University of Southampton

STUDIES IN THE COORDINATION CHEMISTRY OF SOME GROUP VB AND VIB LIGANDS

A Thesis Submitted for
the degree of
Doctor of Philosophy

by

Helen Evelyn Tuttlebee

May 1981

In the beginning God created the heavens
and the earth .....

Genesis 1,1.

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Doctor of Philosophy

STUDIES IN THE COORDINATION CHEMISTRY OF SOME GROUP VB AND VIB LIGANDS

by Helen Evelyn Tuttlebee

The synthesis and properties of palladium(II) and platinum(II) halide complexes of a series of systematically varied dithioether ligands have been studied. The isolated compounds were of the type [M(dithioether)X_2] (M = Pd, Pt; X = Cl, Br, I; dithioether = $RS(CH_2)_nSR$ (n = 2,3), *cis*-RSCH=CHSR, *o*-$C_6H_4(SR)_2$; R = Me,ϕ) which are assigned *cis* planar structures, $[Pd(\phi S(CH_2)_nS\phi)X_2]$ (n = 4,6) which are polymeric with *trans* ligand bridges and $[M(\phi S(CH_2)_{12}S\phi)X_2]$ which are *trans* chelated monomers. The ligand $\phi SCH_2S\phi$ behaves as a monodentate ligand in $[M(\phi SCH_2S\phi)_2X_2]$ compounds.

Iron(III) bromide reacted with some bidentate group VB ligands to form complexes of the type $[FeL_2Br_2][FeBr_4]$, containing a low spin tetragonally distorted octahedral cation and a high spin tetrahedral anion, $[Fe(LO_2)(H_2O)_2Y_2]$ [Y = NO_3, NCS) and also $[(HL)_2Cl_3FeOFeCl_3]$. Iron(III) halide complexes of monodentate group VB ligands have also been prepared.

Cobalt(II) and nickel(II) halides reacted with some mixed donor (N, P, As, Sb, S) methyl-substituted *o*-phenylene ligands to give a range of complexes formulated as $[NiLX_2]$ and $[CoLX_2]$ (X = halide, NO_3, NCS) $[CoL_2X]Y$ (X = halide; Y = X,$\frac{1}{2}CoX_4$, ClO_4, $B\phi_4$) and $[CoL_2](ClO_4)_2$.

A number of air-stable, mixed donor ligands have been tested for their suitability as extractants of nickel for a solvent extraction process. Their cobalt(II), nickel(II), and copper chemistry in both non aqueous and aqueous conditions has been investigated. The didodecyldithiophosphoric acid ligand exhibited the greatest potential.

The above-mentioned formulations have been made on the evidence of infrared, electronic, Mössbauer and ^1H nmr spectral data and also elemental analysis, molecular weight, conductivity and magnetic susceptibility measurements.

Acknowledgements

I am grateful for both a University of Southampton award (one year) and a Science Research Council CASE award involving ICI Organics at Blackely (two years) for the financial support of this research.

I am also grateful and appreciative of my supervisor, Dr W Levason at Southampton University for his oversight, help and constant encouragement over the three year period.

Thanks also go to Dr R Dalton at ICI Organics for his enthusiastic and attentive supervision during my short stay in Manchester and also to Dr S M Nelson of Queen's University, Belfast, for his variable temperature ^{1}H nmr and Mössbauer measurements.

I finally thank Miss Julia Quinn for her accurate and well presented typing, the members of the 'sixth floor' for both their company and help, and last, but not least, my husband for both his acquired tolerance to 'smelly' chemicals and also practical encouragement (housework!).

CONTENTS

CHAPTER ONE: SOME DITHIOETHER COMPLEXES OF THE PALLADIUM(II) AND PLATINUM(II) HALIDES

CHAPTER TWO: THE IRON(III) BROMIDE COMPLEXES OF SOME MONODENTATE AND BIDENTATE GROUP VB LIGANDS

CHAPTER THREE: THE COBALT(II) COMPLEXES OF A SET OF LIGANDS OF THE TYPE o-$C_6H_4(EMe_2)(E'Me_2)$ (E=E'= N,P,As; E=N, E'=Sb and $\bar{E}$=P, E'=S)

CHAPTER FOUR: THE COBALT(II) AND NICKEL(II) COMPLEXES OF SOME AIR-STABLE MIXED DONOR LIGANDS AND THE POTENTIAL USE OF THESE LIGANDS AS EXTRACTANTS FOR NICKEL IN A SOLVENT EXTRACTION PROCESS

Abbreviations

M	Metal
X	Halide, nitrate, thiocyanate, perchlorate etc.

