ca.* 15 cm^3 capacity with plastic caps were used for the scintillator mixture, the solvent and the lithium complex under test. The volume of the mixture under test in the vials was kept constant to 5 cm^3. Three different scintillator mixtures were tried together with the solvents under test; the commercially available ones Unisolve 1 and Unisolve 100, and PNL 1 which was made during this study. PNL 1 consists of p-terphenyl (0.2500 g) and dimethylPOPOP (0.0125 g) in toluene (50 cm^3). The ratio of the solvents under test to the scintillator mixture was 3/2 cm^3. Three more scintillator mixtures were also prepared and studied: PNL 1-A [p-terphenyl (0.2540 g), dimethyl-POPOP (0.0250 g) in toluene (50 cm^3)]; PNL 1-B [p-terphenyl (0.2570 g), POPOP (0.0200 g) in toluene (50 cm^3)]; PNL 1-C [p-terphenyl (0.2450 g), POPOP (0.0280 g) in toluene (50 cm^3)]. The scintillation efficiency of the lithium complexes was examined in PNL 1 and PNL 1-C.

6.4 Analytical techniques

Carbon, hydrogen and nitrogen analysis were carried out on a Perkin-Elmer 240 elemental analyser.

Lithium analysis was carried out on a Pye-Unicam SP9 atomic absorption spectrometer. Wet oxidation was achieved by heating an accurately weighed amount of the compound (*ca*. 0.1 g) in concentrated nitric (5-10 cm^3) and sulfuric acids (5 cm^3), and subsequently adding a few drops of 30% hydrogen peroxide. AR lithium hydroxide monohydrate was used for the preparation of the standard solutions.

6.5 Physical techniques

Infra-red spectroscopy

Infra-red spectra in the region 4000-600 cm^{-1} were recorded on a Perkin-Elmer 781 spectrophotometer. The spectra were recorded mainly as KBr discs. Solution infra-red were recorded in chloroform, and carbon tetrachloride.

Thermal gravimetric analysis

Thermal gravimetric analysis was carried out on a Stanton HT-SM Thermobalance.

Nuclear magnetic resonance spectroscopy

Fourier Transform ^{1}H n.m.r. spectra were recorded on a Bruker WP 80 MHz, a Varian XL-200 MHz and a Varian XVR-400 MHz spectrometer.

Trimethylsilane was used as reference standard and all spectra were recorded in deuterated chloroform unless otherwise stated. For 400 MHz ^{1}H n.m.r. spectra, deuterated chloroform was used as reference standard.

Conductivity measurements

Conductivity measurements were recorded on a PT 1-18 digital conductivity meter.

Magnetic measurements

Magnetic measurements were recorded at room temperature on a Johnson Matthey magnetic susceptibility balance. The instrument was calibrated with mercury(II) tetrathiocyanocobaltate(II).

Mass spectrometry

Mass spectra were recorded on a VG 7070H mass spectrometer with Finnigan INCOS II data system.

High performance liquid chromatography

A Waters M6000 pump, Waters R401 refractive index detector and Rheodyne 712S injection valve was used. A stainless steel column, 2 x 25 cm long, 10 mm internal diameter and 12 mm outside diameter, packed with Lichroprep 5-20 µm silica gel was also employed. The mobile phase was a 1:1 mixture of ethyl acetate and light petrol (b.p. 60-80 ^{o}C).

Melting points

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

Solvent systems used for thin layer chromatography

The following solvent systems were employed in the course of this work for thin layer chromatography.

Toluene/Ethanol/Ethyl acetate (9:2:1)
Chloroform

6.6 Reactions

6.6.1 Reaction of 1,2-naphthoquinone 1-oxime with lithium hydroxide monohydrate in ethanol in 1:1 molar ratio

A solution of 1,2-naphthoquinone 1-oxime (5.35 g, 31.0 mmol) in ethanol (125 cm^3) was added portionwise and with continuous stirring to a suspension of lithium hydroxide monohydrate (1.30 g, 31.0 mmol) in ethanol (40 cm^3). The resultant mixture was heated on a water bath at *ca.* 65 °C for 0.5 h and then filtered hot. The green filtrate on standing gave dark green crystalline *(1,2-naphthoquinone 1-oximato)lithium(I), 1/2 ethanol*

(5.15 g, 82%) (Found: C, 64.9; H, 5.1; Li, 3.6; N, 6.7. $C_{22}H_{18}Li_2N_2O_5$ requires C, 65.4; H, 4.5; Li, 3.4; N, 6.9%), which was filtered off, washed with ethanol (3 x 5 cm^3) and light petrol (b.p. 30-40 °C) (3 x 50 cm^3) and dried at 40 °C/1.0 mm.

6.6.2 *Pyrolysis of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol*

(1,2-Naphthoquinone 1-oximato)lithium(I), 1/2 ethanol (4.0814 g) was heated at 110-120 °C/1.0 mm for 30 h. The green crystalline residue was *(1,2-naphthoquinone 1-oximato)lithium(I)* (3.5603 g, 98%) (Found: C, 66.9; H, 3.8; Li, 3.9; N, 7.5. $C_{10}H_6LiNO_2$ requires C, 66.1; H, 3.4; Li, 3.9; N, 7.8%). The distillate, collected in a flamed out trap cooled in a solid carbon dioxide/acetone bath was shown to be ethanol(i.r.).

6.6.3 *Reaction of 1,2-naphthoquinone 1-oxime with lithium hydroxide in ethanol in 2:1 molar ratio*

Solid 1,2-naphthoquinone 1-oxime (4.30 g, 25.0 mmol) was added portionwise and with stirring to a suspension of lithium hydroxide (0.30 g, 12.5 mmol) in ethanol (45 cm^3). The resultant mixture, was heated on a water bath at *ca.* 60 °C for 0.5 h and then filtered hot. The green filtrate on standing gave green crystalline *(1,2-naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I), ethanol* (2.27 g, 45%) (Found: C, 65.9; H, 5.0; Li, 1.8; N, 7.4. $C_{22}H_{19}LiN_2O_5$ requires C, 66.3; H, 4.8; Li, 1.7; N, 7.0%), which was filtered off, washed with ethanol (3 x 5 cm^3) and light petrol (b.p. 30-40 °C) (3 x 50 cm^3) and dried at 40 °C/1.0 mm.

(1,2-Naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I), ethanol (9.74 g, 68%) (Found: C, 65.9; H, 4.6; Li, 1.8; N, 6.8%), was also obtained and isolated as described above when a suspension of lithium hydroxide monohydrate (1.50 g, 36.0 mmol) in ethanol (120 cm^3) was added to a solution of 1,2-naphthoquinone 1-oxime (12.40 g, 72.0 mmol) in ethanol (200 cm^3) and the resultant mixture stirred for 0.5 h at *ca.* 60 °C.

6.6.4 Pyrolysis of (1,2-naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I), ethanol

(1,2-Naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I), ethanol (4.9929 g) was heated at 90-95 °C/1.0 mm for 20 h to give light green *(1,2-naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I)* (4.4020 g, 99%) (Found: C, 68.4; H, 4.0; Li, 1.9; N, 7.5. $C_{20}H_{13}LiN_2O_4$ requires C, 68.2; H, 3.4; Li, 2.0; N, 7.9%). The distillate collected in a previously flamed out trap cooled in a solid carbon dioxide/acetone bath was shown to be ethanol (i.r.).

6.6.5 *Reaction of 1,2-naphthoquinone 2-oxime with lithium hydroxide monohydrate in ethanol in 1:1 molar ratio*

A solution of 1,2-naphthoquinone 2-oxime (5.35 g, 31.0 mmol) in ethanol (125 cm^3) was added portionwise and with stirring to a suspension of lithium hydroxide monohydrate (1.30 g, 31.0 mmol) in ethanol (40 cm^3). The reaction mixture was heated on a water bath at *ca.* 65 °C for 0.5 h and then filtered hot. The brick/brown filtrate on standing gave no solid and was subsequently concentrated to dryness under nitrogen. The brick/brown solid thus obtained was washed with light petrol (b.p. 30-40 °C) (3 x 70 cm^3) and was then refluxed in toluene for 1.5 h. Filtration gave brown *(1,2-naphthoquinone 2-oximato)lithium(I), 1/2 ethanol* (6.52 g 93%) (Found: C, 64.8; H, 5.0; Li, 3.5; N, 6.2. $C_{22}H_{18}Li_2N_2O_5$ requires C, 65.4; H, 4.5; Li, 3.4; N, 6.9%), which was dried at 50 °C/1.0 mm.