Ligands (L)

bipy	Bipyridyl
dapm	1,3-Bis(dimethylarsino)propane
dias	1,2-Bis(dimethylarsino)benzene
dpe	1,2-Bis(diphenylphosphino)ethane
dppm	1,3-Bis(dimethylphosphino)propane
dppp	1,3-Bis(diphenylphosphino)propane
HAc	Diphenylphosphinoacetic acid
HB	o-Diphenylphosphinobenzoic acid
Me$_4$en	1,2-Bis(dimethylamino)ethane
Me$_4$pn	1,2-Bis(dimethylamino)propane
Me$_4$tn	1,3-Bis(dimethylamino)propane
Me$_6$tren	Tris(2-dimethylaminoethyl)amine
NAs$_{me}$	(o-Dimethylaminophenyl)dimethylarsine
NN$_{me}$	1,2-Bis(dimethylamino)benzene
NP$_3$	Tris(2-diphenylphosphinoethyl)amine
PAs$_{me}$	(o-Dimethylphosphinophenyl)dimethylarsine
PA$_{\phi}$	(o-Diphenylphosphinophenyl)diphenylarsine
phen	1,10-Phenanthroline
PN$_{me}$	(o-Dimethylaminophenyl)dimethylphosphine
PN$_{\phi}$	(o-Dimethylaminophenyl)diphenylphosphine
PO$_{me}$	(o-Dimethylphosphino)anisole
PO$_{\phi}$	(o-Diphenylphosphino)anisole
PP$_{me}$	1,2-Bis(dimethylphosphino)benzene
PP$_{\phi}$	1,2-Bis(diphenylphosphino)benzene
PS$_{me}$	(o-Methylthiophenyl)dimethylphosphine
PS$_{\phi}$	(o-Methylthiophenyl)diphenylphosphine
py	pyridine
QAS	Tris(o-diphenylarsinophenyl)arsine

SbA_ϕ	(*o*-Diphenylstibinophenyl)diphenylarsine
SbN_{me}	(*o*-Dimethylaminophenyl)dimethylstibine
vaa	Cis-1,2-bis(diphenylarsino)ethylene
vpp	Cis-1,2-bis(diphenylphosphino)ethylene

Substituent R groups (R = alkyl, alkenyl or aryl)

Bu^n, Bu^t	Normal, tertiary butyl respectively
Cy	Cyclohexyl
Et	Ethyl
Me	Methyl
Pr^n, Pr^i	Normal, isopropyl respectively
ϕ	Phenyl

Solvents

Ac_2O	Acetone
DM or (d)	Dichloromethane
DMSO	Dimethylsulphoxide
DMF	N,N-Dimethylformamide
Et_2O	Diethyl ether
$MeNO_2$ or (N)	Nitromethane
MeCN	Acetonitrile
THF	Tetrahydrofuran
TMS	Tetramethylsilane

Physical parameters

E_{max}	Energy of band maximum (cm^{-1})
T	Temperature (K)
ν(M-X)	Stretching frequency of the M-X bond (cm^{-1})
Λ_M	Molar conductivity ($cm^2\ \Omega^{-1}$)
μ_{eff}	Effective magnetic moment (BM)
χ_{corr}	Diamagnetically corrected molar susceptibility ($m^3\ mol^{-1}$)
ϵ_{mol}	Molar extinction coefficient (ℓcm^{-1})

Tables

Figures

CHAPTER ONE

Some Dithioether Complexes of the Palladium(II) and Platinum(II) Halides

1.1 LITERATURE SURVEY

1.11 The Chemistry of Palladium and Platinum

Palladium and platinum belong to the 2nd and 3rd row of the transition series. They are rare metals and are widely used in catalytic processes [1], e.g. (a) Wacker process where ethylene is oxidised to acetaldehyde in the presence of palladium(II) chloride (a homogeneous catalysis) and (b) the platforming of crude oils. Palladium is used for H_2 purification and platinum for electrical contacts in printed circuitry. The preparation of crystalline Pt derivatives has been a widely used technique for the characterisation of many organic compounds. [1]

Palladium and platinum have been found to exist in the following oxidation states: 0, +1, +2, +4, +5 and +6, the principal ones of which are +2 and +4.

Atomic and Ionic Radii (Å) [2]

	Pd	Pt
M(O) metal	1.375	1.387
M(II) covalent, square planar	1.31	1.31
M(IV) covalent, octahedral	1.31	1.31

The similarity between the corresponding Pd and Pt radii is common among pairs of elements in the same group in the 2nd and 3rd transition series [2]. This arises from the lanthanide 'contraction' of the atomic radius which is due to the imperfect shielding of the outer d electrons from the nuclear charge, by the 4f subshell.

The 2nd, 3rd and 4th ionisation potentials of Pt [2] are lower than the respective Pd values. A 5d electron on Pt will feel a lower effective nuclear charge than a 4d electron on Pd owing to the 4f electrons providing a better shield for the outer d electrons.

Ionisation potentials of Palladium and Platinum (eV)

Ionisation potential	Pd	Pt
$M^{+} \rightarrow M^{2+}$	19.42	18.56
$M^{2+} \rightarrow M^{3+}$	39.92	28.50

Ionisation potential	Pd	Pt
$M^{3+} \rightarrow M^{4+}$	48.80	41.10

The Pauling electronegativities [2] of Pt and Pd are identical, i.e. 2.2 and thus they exhibit a similar type bonding with other elements. The heat of sublimation [2] of Pd is less than Pt which leads to a larger enthalpy of formation for the Pd(II) compared to the Pt(II) compounds.

The oxidation potential in aqueous solution for the equilibrium M (metal) $\rightleftharpoons$ M(II) is more negative for Pt than for Pd and it is therefore more difficult to oxidise platinum metal, i.e. it is easier to reduce Pt(II) than Pd(II) [3,4].

The oxidation potential in aqueous solution for the equilibrium M(II) $\rightleftharpoons$ M(IV) is the reverse, i.e. Pt(II) compounds are easier to oxidise than Pd(II) compounds. Oxidation becomes more favourable in these two equilibria by increasing the atomic weight of the halogen present. The conclusion here is that the Pd(II) and Pt(II) complexes of the heavier halides are the more stable in aqueous solution.

The most common oxidation state is +2 (d^8). The M(II) ion (M = Pd, Pt) in fact will complex readily with ligands containing donors from most groups of the periodic table. In this oxidation state there are no complexes where the coordination number is less than four and all those where it is four are of square planar geometry or only slightly distorted from this, e.g. $[(PMe_3)_2PtCl_2]$ [5]. This square planar geometry leads to the possibility of cis and trans isomers. The discovery of the 'trans effect', discussed later, has led to the systematic synthesis of particular cis or trans isomers.

There are a number of 5-coordinate complexes and these contain ligands such as $SnCl_3^-$ and phosphorus, arsenic and antimony donors. The increasing ability to stabilise 5-coordination within the group VB elements is N <<< P < As < Sb.

The Pd(II) and Pt(II) ions both exhibit large crystal field splittings.

Four-coordinate and five-coordinate structures (trigonal bipyramidal or square-pyramidal) are likely to be observed since leaving