6.6.6 *Pyrolysis of (1,2-naphthoquinone 2-oximato) lithium(I), 1/2 ethanol*

(1,2-Naphthoquinone 2-oximato)lithium(I), 1/2 ethanol (6.1440 g) was heated at 90-95 °C/1.0 mm for 22 h to give light brown *(1,2-naphthoquinone 2-oximato) lithium(I)* (5.3849 g, 99%) (Found: C, 66.8; H, 3.7; Li, 3.7; N, 7.6. $C_{10}H_6LiNO_2$ requires C, 67.1; H, 3.4; Li, 3.9; N, 7.8%). The distillate was shown to be ethanol (i.r.).

6.6.7 Reaction of 1,2-naphthoquinone 2-oxime with lithium hydroxide in ethanol in 2:1 molar ratio

1,2-Naphthoquinone 2-oxime (7.20 g, 42.0 mmol) in ethanol (150 cm^3) was added portionwise and with stirring to a suspension of lithium hydroxide (0.50 g, 21.0 mmol) in ethanol (40 cm^3). The reaction mixture was heated on a water bath at *ca*. 60 °C for 0.5 h and then filtered hot. The filtrate on standing gave no solid and was subsequently concentrated to dryness under nitrogen. The brown residue thus obtained was washed with light petrol (b.p. 30-40 °C) (3 x 70 cm^3), recrystallised from methanol and dried at 45 °C/1.0 mm to give light brown *(1,2-naphthoquinone 2-oxime)(1,2-naphthoquinone 2-oximato)lithium(I), ethanol* (6.50 g, 78%) (Found: C, 66.3; H, 4.2; Li, 1.8; N, 7.4. $C_{22}H_{19}LiN_2O_5$ requires C, 66.3; H, 4.8; Li, 1.7; N, 7.0%).

In another experiment, a suspension of lithium hydroxide monohydrate (1.50 g, 36.0 mmol) in ethanol (120 cm^3) was added with stirring to a solution of 1,2-naphthoquinone 2-oxime (12.40 g, 72.0 mmol) in ethanol (200 cm^3). The reaction mixture was heated on a water bath at *ca*. 60 °C for 0.5 h and then filtered hot. The filtrate on standing gave no solid and was subsequently concentrated to dryness under nitrogen. The brown residue thus obtained was washed with light petrol (b.p. 30-40 °C) (3 x 50 cm^3) and refluxed gently in distilled toluene for 1.5 h. Filtration of the mixture gave light brown (1,2-naphthoquinone 2-oxime) (1,2-naphthoquinone 2-oximato)lithium(I), ethanol (11.80 g, 83%)(Found: C, 66.1; H, 4.5; Li, 1.8; N, 7.5. $C_{22}H_{19}LiN_2O_5$ requires C, 66.3; H, 4.8; Li, 1.7; N, 7.0%), which was dried at 50 °C/1.0 mm.

6.6.8 *Pyrolysis of (1,2-naphthoquinone 2-oxime)(1,2-naphthoquinone 2-oximato)lithium(I), ethanol*

(1,2-Naphthoquinone 2-oxime) (1,2-naphthoquinone 2-oximato)lithium(I), ethanol (6.3449 g) was heated at 90-95 °C/1.0 mm for 54 h to give brown *(1,2-naphthoquinone 2-oxime) (1,2-naphthoquinone 2-oximato)lithium(I)* (5.5784 g, 99%) (Found: C, 68.0; H, 4.0; Li, 1.8; N, 7.6. $C_{20}H_{13}LiN_2O_4$ requires C, 68.2; H, 3.4; Li, 1.9; N, 7.9%).

6.6.9 *Reaction of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol with triphenylphosphine at 20 °C in 1:3 molar ratio*

(1,2-Naphthoquinone 1-oximato)lithium(I), 1/2 ethanol (1.00 g, 5.0 mmol) in acetone (55 cm^3) was added to a stirred solution of triphenylphosphine (3.89 g, 15.0 mmol) in acetone (25 cm^3). After 7 h a multicomponent mixture (*ca.* 10 components by t.l.c.) resulted. This mixture was not studied further.

6.6.10 Reaction of (1,2-naphthoquinone 2-oximato) lithium(I), 1/2 ethanol with triphenylphosphine at 20 °C in 1:3 molar ratio

(1,2-Naphthoquinone 2-oximato)lithium(I), 1/2 ethanol (1.00 g, 5.0 mmol) in acetone (50 cm^3) was added to a stirred solution of triphenylphosphine (3.89 g, 15.0 mmol) in acetone (25 cm^3). After 4 h a multicomponent mixture (*ca.* 15 components by t.l.c.) resulted. This mixture was not studied further.

6.6.11 Reaction of bis(1,2-naphthoquinone 1-oximato) copper(II) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) /water mixture or in anhydrous methanol

DMAD (2.79 g, 19.6 mmol) in EGDE (10 cm^3) was added to bis(1,2-naphthoquinone 1-oximato)copper(II) (2.00 g, 4.9 mmol) in 7:1 EGDE/water mixture (80 cm^3). The reaction mixture was heated under reflux for 3 h. After cooling, filtration gave paramagnetic crude brown *dihydrated complex of hydrolysed DMAD* (3) (0.63 g) (Found: C, 22.9; H, 1.2; Cu, 35.0; N, 1.7%) (confirmed by comparative i.r. with an authentic sample; *cf.* 6.6.12), which was washed with methanol and dried at

60 °C/1.0 mm. Removal of the solvent from the filtrate afforded a residue (multicomponent by t.l.c.) which was mixed with charcoal in EGDE (50 cm^3). The resultant mixture was heated under reflux for 1 h and filtered. Removal of the solvent from the filtrate gave a yellow/orange residue, which on washing with ice cold diethyl ether (2 x 2 cm^3) and recrystallisation from 1:1 hexane/ethyl acetate afforded yellow 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (1) (1.20 g, 77%), m.p. 153- 155 °C (lit.[3] 159-160 °C) (Found: C, 60.5; H, 4.2; N, 4.4. Calc. for $C_{16}H_{13}NO_6$: C, 60.9; H, 4.1; N, 4.4%); *m/z* 315 (M^+).

In another experiment, DMAD (2.79 g, 19.6 mmol) and bis(1,2-naphthoquinone 1-oximato)copper(II) (2.00 g, 4.9 mmol) were heated under reflux in anhydrous methanol (60 cm^3). Filtration of the mixture gave a brown paramagnetic solid (0.79 g) (Found: C, 46.5; H, 3.0; Cu, 22.3; N, 4.0%); ν_{max}(KBr) 3600-3400 (OH), 3040 (CH), 2980 (Me), 1720 (C=O), 1600 (C=C), 1435 (C-O) cm^{-1}; which was washed with methanol and dried at 45 °C /1.0 mm. 4-Hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (1) (0.84 g, 54%) (identified by comparative m.p., i.r. and ^1H n.m.r.) was obtained from the filtrate. A portion of the brown solid (0.29 g) was stirred with hydrochloric acid (20 cm^3) for 1 h and then the resultant mixture extracted with diethyl ether (3 x 30 cm^3). The combined extracts were washed with water, dried over magnesium sulphate and concentrated to dryness at 20 °C/14.0 mm. The residue was heated with charcoal in methanol (30 cm^3) for 1 h and the mixture filtered. Removal of the solvent from the filtrate gave a yellow/brown residue (0.07 g); $\nu_{max}(CHCl_3)$ 3600-3400 (OH), 3020 (CH), 2980 (Me), 1730 (C=O), 1660 (C=O), 1600 (C=C), 1440, 1405 (C-O) cm^{-1}; $\delta_H(CDCl_3)$ (200 MHz) 3.91 (s, $COC\underline{H}_3$), 5.35 (s, $NO\underline{H}$), 7.22-8.20 (m, aromatic).