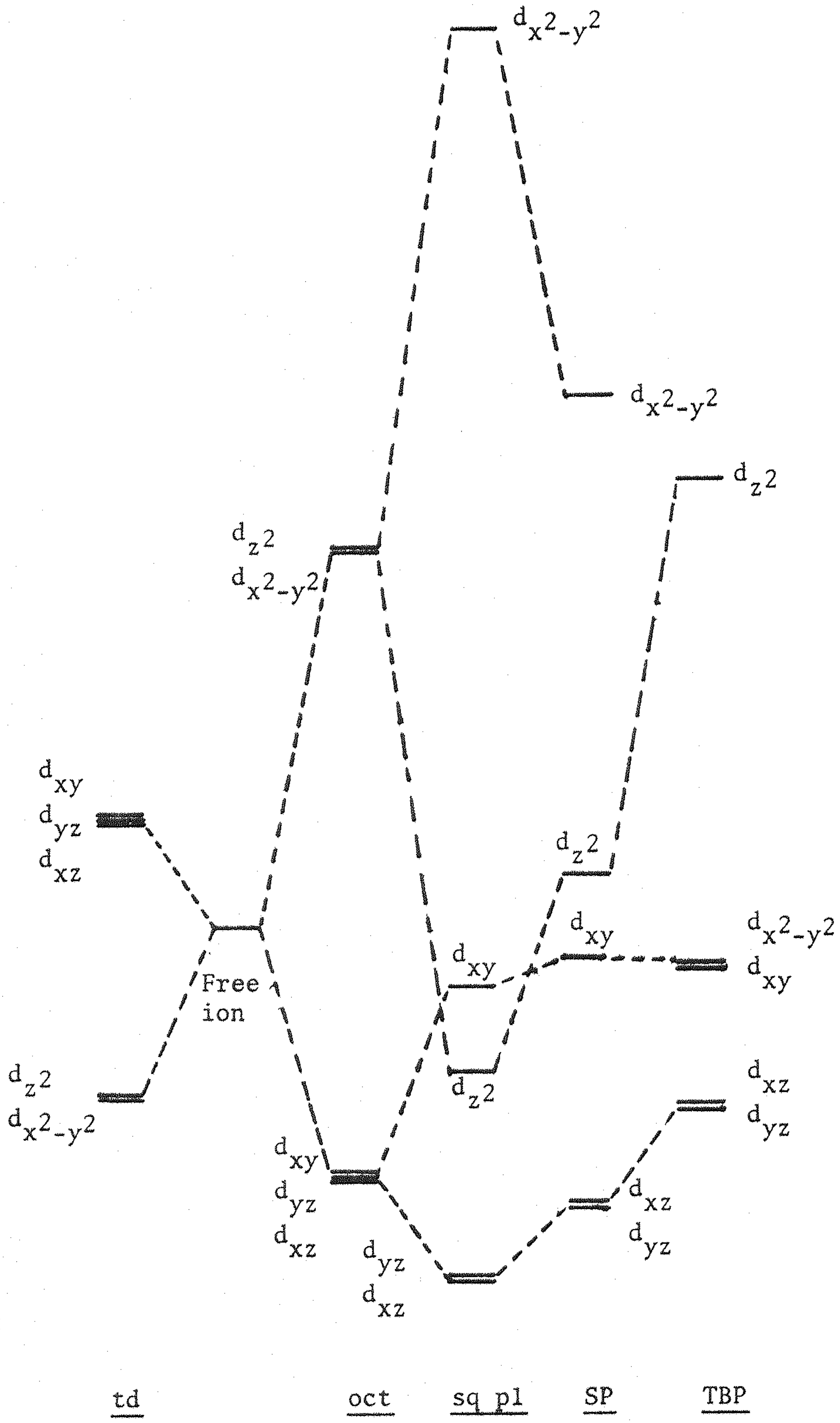


Figure 1.1 The relative energies of the d orbitals in crystal fields

the highest d-orbital empty will give rise to a considerable ligand field stabilisation.(Fig 1.1)

A six-coordinate structure would be expected to be rare and distorted towards a square planar structure. The energy of the $d_{x^2-y^2}$ orbital would be raised and could then be left empty thus leading to a diamagnetic product. The d_{z^2} orbital would simultaneously be lowered giving overall stabilisation relative to a regular octahedral structure.

An octahedral geometry is seen in the +4 oxidation state. Pt(IV) compounds are more abundant than those of Pd(IV) and this is due to the higher ionisation energy required to produce the Pd^{4+} ion. Pt(II) is able to undergo reactions by an oxidative-addition mechanism which is less likely to occur for Pd(II).

The metals palladium and platinum in oxidation states below +4 are commonly termed as class 'b' or 'soft' acids [6,7,8,9,10]. Chatt [6] showed that metal ions could be divided into two groups, class 'a' and class 'b'. Class 'a' metals are those that prefer to form complexes with elements of low atomic number in a given group of the periodic table and class 'b' prefer those of higher atomic number. The stabilities of the halide complexes of a class 'b' metal decrease in the order $I^- > Br^- > Cl^- > F^-$.

Pearson's theory [7] stated that 'hard' acids form their stronger complexes with 'harder' bases and 'soft' acids with 'softer' bases. 'Hard' and 'soft' are related to polarisability and the halide ions for example, increase in softness with increase in atomic number. The terms 'hard' and 'soft' acids may be replaced by Chatt's class 'a' and class 'b' metals.