6.6.12 Reaction of copper hydroxide with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture

DMAD (1.45 g, 10 mmol) was mixed with copper hydroxide (0.50 g, 5 mmol) in 5:1 EGDE/water (30 cm^3). The reaction mixture was heated under reflux for 10 h. Filtration gave pale green *dihydrated copper complex of hydrolysed DMAD* (3) (0.55 g, 51%) (Found: C, 21.8; H, 2.2; Cu, 30.8. $C_4H_4CuO_6$ requires C, 22.7; H, 1.9; Cu, 30.0%); $\nu_{max}(KBr)$ 3560-3320 (OH), 1690-1660 (C=O), 1430 (C-O) cm^{-1}; which was washed with water and methanol and dried at 60 °C/1.0 mm.

6.6.13 *Reaction of bis(1,2-naphthoquinone 2-oximato) copper(II) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE) /water mixture or in anhydrous methanol*

DMAD (2.79 g, 19.6 mmol) in EGDE (10 cm^3) was added to bis(1,2-naphthoquinone 2-oximato)copper(II) (2.00 g, 4.9 mmol) in 7:1 EGDE/water mixture (80 cm^3). The reaction mixture was heated under reflux for 3 h. After cooling, filtration gave paramagnetic crude brown *dihydrated copper complex of hydrolysed DMAD* (3) (0.60 g) (Found: C, 23.4; H, 1.1; Cu, 32.9; N, 1.8%) (confirmed by comparative i.r. with an authentic sample; *cf.* 6.6.12), which was washed with methanol and dried at 60 °C/1.0 mm. Removal of the solvent from the filtrate afforded a residue (multicomponent by t.l.c.) which was mixed with charcoal in EGDE (50 cm^3). The resultant mixture was heated under reflux for 1 h and filtered. Removal of the solvent from the filtrate gave a brownish/orange residue which was mixed with silica and chromatographed. Elution with toluene gave a dark yellow residue (trace). Subsequent elution with 8:2 toluene/ethyl acetate gave a brownish/yellow extract. Removal of the solvent from this extract afforded 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (2) (0.50 g, 32%), m.p. 156- 158 °C (lit.[3] 163-164 °C) (Found: C, 60.7; H, 4.1; N, 4.4. Calc. for $C_{16}H_{13}NO_6$: C, 60.9; H, 4.1; N, 4.4%); m/z 315 (M^+), which was washed with ice cold diethyl ether (2 x 2 cm^3) and dried at 30 ^{o}C/1.0 mm.

In another experiment, DMAD (2.79 g, 19.6 mmol) and bis(1,2-naphthoquinone 2-oximato)copper(II) (2.00 g, 4.9 mmol) were heated under reflux in anhydrous methanol (60 cm^3). Filtration of the mixture gave brown/purple paramagnetic *monohydrated copper complex of hydrolysed 1,4-oxazine* (4) (1.40 g) (Found: C, 52.3; H, 3.4; Cu, 10.0; N, 4.5. $C_{30}H_{22}CuN_2O_{13}$ requires C, 52.8; H, 3.2; Cu, 9.3; N, 4.1%); ν_{max}(KBr) 3400 (OH), 3020 (CH), 2980 (Me), 1735 (C=O), 1610 (C=C), 1440 (C-O) cm^{-1}; μ_{eff} 0.55 BM; which was washed with methanol and dried at 45 ^{o}C/1.0 mm. 4-Hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (2) (0.58 g, 38%) (identified by comparative m.p., i.r. and ^{1}H n.m.r.) was obtained from the filtrate. A portion of the brown/purple copper complex (0.30 g) was stirred with hydrochloric acid (20 cm^3) for 1 h and the resultant mixture extracted with diethyl ether (3 x 40 cm^3). The combined extracts were washed with water, dried over magnesium sulphate and concentrated to dryness at 20 ^{o}C/14.0 mm. The residue was heated with charcoal in methanol (30 cm^3) for 1 h and the mixture filtered. Removal of the solvent from the filtrate gave a light brown residue (0.06 g); ν_{max}($CHCl_3$) 3600-3400 (OH), 3020 (CH), 2980 (Me), 1740 (C=O), 1655 (C=O), 1600 (C=C), 1440, 1405 (C-O) cm^{-1}; δ_H($CDCl_3$) (200 MHz) 3.94 (3H, s, $COC\underline{H}_3$), 5.35 (1H, s, NO$\underline{H}$), 7.27-8.24 (6H, m, aromatic).

6.6.14 *Reaction of bis(1,2-naphthoquinone 2-oximato) copper(II) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/glacial acetic acid mixture*

DMAD (0.69 g, 4.8 mmol) in EGDE (10 cm^3) was added to glacial acetic acid (0.14 g, 2.3 mmol) and bis(1,2-naphthoquinone 2-oximato)copper(II) (0.50 g, 1.2 mmol) in EGDE (25 cm^3). The reaction mixture was heated under reflux for 3 h and filtered. The concentrated filtrate was extracted with diethyl ether (3 x 40 cm^3). The combined extracts were washed with water, dried over magnesium sulphate and concentrated to dryness at 20 °C/14.0 mm. The residue was then heated under reflux with charcoal in EGDE (50 cm^3) for 1 h and filtered. Removal of the solvent from the filtrate gave a brown sticky solid which on recrystallisation from 1:1 hexane/ethyl acetate afforded a yellow/brown solid. Preparative t.l.c. of this solid in chloroform gave the 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine 2 (0.08 g, 21%) (identified by m.p. and i.r.).

6.6.15 *Reaction of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture or in anhydrous methanol*

DMAD (2.20 g, 15.5 mmol) in EGDE (10 cm^3) was added to bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (1.50 g, 3.9 mmol) in 7:1 EGDE/water (40 cm^3). The reaction mixture was heated under reflux for 2 h and filtered. Removal of the solvent from the filtrate afforded a residue (multicomponent by t.l.c.) which was heated under reflux with charcoal in EGDE (50 cm^3) for 1.5 h and filtered. Concentration of the filtrate at 40 °C/14.0 mm gave an orange solid which on washing with ice cold diethyl ether (3 x 5 cm^3) and recrystallisation from 1:1 hexane/ethyl acetate afforded light yellow 6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (**8**) (0.94 g, 79%), m.p. 190-192 °C (lit.[3] 186-188 °C) (Found: C, 47.8; H, 3.8; N, 4.7. Calc. for $C_{12}H_{10}ClNO_6$: C, 48.1 H, 3.3; N, 4.7%); *m/z* 299 (M^+).

The 6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine **8** (50%) was also obtained by using anhydrous methanol as solvent.

6.6.16 *Action of heat on 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine* **(1)** *in methanol under aerobic conditions*

4-Hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (1) was recovered (*ca.* 95%) (identified by t.l.c., m.p., and i.r.) after heating under reflux in methanol.

6.6.17 *Action of 1,2-naphthoquinone 1-oxime on 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine* **(1)** *in methanol under aerobic conditions*

1,2-Naphthoquinone 1-oxime (0.06 g, 0.3 mmol) in methanol (25 cm^3) was added to 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine (1) (0.10 g, 0.3 mmol) in methanol (25 cm^3). The reaction mixture was heated under reflux for 24 h. T.l.c. indicated the presence of only the reactants in the mixture and no products.

6.6.18 *Aerobic oxidation of 1,4-oxazines in the presence of $Cu(qo)_2$ complexes*

The 1,4-oxazine 1 (0.50 g, 1.6 mmol) was heated under reflux in methanol (75 cm^3) in the presence of bis(1,2-naphthoquinone 1-oximato)copper(II) (0.03 g, 0.07 mmol) for 20 h, and the reaction mixture was then filtered. The filtrate was chromatographed on silica. Elution with toluene/ethyl acetate gave *methyl 1,3-oxazole-2-carboxylate* **(9)** (0.23 g, 63%), m.p. 145-146 °C (Found:

C, 68.8; H, 4.1; N, 6.1. $C_{13}H_9NO_3$ requires C, 68.7; H, 4.0; N, 6.2%); *m/z* 227 (M^+), which was washed with ice cold toluene (2 x 1 cm^3) and dried at 60 °C/1.0 mm.