The thermodynamic data for the Pd(II) and Pt(II) complexes, the ΔG and ΔH values, decrease as the atomic number of the halogen increases, i.e. they become more stable and more likely to form, and therefore indicate that Pd(II) and Pt(II) are class 'b' metal ions or 'soft' acids. This is shown in the preference of these M(II) ions for halogens, cyanides, phosphorus, arsenic, sulphur and selenium and their relatively low affinity for oxygen and fluorine.

In traversing the first period, considering a combination of the ligand with a class 'b' metal, there is increasing lone pair repulsion between the electrons in the d-orbitals and the increasing number of non-bonding lone pairs in the p-orbitals of the ligand donor atom. The coordinating affinity for strong class 'b' metals decreases rapidly in the order N >> O >> F. In the case of strong class 'a' metals where electrostatic bonding occurs the order is F > O > N.

Pt(II) is more inert kinetically than Pd(II) and thus ligand replacement reactions can be followed more easily. (Pd(II) reaction rates are $10^5 - 10^6$ x faster than Pt(II)). Ligand substitution reactions of square planar Pt(II) complexes occur with retention of configuration.

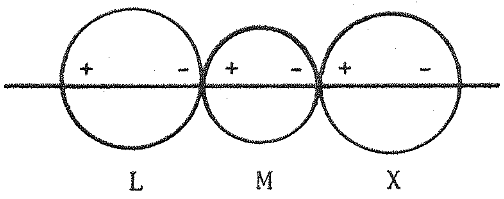
The phenomenon that a ligand has a greater labilising effect on a group trans to it than it does on groups in the cis position in square planar compounds is referred to as the trans effect. [1,2,12]. This is important in Pd(II) and Pt(II) complexes and can be utilised to obtain a required cis or trans product. An approximate order of decreasing trans effect for Pd(II) and Pt(II) has been previously proposed.

$$C_2H_4 \sim NO \sim CO \sim CN^- > R_3Sb > R_3P > R_3As \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^-$$

$$> SCN^- > NO_2^- > I^- > Br^- > NH_3 > OH^- > H_2O$$

This represents the decreasing ability for these ligands to facilitate substitution in a position trans to themselves. The trans effect is a kinetic phenomenon, i.e. a ligand will alter the rate of substitution at the position trans to itself. Two attempted explanations of the trans effect have been made:

(a) The polarisation or σ-trans effect theory (a ground state theory) where the primary charge on the metal induces a dipole in the ligand L, which in turn induces a dipole in the metal. The orientation of the latter is such as to repel negative charge in the trans ligand X. X is then less attracted to the metal because of the presence of L and the M-X bond is weakened and lengthened compared to a cis-(M-X) bond.



An incoming nucleophile will be first directed toward X and a trigonal bipyramidal transition state stabilised. The polarisability of the metal will be important here. The trans effect of a ligand should be less in Pd(II) than in Pt(II). (Pd(II) complexes are less covalent then Pt(II) complexes).

(b) This theory refers to strong π-acid ligands (e.g. phosphines) which are very effective in their ability to stabilise a 5-coordinate transition state, (a transition state theory). A bimolecular reaction is assumed and for which there is generally good evidence. The ligand withdraws metal π d_{xz} electron density into its own empty π or π^* orbitals and away from the ligand in the trans position (X). [13].

Theory (b) applies to the transition state and (a) to the ground state.