The 1,4-benzoxazine **8** (0.50 g, 1.6 mmol) was heated under reflux in methanol (80 cm^3) in the presence of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) (0.03 g, 0.08 mmol) for 8 h, and the reaction mixture was then filtered. The filtrate was chromatographed on silica. Elution with 8:2 toluene/ethyl acetate gave an orange solid which upon crystallisation from hexane afforded methyl 5-chloro-1,3-benzoxazole-2-carboxylate (7) (0.14 g, 40%), m.p. 116-117 °C (lit.[4] 120-121 °C) (Found: C, 51.2; H, 2.9; N, 6.6. Calc. for $C_9H_6ClNO_3$: C, 51.1; H, 2.8; N, 6.6%); *m/z* 211 (M^+).

6.6.19 Reaction of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 20 °C in 1:2 molar ratio

DMAD (1.90 g, 13.4 mmol) in EGDE (10 cm^3) was stirred with (1,2-naphthoquinone 1-oximato)lithium(I), 1/2 ethanol (1.50 g, 7 mmol) in 7:1 EGDE/water mixture (50 cm^3). After 1 h filtration gave a white solid (0.07 g) (Found: Li, 12.0%) (alkaline) which was washed with EGDE and dried at 60 °C/1.0 mm. The filtrate was concentrated under nitrogen and the resultant viscous residue extracted with diethyl ether (4 x 30 cm^3) to leave a greenish/brown solid (L) as crude *hydrated lithium salt of hydrolysed addition product* (15) (1.70 g) (Found: C, 53.4; H, 3.9; Li, 2.3; N, 3.9%) (confirmed by comparative i.r. with an authentic sample; *cf.* 6.6.25), which was washed with EGDE and dried at 50 °C/1.0 mm. The combined diethyl ether extracts were dried over magnesium sulphate, concentrated and chromatographed on silica. Elution with 8:2 toluene/ethyl acetate gave an orange eluate. Removal of the solvent from this eluate gave a yellow/orange residue which on washing with ice cold diethyl ether (2 x 1 cm^3) and crystallisation from 1:1 hexane/ethyl acetate afforded yellow *addition product* (13/14) (0.90 g, 41%), m.p. 104-106 °C (Found: C, 60.6; H, 4.2; N, 4.3. $C_{16}H_{13}NO_6$ requires C, 60.9; H, 4.1; N, 4.4%); *m/z* 315 (M^+).

A portion of the greenish/brown solid (L) (0.60 g) was stirred with aqueous hydrochloric acid (20 cm^3, 2M) for 0.5 h and the resultant mixture extracted with diethyl ether (3 x 20 cm^3). The combined extracts were washed with water, dried over magnesium sulphate and concentrated to dryness at 20 °C/14.0 mm. The residue was heated with charcoal in methanol (20 cm^3) for 0.5 h and the mixture filtered. Removal of the solvent from the filtrate gave a yellowish/brown residue (0.10 g); $\nu_{max}(CHCl_3)$ 3600-3200 (OH), 3020 (CH), 2980 (Me), 1720 (C=O), 1640 (C=O), 1440 (C-O) cm^{-1}; $\delta_H(CDCl_3)$ (80 MHz)

3.78, 3.85 (3H, s, $COCH_3$), 6.40-8.75 (7H, m, vinylic/aromatic).

6.6.20 *Reaction of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 0 °C in 1:2 molar ratio*

DMAD (1.76 g, 12.4 mmol) in EGDE (10 cm^3) and 1,2-naphthoquinone 1-oximato)lithium(I), 1/2 ethanol (1.25 g, 6 mmol) in 7:1 EGDE/water (50 cm^3) were stirred at 0 °C for 2 h. Using the separation procedure described in 6.6.19, a white solid (0.04 g) (Found: Li, 11.6%) (alkaline), a greenish/brown solid (L) (1.24 g) (identified by comparative i.r. with an authentic sample; *cf.* 6.6.25) and a yellow addition product (**13/14**) (0.85 g, 44%) (identified by m.p. and i.r. with an authentic sample; *cf.* 6.6.19) were obtained.

6.6.21 *Reaction of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 50 °C in 1:2 molar ratio*

DMAD (2.80 g, 19.7 mmol) in EGDE (15 cm^3) and (1,2-naphthoquinone 1-oximato)lithium(I), 1/2 ethanol

(2.00 g, 9.9 mmol) in 7:1 EGDE/water (65 cm^3) were stirred at 50 °C for 0.25 h. Using the separation procedure described in 6.6.19, a white solid (0.20 g) (Found: Li, 11.9%) (alkaline), a greenish/brown solid (L) (1.75 g) (identified by comparative i.r. with an authentic sample; *cf.* 6.6.25) and a yellow addition product (**13/14**) (0.95 g, 30%) (identified by m.p. and i.r. with an authentic sample; *cf.* 6.6.19) were obtained.

6.6.22 Reaction of (1,2-naphthoquinone 1-oximato) lithium(I), 1/2 ethanol with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 20 °C in 1:4 molar ratio

DMAD (2.81 g, 19.8 mmol) in EGDE (10 cm^3) and (1,2-naphthoquinone 1-oximato)lithium(I), 1/2 ethanol (1.00 g, 5.0 mmol) in 7:1 EGDE/water mixture (40 cm^3) were stirred at 20 °C for 0.5 h. Using the separation procedure described in 6.6.19, a greenish/brown solid (L) (1.40 g) (Found: Li, 2.3%) (identified by comparative i.r. with an authentic sample; *cf.* 6.6.25) and a yellow addition product (**13/14**) (0.80 g, 51%), m.p. 104-106 °C (Found: C, 60.7; H, 4.1; N, 4.3. $C_{16}H_{13}NO_6$ requires C, 60.9; H, 4.1; N, 4.4%); *m/z* 315 (M^+), were obtained.

6.6.23 *Reaction of (1,2-naphthoquinone 1-oximato) lithium(I) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 20 °C in 1:4 molar ratio*

DMAD (1.02 g, 7.2 mmol) in EGDE (5 cm^3) and (1,2-naphthoquinone 1-oximato)lithium(I) (0.32 g, 1.8 mmol) in 7:1 EGDE/water mixture (30 cm^3) were stirred at 20 °C for 3/4 h. Using the separation procedure described in 6.6.19, a greenish/brown solid (L) (0.28 g) (identified by comparative i.r. with an authentic sample; *cf.* 6.6.25) and a yellow addition product (**13/14**) (0.30 g, 53%) (identified by m.p. and i.r. with an authentic sample; *cf.* 6.6.19, 6.6.22) were obtained.

6.6.24 *Reaction of (1,2-naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato)lithium(I) with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 20 °C in 1:4 molar ratio*

DMAD (1.96 g, 13.8 mmol) in EGDE (10 cm^3) and (1,2-naphthoquinone 1-oxime) (1,2-naphthoquinone 1-oximato) lithium(I) (1.22 g, 3.5 mmol) in 7:1 EGDE/water mixture (40 cm^3) were stirred at 20 °C for 0.5 h. Using the separation procedure described in 6.6.19, a greenish/ brown solid (L) (1.04 g) (Found: Li, 2.1%) (identified by comparative i.r. with an authentic sample; *cf.* 6.6.25) and a yellow addition product (13/14) (0.55 g, 51%), m.p. 104-105 °C (Found: C, 60.5; H, 4.3; N, 4.2. $C_{16}H_{13}NO_6$ requires C, 60.9; H, 4.1; N, 4.4%), were obtained.

6.6.25 *Reaction of lithium hydroxide monohydrate with the addition product (13/14) in ethylene glycol dimethyl ether (EGDE)/water mixture*

A mixture of the addition product (13/14) (0.15 g, 0.5 mmol) in EGDE (15 cm^3) and lithium hydroxide monohydrate (0.02 g, 0.5 mmol) in water (1 cm^3) were stirred at 20 °C for 2 h. Removal of the solvent at 40 °C/14.0 mm gave light brown *monohydrated lithium salt of hydrolysed addition product* (15) (0.13 g, 87%) (Found: C, 54.6; H, 3.9; Li, 2.2; N, 3.9. $C_{15}H_{12}LiNO_7$ requires C, 55.4; H, 3.7; Li, 2.1; N, 4.3%); ν_{max}(KBr) 3480-3340 (OH), 3040 (CH), 2980 (Me), 1720 (C=O), 1660 (C=O), 1580 (C=C), 1435 (C-0) cm^{-1}; $\delta_H[(CD_3)_2SO]$ (80 MHz) 3.49, 3.62 (3H, s, $COC\underline{H}_3$), 6.27-8.14 (7H, m, vinylic/ aromatic); which was washed with ice cold water (2 x 1 cm^3) and diethyl ether (4 x 5 cm^3) and dried at 30 °C/1.0 mm.

6.6.26 *Reaction of lithium hydroxide monohydrate with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture*

DMAD (0.68 g, 4.8 mmol) in EGDE (10 cm^3) and lithium hydroxide monohydrate (0.20 g, 4.8 mmol) in water (2 cm^3) were stirred at 20 $^\circ$C for 2 h. Removal of the solvent at 40 $^\circ$C/14.0 mm gave yellowish/white crystals of *monohydrated lithium methylacetylene dicarboxylate* (0.48 g, 67%) (Found: C, 38.6; H, 3.6; Li, 5.0. $C_5H_5LiO_5$ requires C, 39.5; H, 3.3; Li, 4.6%); ν_{max}(KBr) 3480-3340 (OH), 2980 (Me), 1640-1610 (C=O), 1380-1340 (C-O) cm^{-1}; $\delta_H(D_2O)$ (80 MHz) 3.85 (3H, s, COC$\underline{H}_3$); which was washed with ice cold water (2 x 1 cm^3) and diethyl ether (4 x 5 cm^3) and dried at 30 $^\circ$C/1.0 mm.

6.6.27 *Reaction of lithium hydroxide monohydrate with the 4-hydroxy-2,3-dimethoxycarbonyl-1,4-oxazine* 1 *inethylene glycol dimethyl ether (EGDE)/water mixture*

The 1,4-oxazine 1 (1.01 g, 3.2 mmol) in EGDE (20 cm^3) and lithium hydroxide monohydrate (0.13 g, 3.1 mmol) in water (5 cm^3) were stirred at 20 $^\circ$C for 3 h. Removal of the solvent at 40 $^\circ$C/14.0 mm gave pale yellow *monohydrated dilithium salt of hydrolysed 1,4-oxazine* (0.83, 81%) (Found: C, 54.8; H, 3.8; Li, 4.2; N, 3.9. $C_{15}H_{11}Li_2NO_7$ requires C, 54.4; H, 3.3; Li, 4.2; N, 4.2%); ν_{max}(KBr) 3460-3360 (OH), 3040 (CH), 2980 (Me), 1740 (C=O), 1660-1640 (C=O), 1430-1400 (C-O) cm^{-1}; $\delta_H[(CD_3)_2SO]$ (80 MHz) 3.94 (3H, s, $COC\underline{H}_3$), 7.06-8.55 (6H, m, aromatic).

6.6.28 *Reaction of (1,2-naphthoquinone 2-oximato) lithium(I), 1/2 ethanol with dimethylacetylene dicarboxylate (DMAD) in ethylene glycol dimethyl ether (EGDE)/water mixture at 20 °C in 1:2 and 1:4 molar ratio*

i) 1:2 molar ratio

DMAD (2.10 g, 14.8 mmol) in EGDE (10 cm^3) and (1,2-naphthoquinone 2-oximato)lithium(I), 1/2 ethanol (1.50 g, 7.4 mmol) in 7:1 EGDE/water (40 cm^3) were stirred at 20 °C. After 0.5 h, filtration gave a white solid (0.12 g) (Found: Li, 9.1%) (alkaline) which was washed with EGDE and dried at 50 °C/1.0 mm. The filtrate was concentrated under nitrogen and the resultant residue extracted with diethyl ether (4 x 40 cm^3) to leave a dark brown solid (0.95 g) (Found: Li, 2.0%); ν_{max}(KBr) 3500-3480 (OH), 3040 (CH), 2980 (Me), 1720 (C=O), 1670-1600 (C=O, C=C), 1440 (C-O) cm^{-1}; which was washed with EGDE and dried at 50 °C/1.0 mm. The combined diethyl ether extracts were dried over magnesium sulphate, concentrated and chromatographed on silica. Elution with toluene/ethyl acetate mixtures gave an orange/brown extract which was heated with charcoal in methanol (30 cm^3) for 1 h and filtered. Removal of the solvent from the filtrate gave a dark orange residue (multicomponent by t.l.c.) which was subjected to preparative t.l.c. Development of the t.l.c. plates in chloroform gave the 1,4-oxazine **2** (0.29 g, 13%) (identified by m.p., i.r., ^1H n.m.r. and m.s. with an authentic sample; cf. 6.6.13) and the *addition product* **18** (0.13 g, 5%); $\nu_{max}(CCl_4)$ 2980 (Me), 1725 (C=O), 1690, 1660 (C=O), 1600 (C=C), 1430 (C-O) cm^{-1}; $\delta_H(CDCl_3)$ (200 MHz) 3.76, 3.80, 3.88, 3.89 (6H, s, $COC\underline{H}_3$), 6.40-8.20 (7H, m, vinylic/aromatic); *m/z* 315 (M^+)

ii) 1:4 molar ratio

DMAD (4.20 g, 29.6 mmol) in EGDE (15 cm^3) and (1,2-naphthoquinone 2-oximato)lithium(I), 1/2 ethanol (1.50 g, 7.4 mmol) in 7:1 EGDE/water (40 cm^3) were stirred at 20 °C for 0.5 h. Using the separation procedure described for the 1:2 molar ratio (*vide supra*), a white solid (0.13 g) (Found: Li, 9.0%) (alkaline), a brown solid (1.65 g) (Found: Li, 2.2%) (same i.r. to that recovered from the 1:2 molar ratio), the 1,4-oxazine **2** (0.35 g, 15%) (identified by m.p. and i.r. with an authentic sample; *cf.* 6.6.13), and the addition product **18** (*vide supra*) (0.15 g, 6%) were obtained.

6.7 References

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APPENDICES

APPENDIX 1

INDIUM COMPLEXES DERIVED FROM THE MONO-OXIMES OF 1,2-NAPHTHOQUINONE

One of the proposed aims of this work, was the synthesis and study of indium naphthoquinoneoximato complexes and the evaluation of their use in liquid scintillation counting.

Synthesis of the complexes was achieved by using the direct reaction of indium trichloride with the potassium complexes of 1,2-naphthoquinone mono-oximes in water. However, the products obtained were highly insoluble species, which probably contained hydroxy or oxo bridges. Attempts to obtain complexes of type InL_3 (LH = 1,2-naphthoquinone 1-oxime, 1,2-naphthoquinone 2-oxime) by using acetonitrile as solvent were also unsuccessful.

In view of the nature and insolubility of these compounds, their application in liquid scintillation counting and further chemical characterisation was not attempted.

APPENDIX 2

DETAILS OF THE CRYSTAL STRUCTURE OF Li(1-nqo)(1-nqoH).EtOH

Table 1 Fractional atomic coordinates and thermal parameters (Å^2) for Li(1-nqo)(1-nqoH).EtOH

Atom	x	y	z	U_{iso} or U_{eq}
N(1a)	0.3848(5)	0.2005(7)	0.3142(14)	0.045(7)
O(1a)	0.4093(4)	0.2815(6)	0.3704(12)	0.051(6)
O(2a)	0.3232(5)	0.0476(5)	0.2021(13)	0.059(6)
N(1b)	0.2478(6)	0.2978(7)	0.3746(15)	0.048(7)
O(1b)	0.2934(5)	0.3646(7)	0.4292(16)	0.052(7)
O(2b)	0.1714(4)	0.1598(6)	0.2666(14)	0.063(6)
O(1e)	0.2625(5)	0.0983(6)	0.5854(14)	0.061(7)
Li	0.2751(11)	0.1511(14)	0.3479(30)	0.047(6)
C(1a)	0.4278(6)	0.1403(8)	0.2297(19)	0.036(3)
C(2a)	0.3892(7)	0.0548(8)	0.1806(18)	0.040(3)
C(3a)	0.4306(7)	-0.0203(10)	0.0929(20)	0.051(4)
C(4a)	0.5005(8)	-0.0125(11)	0.0667(22)	0.059(5)
C(5a)	0.6111(7)	0.0745(9)	0.0813(19)	0.046(4)
C(6a)	0.6505(8)	0.1561(10)	0.1205(21)	0.053(4)
C(7a)	0.6163(7)	0.2343(10)	0.1857(20)	0.053(4)
C(8a)	0.5447(7)	0.2303(9)	0.2261(18)	0.041(4)
C(9a)	0.5027(6)	0.1495(9)	0.1945(18)	0.044(4)
C(10a)	0.5377(6)	0.0725(8)	0.1171(17)	0.041(3)
C(1b)	0.1821(7)	0.3197(8)	0.3651(18)	0.043(3)
C(2b)	0.14C7(7)	0.2351(10)	0.2992(20)	0.046(4)

Table 1 (continued)

C(3b)	0.0644(7)	0.2481(11)	0.2812(21)	0.055(4)
C(4b)	0.0342(8)	0.3289(10)	0.3204(21)	0.065(5)
C(5b)	0.0352(8)	0.4972(11)	0.4130(19)	0.059(4)
C(6b)	0.0695(9)	0.5746(12)	0.4675(23)	0.065(5)
C(7b)	0.1421(8)	0.5740(12)	0.4990(23)	0.068(5)
C(8b)	0.1792(8)	0.4914(10)	0.4614(20)	0.056(4)
C(9b)	0.1453(6)	0.4083(9)	0.4041(19)	0.042(3)
C(10b)	0.0708(7)	0.4133(10)	0.3781(21)	0.062(4)
C(1e)	0.3263(12)	0.1881(14)	0.8096(32)	0.093(7)
C(2e)	0.3134(10)	0.0967(13)	0.7220(28)	0.080(5)

Table 2 Fractional atomic coordinates for the hydrogen atoms for Li(1-nqo)(1-nqoH).EtOH

Atom	x	y	z	
H(3a)	0.402(5)	-0.081(8)	0.082(16)	0.04(4)
H(4a)	0.532(7)	-0.058(11)	0.012(21)	0.11(6)
H(5a)	0.644(6)	0.021(9)	-0.000(18)	0.07(5)
H(6a)	0.700(7)	0.145(9)	0.073(20)	0.13(6)
H(7a)	0.642(6)	0.303(10)	0.246(19)	0.11(5)
H(8a)	0.518(5)	0.289(8)	0.261(17)	0.05(4)
H(3b)	0.038(5)	0.183(8)	0.270(15)	0.04(4)
H(4b)	-0.021(6)	0.323(7)	0.306(15)	0.06(4)
H(5b)	-0.017(7)	0.474(10)	0.396(19)	0.08(6)
H(6b)	0.045(6)	0.627(9)	0.493(16)	0.03(4)
H(7b)	0.172(8)	0.627(10)	0.544(20)	0.12(6)
H(8b)	0.231(4)	0.487(6)	0.510(12)	0.02(3)
H(10b)	0.336(8)	0.358(12)	0.465(23)	0.20(8)
H(1e1)	0.269(7)	0.202(8)	0.867(17)	0.08(4)
H(1e2)	0.336(6)	0.234(9)	0.715(19)	0.06(5)
H(1e3)	0.379(9)	0.188(12)	0.904(26)	0.22(8)
H(2e1)	0.292(7)	0.045(11)	0.830(22)	0.18(7)
H(2e2)	0.356(5)	0.074(8)	0.654(15)	0.04(4)
H(10e)	0.224(7)	0.048(11)	0.612(23)	0.12(6)

Table 3 Anisotropic thermal parameters (Å^2) for Li(1-nqo)(1-nqoH).EtOH

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1a)	0.056(7)	0.035(6)	0.043(7)	0.001(6)	-0.002(6)	-0.003(6)
O(1a)	0.048(5)	0.041(5)	0.063(7)	-0.015(5)	0.005(5)	-0.014(4)
O(2a)	0.058(5)	0.041(5)	0.079(7)	-0.019(6)	0.011(6)	-0.012(5)
N(1b)	0.049(7)	0.037(6)	0.059(8)	0.004(6)	-0.004(7)	-0.009(6)
O(1b)	0.038(6)	0.042(6)	0.077(8)	-0.012(6)	0.002(6)	-0.006(5)
O(2b)	0.055(5)	0.050(5)	0.084(8)	0.001(6)	-0.012(6)	-0.005(5)
O(1e)	0.044(6)	0.065(7)	0.075(9)	0.035(6)	-0.020(6)	-0.030(5)

Table 4 Bond lengths (Å) for Li(1-nqo)(1-nqoH).EtOH

Li	-N(1a)	2.198(23)	Li	-O(2a)	2.033(22)
Li	-N(1b)	2.150(22)	Li	-O(2b)	2.046(22)
Li	-O(1e)	1.923(24)	C(1a)	-N(1a)	1.332(16)
C(1a)	-C(2a)	1.459(17)	C(1a)	-C(9a)	1.441(16)
N(1a)	-O(1a)	1.305(13)	C(2a)	-O(2a)	1.256(16)
C(2a)	-C(3a)	1.470(18)	C(3a)	-C(4a)	1.335(20)
C(4a)	-C(10a)	1.443(20)	C(5a)	-C(6a)	1.404(19)
C(5a)	-C(10a)	1.407(18)	C(6a)	-C(7a)	1.371(20)
C(7a)	-C(8a)	1.383(19)	C(8a)	-C(9a)	1.411(18)
C(9a)	-C(10a)	1.397(17)	C(1b)	-N(1b)	1.277(17)
C(1b)	-C(2b)	1.511(18)	C(1b)	-C(9b)	1.462(17)
N(1b)	-O(1b)	1.340(15)	C(2b)	-O(2b)	1.237(16)
C(2b)	-C(3b)	1.456(19)	C(3b)	-C(4b)	1.311(21)
C(4b)	-C(10b)	1.444(21)	C(5b)	-C(6b)	1.335(23)
C(5b)	-C(10b)	1.389(21)	C(6b)	-C(7b)	1.388(23)
C(7b)	-C(8b)	1.391(22)	C(8b)	-C(9b)	1.406(19)
C(9b)	-C(10b)	1.420(18)	C(1e)	-C(2e)	1.47(3)
C(2e)	-O(1e)	1.392(22)			

Table 4 (continued)

C(3a) -H(3a)	1.03(9)	C(4a) -H(4a)	.96(9)
C(5a) -H(5a)	1.14(9)	C(6a) -H(6a)	1.02(9)
C(7a) -H(7a)	1.17(9)	C(8a) -H(8a)	1.00(9)
O(1b) -H(1ob)	.84(9)	C(3b) -H(3b)	1.05(9)
C(4b) -H(4b)	1.04(9)	C(5b) -H(5b)	1.05(9)
C(6b) -H(6b)	.89(9)	C(7b) -H(7b)	.99(9)
C(8b) -H(8b)	1.05(8)	C(1e) -H(1e1)	1.18(9)
C(1e) -H(1e2)	.97(9)	C(1e) -H(1e3)	1.21(9)
C(2e) -H(2e1)	1.16(9)	C(2e) -H(2e2)	.99(9)
O(1e) -H(1oe)	1.04(9)		

Table 5 Bond angles (°) for Li(1-nqo)(1-nqoH).EtOH

O(2a)-Li-N(1a)	75.5(8)	N(1b)-Li-N(1a)	85.8(8)
N(1b)-Li-O(2a)	148(1)	O(2b)-Li-N(1a)	148(1)
O(2b)-Li-O(2a)	108(1)	O(2b)-Li-N(1b)	75.0(8)
O(1e)-Li-N(1a)	110(1)	O(1e)-Li-O(2a)	105(1)
O(1e)-Li-N(1b)	105(1)	O(1e)-Li-O(2b)	100(1)
C(2a)-C(1a)-N(1a)	110(1)	C(9a)-C(1a)-N(1a)	128(1)
C(9a)-C(1a)-C(2a)	121(1)	C(1a)-N(1a)-Li	114.9(9)
O(1a)-N(1a)-Li	125.3(9)	O(1a)-N(1a)-C(1a)	120(1)
O(2a)-C(2a)-C(1a)	122(1)	C(3a)-C(2a)-C(1a)	116(1)
C(3a)-C(2a)-O(2a)	121(1)	C(2a)-O(2a)-Li	117(1)
C(4a)-C(3a)-C(2a)	122(1)	C(10a)-C(4a)-C(3a)	121(1)
C(10a)-C(5a)-C(6a)	120(1)	C(7a)-C(6a)-C(5a)	119(1)
C(8a)-C(7a)-C(6a)	120(1)	C(9a)-C(8a)-C(7a)	123(1)
C(8a)-C(9a)-C(1a)	126(1)	C(10a)-C(9a)-C(1a)	118(1)
C(10a)-C(9a)-C(8a)	116(1)	C(5a)-C(10a)-C(4a)	116(1)
C(9a)-C(10a)-C(4a)	122(1)	C(9a)-C(10a)-C(5a)	122(1)
C(2b)-C(1b)-N(1b)	109(1)	C(9b)-C(1b)-N(1b)	131(1)
C(9b)-C(1b)-C(2b)	120(1)	C(1b)-N(1b)-Li	117(1)
O(1b)-N(1b)-Li	124(1)	O(1b)-N(1b)-C(1b)	118(1)
O(2b)-C(2b)-C(1b)	120(1)	C(3b)-C(2b)-C(1b)	116(1)
C(3b)-C(2b)-O(2b)	124(1)	C(2b)-O(2b)-Li	116(1)
C(4b)-C(3b)-C(2b)	121(1)	C(10b)-C(4b)-C(3b)	126(1)
C(10b)-C(5b)-C(6b)	122(1)	C(7b)-C(6b)-C(5b)	121(2)
C(8b)-C(7b)-C(6b)	118(1)	C(9b)-C(8b)-C(7b)	122(1)
C(8b)-C(9b)-C(1b)	124(1)	C(10b)-C(9b)-C(1b)	119(1)

Table 5 (continued)

C(10b)-C(9b) -C(8b)	117(1)	C(5b) -C(10b)-C(4b)	122(1)
C(9b) -C(10b)-C(4b)	118(1)	C(9b) -C(10b)-C(5b)	120(1)
O(1e) -C(2e) -C(1e)	115(2)	C(2e) -O(1e) -Li	126(1)
H(3a) -C(3a) -C(2a)	111(6)	H(3a) -C(3a) -C(4a)	125(6)
H(4a) -C(4a) -C(3a)	127(9)	H(4a) -C(4a) -C(10a)	112(9)
H(5a) -C(5a) -C(6a)	111(6)	H(5a) -C(5a) -C(10a)	128(6)
H(6a) -C(6a) -C(5a)	107(8)	H(6a) -C(6a) -C(7a)	133(8)
H(7a) -C(7a) -C(6a)	127(6)	H(7a) -C(7a) -C(8a)	111(6)
H(8a) -C(8a) -C(7a)	120(6)	H(8a) -C(8a) -C(9a)	116(6)
H(10b)-O(1b) -N(1b)	129(2)	H(3b) -C(3b) -C(2b)	111(6)
H(3b) -C(3b) -C(4b)	126(6)	H(4b) -C(4b) -C(3b)	110(6)
H(4b) -C(4b) -C(10b)	125(6)	H(5b) -C(5b) -C(6b)	139(8)
H(5b) -C(5b) -C(10b)	99(8)	H(6b) -C(6b) -C(5b)	120(7)
H(6b) -C(6b) -C(7b)	118(7)	H(7b) -C(7b) -C(6b)	128(9)
H(7b) -C(7b) -C(8b)	114(9)	H(8b) -C(8b) -C(7b)	117(5)
H(8b) -C(8b) -C(9b)	118(5)	H(1e1)-C(1e) -C(2e)	99(6)
H(1e2)-C(1e) -C(2e)	107(8)	H(1e2)-C(1e) -H(1e1)	109(9)
H(1e3)-C(1e) -C(2e)	113(8)	H(1e3)-C(1e) -H(1e1)	122.8(9)
H(1e3)-C(1e) -H(1e2)	105(1)	H(2e1)-C(2e) -C(1e)	108(8)
H(2e1)-C(2e) -O(1e)	106(7)	H(2e2)-C(2e) -C(1e)	112(6)
H(2e2)-C(2e) -O(1e)	101(6)	H(2e2)-C(2e) -H(2e1)	115(9)
H(10e)-O(1e) -Li	121(9)	H(10e)-O(1e) -C(2e)	110(9)

Table 6 Intermolecular distances (Å) for

Li(1-nqo)(1-nqoH).EtOH

Atom1	Atom2	dist	S	a	b	c
H(1e1)	...Li	3.63	1	0.0	0.0	1.0
C(2e)	...Li	4.00	2	0.0	0.0	0.0
O(1e)	...Li	4.09	2	0.0	0.0	0.0
H(2e1)	...Li	3.05	2	0.0	0.0	0.0
H(10e)	...Li	3.32	2	0.0	0.0	0.0
H(1e3)	...C(1a)	2.66	1	0.0	0.0	1.0
C(4a)	...O(1a)	3.41	4	1.0	-1.0	0.0
H(4a)	...O(1a)	2.68	4	1.0	-1.0	0.0
H(1e3)	...C(2a)	2.79	1	0.0	0.0	1.0
H(10e)	...C(2a)	2.63	2	0.0	0.0	0.0
H(2e1)	...O(2a)	2.81	1	0.0	0.0	1.0
C(2e)	...O(2a)	3.29	2	0.0	0.0	0.0
O(1e)	...O(2a)	2.76	2	0.0	0.0	0.0
H(2e1)	...O(2a)	2.71	2	0.0	0.0	0.0
H(10e)	...O(2a)	1.75	2	0.0	0.0	0.0
H(10e)	...C(3a)	2.93	2	0.0	0.0	0.0
H(8a)	...C(3a)	3.07	4	1.0	0.0	0.0
C(10b)	...C(5a)	3.48	3	-1.0	0.0	0.0
C(2b)	...C(6a)	3.47	3	-1.0	0.0	0.0
H(1e1)	...C(6a)	3.01	3	-1.0	0.0	1.0
H(1e1)	...C(7a)	3.04	3	-1.0	0.0	1.0
C(4b)	...C(8a)	3.46	3	-1.0	0.0	1.0
H(7b)	...O(1b)	2.92	2	0.0	1.0	0.0
H(5a)	...O(1b)	2.57	4	1.0	-1.0	0.0
H(3a)	...O(2b)	2.93	2	0.0	0.0	-1.0
H(4b)	...C(1e)	3.01	3	-1.0	0.0	1.0
H(2e1)	...O(1e)	2.95	2	0.0	0.0	0.0
H(7a)	...O(1e)	2.94	3	0.0	0.0	1.0

Table 7 Intramolecular distances (Å) for Li(1-nqo)(1-nqoH).EtOH

C(1a) ...Li	3.01	O(1a) ...Li	3.14
C(2a) ...Li	2.83	C(3a) ...Li	4.25
C(1b) ...Li	2.97	O(1b) ...Li	3.10
C(2b) ...Li	2.82	C(3b) ...Li	4.23
C(1e) ...Li	3.58	C(2e) ...Li	2.96
H(10b)...Li	3.27	H(1e2)...Li	3.17
H(2e2)...Li	2.93	H(10e)...Li	2.62
O(1a) ...C(1a)	2.28	O(2a) ...C(1a)	2.38
C(3a) ...C(1a)	2.49	C(4a) ...C(1a)	2.83
C(8a) ...C(1a)	2.54	C(10a)...C(1a)	2.43
H(8a) ...C(1a)	2.72	C(2a) ...N(1a)	2.29
O(2a) ...N(1a)	2.59	C(8a) ...N(1a)	3.11
C(9a) ...N(1a)	2.50	N(1b) ...N(1a)	2.96
O(1b) ...N(1a)	3.01	H(8a) ...N(1a)	2.83
H(10b)...N(1a)	2.67	C(8a) ...O(1a)	2.86
C(9a) ...O(1a)	2.86	N(1b) ...O(1a)	3.05
O(1b) ...O(1a)	2.52	H(8a) ...O(1a)	2.21
H(10b)...O(1a)	1.90	H(1e2)...O(1a)	2.97
C(4a) ...C(2a)	2.45	C(9a) ...C(2a)	2.53
C(10a)...C(2a)	2.85	H(3a) ...C(2a)	2.08
C(3a) ...O(2a)	2.38	O(2b) ...O(2a)	3.31
O(1e) ...O(2a)	3.14	H(3a) ...O(2a)	2.51
C(9a) ...C(3a)	2.86	C(10a)...C(3a)	2.42
H(4a) ...C(3a)	2.06	C(5a) ...C(4a)	2.42
C(9a) ...C(4a)	2.48	H(3a) ...C(4a)	2.10

Table 7 (continued)

H(5a) ...C(4a)	2.79	C(7a) ...C(5a)	2.40
C(8a) ...C(5a)	2.75	C(9a) ...C(5a)	2.45
H(4a) ...C(5a)	2.45	H(6a) ...C(5a)	1.95
C(8a) ...C(6a)	2.39	C(9a) ...C(6a)	2.84
C(10a)...C(6a)	2.43	H(5a) ...C(6a)	2.11
H(7a) ...C(6a)	2.28	C(9a) ...C(7a)	2.46
C(10a)...C(7a)	2.78	H(6a) ...C(7a)	2.20
H(8a) ...C(7a)	2.08	C(10a)...C(8a)	2.38
H(7a) ...C(8a)	2.11	H(8a) ...C(9a)	2.05
H(4a) ...C(10a)	2.00	H(5a) ...C(10a)	2.30
O(1b) ...C(1b)	2.24	O(2b) ...C(1b)	2.39
C(3b) ...C(1b)	2.52	C(4b) ...C(1b)	2.81
C(8b) ...C(1b)	2.54	C(10b)...C(1b)	2.48
H(8b) ...C(1b)	2.76	H(10b)...C(1b)	3.03
C(2b) ...N(1b)	2.27	O(2b) ...N(1b)	2.56
C(8b) ...N(1b)	3.10	C(9b) ...N(1b)	2.50
O(1e) ...N(1b)	3.24	H(8b) ...N(1b)	2.88
H(10b)...N(1b)	1.98	C(8b) ...O(1b)	2.81
C(9b) ...O(1b)	2.86	H(8b) ...O(1b)	2.17
H(1e2)...O(1b)	2.92	C(4b) ...C(2b)	2.41
C(9b) ...C(2b)	2.57	C(10b)...C(2b)	2.91
H(3b) ...C(2b)	2.08	C(3b) ...O(2b)	2.38
O(1e) ...O(2b)	3.04	H(3b) ...O(2b)	2.53
C(9b) ...C(3b)	2.88	C(10b)...C(3b)	2.45
H(4b) ...C(3b)	1.93	C(5b) ...C(4b)	2.48
C(9b) ...C(4b)	2.46	H(3b) ...C(4b)	2.10
H(5b) ...C(4b)	2.33	C(7b) ...C(5b)	2.38
C(8b) ...C(5b)	2.74	C(9b) ...C(5b)	2.43

Table 7 (continued)

H(4b) ...C(5b)	2.80	H(6b) ...C(5b)	1.94
C(8b) ...C(6b)	2.38	C(9b) ...C(6b)	2.80
C(10b)...C(6b)	2.38	H(5b) ...C(6b)	2.23
H(7b) ...C(6b)	2.15	C(9b) ...C(7b)	2.45
C(10b)...C(7b)	2.79	H(6b) ...C(7b)	1.97
H(8b) ...C(7b)	2.09	C(10b)...C(8b)	2.40
H(7b) ...C(8b)	2.01	H(8b) ...C(9b)	2.12
H(4b) ...C(10b)	2.21	H(5b) ...C(10b)	1.87
O(1e) ...C(1e)	2.41	H(2e1)...C(1e)	2.14
H(2e2)...C(1e)	2.06	H(1e1)...C(2e)	2.02
H(1e2)...C(2e)	1.99	H(1e3)...C(2e)	2.24
H(10e)...C(2e)	2.00	H(1e1)...O(1e)	2.55
H(1e2)...O(1e)	2.55	H(2e1)...O(1e)	2.04
H(2e2)...O(1e)	1.86		

APPENDIX 3

LITHIUM COMPLEXES DERIVED FROM CARBOXYLIC AND DITHIOCARBAMIC ACIDS

Lithium complexes derived from carboxylic acids

Lithium complexes of carboxylic acids were prepared by a standard method, involving the reaction of the acid and lithium ethoxide in absolute ethanol. The crude products were recrystallised from ethanol except in the case of the 5-methyl and 5-chloro lithium salicylato derivatives, which were recrystallised from a 1:10 and 1:1 methanol/toluene mixture respectively. The elemental analysis results are given in Table 1.

Reaction of benzylamine with lithium chloride and carbon disulphide in carbon tetrachloride

Carbon disulphide (1.76 g, 23.0 mmol) in carbon tetrachloride (5 cm^3) was added to lithium chloride (0.50 g, 12.0 mmol) and benzylamine (2.55 g, 24.0 mmol) in carbon tetrachloride (20 cm^3) was added subsequently with stirring. The reaction mixture was heated under reflux for 4 h. After cooling, filtration afforded a white solid, which was washed with ice cold water and ice cold ethanol, and dried at 70 °C/1.0 mm to give *(benzylamine dithiocarbamic acid) (benzylamine dithiocarbamato)lithium(I)* (3.32 g, 75%)

(Found: C, 51.9; H, 4.8; Li, 1.8; N, 7.0. $C_{16}H_{17}LiN_2S_4$ requires C, 51.6; H, 4.6; Li, 1.9; N, 7.5%).

Reaction of morpholine with lithium chloride and carbon disulphide in carbon tetrachloride

Carbon disulphide (1.79 g, 23.0 mmol) in carbon tetrachloride (5 cm^3) was added to lithium chloride (0.50 g, 12.0 mmol) and morpholine (2.05 g, 23.0 mmol) carbon tetrachloride (10 cm^3) was added subsequently with stirring. The reaction mixture was heated under reflux for 4 h. After cooling, filtration afforded a white solid, which was washed with ice cold water and ice cold ethanol, and dried at 75 °C/1.0 mm to give *(morpholine dithiocarbamic acid) (morpholine dithiocarbamato)lithium(I)* (2.80 g, 73%) (Found: C, 36.5; H, 3.0; Li, 1.9; N, 8.1. $C_{10}H_9LiN_2S_4O_2$ requires C, 37.0; H, 2.8; Li, 2.1; N, 8.4%).

Table 1 Analytical results for lithium complexes derived from carboxylic acids

Lithium complex	Found (%)				Calculated (%)			
	C	H	Li	N	C	H	Li	N
Li(glyco)	29.3	3.7	8.4	-	29.3	3.7	8.4	-
Li(prol)(prolH)	52.7	2.9	3.0	11.9	53.1	3.1	3.1	12.4
Li(sal)(salH)	59.3	3.8	2.6	-	59.6	3.9	2.5	-
Li(5-Cl-sal)	46.9	2.8	3.7	-	46.8	2.8	3.9	-
Li(5-Me-sal)	60.7	4.5	4.2	-	60.8	4.4	4.4	-
Li(deca)	67.1	10.8	3.4	-	67.4	10.8	3.8	-

glycoH = glycolic acid
prolH = L-proline
salH = salicylic acid
5-Cl-salH = 5-chloro-salicylic acid
5-Me-salH = 5-methyl-salicylic acid
decaH = decanoic acid

TITLE Lithium and Indium Quinoneoximic Complexes And their Application In Scintillation Counting

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