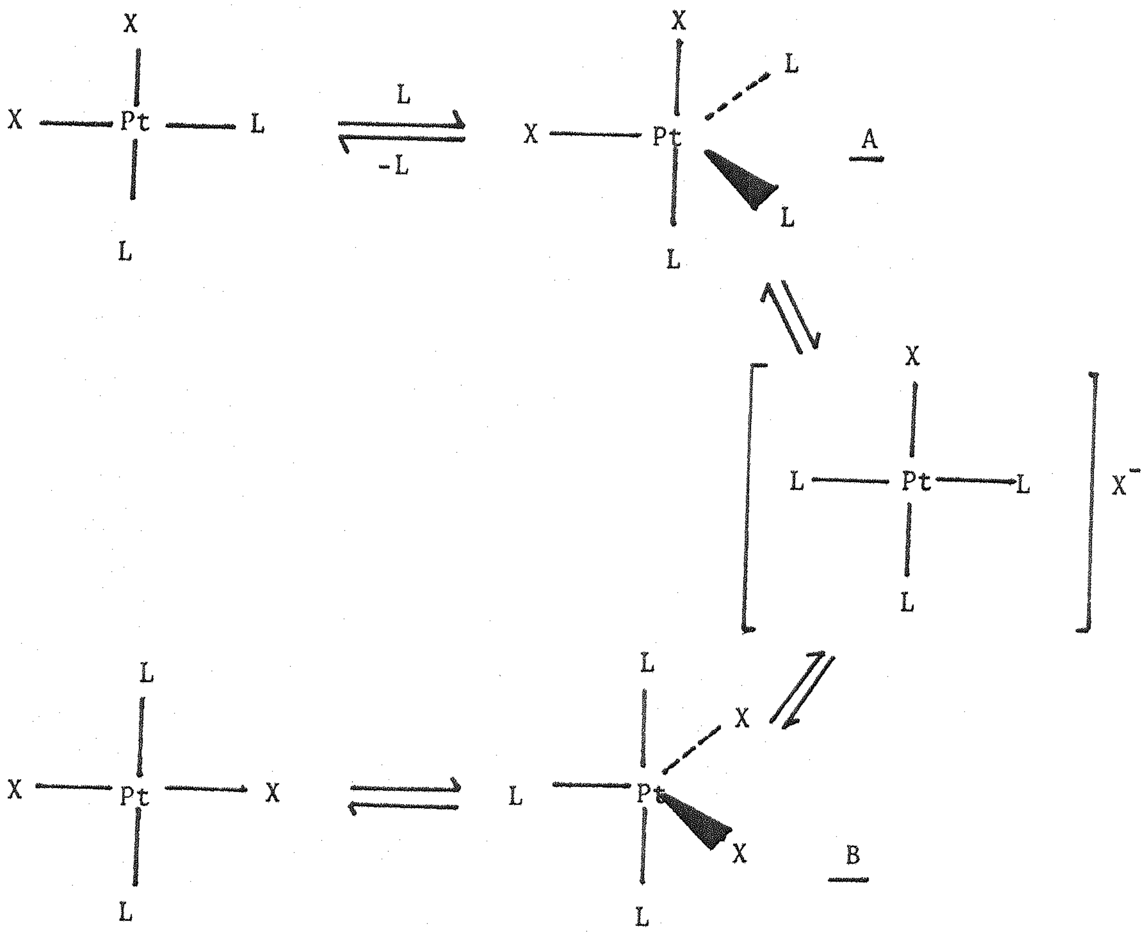
Data obtained from infrared or X-ray diffraction studies sometimes show trans bond weakening. However ν(M-X) cannot be considered as independent of the other vibrational modes in a complex. Trans bond lengthening can also be considered as due simply to a ground state trans effect frequently called 'trans influence'. The trans-effect has been studied kinetically by determining nucleophilic displacement reaction rates [14,15,16,17,18]. For example Gosling and Tobe [15] have studied the replacement of chloride trans to diethylsulphide in $[Pt(SEt_2)Cl_3]^-$ by a variety of amines (and a reverse reaction) in methanol at 30°C. The rate constants are compared with those of the corresponding reactions of the dimethylsulphide analogue [19]. The greater reactivity found for the diethylsulphide complexes compared to the dimethylsulphide implies a greater trans effect for the former.

The general rule for the Pd(II) and Pt(II) complexes $[ML_2X_2]$, where X = an anionic ligand and L = a neutral ligand, is that the cis-isomers are enthalpy favoured but in solution entropy changes favour the trans form. These factors are often finely balanced and changes of metal, ligand, solvent or temperature may significantly affect the equilibrium position. Equilibria positions between cis and trans-isomers have been measured by dipole-moment determinations [20], infrared spectrometry [21] and nmr spectrometry [22]. The trans geometry appears to be more favoured by Pd(II) than by Pt(II) [22]. It was only in 1966 that cis geometry was definitely established for some Pd(II) compounds [23].

The tendency towards more stable trans-isomers increases along the series $Cl^- < Br^- < I^-$ for anionic ligands [22] and $R_2S < R_2Se < R_2Te$ for neutral ligands [22]. Two main mechanisms of isomerism have been proposed [24]:

(a) The consecutive displacement mechanism

This is the best authenticated mechanism and involves only stereospecific ligand substitution steps.



Scheme 1.1

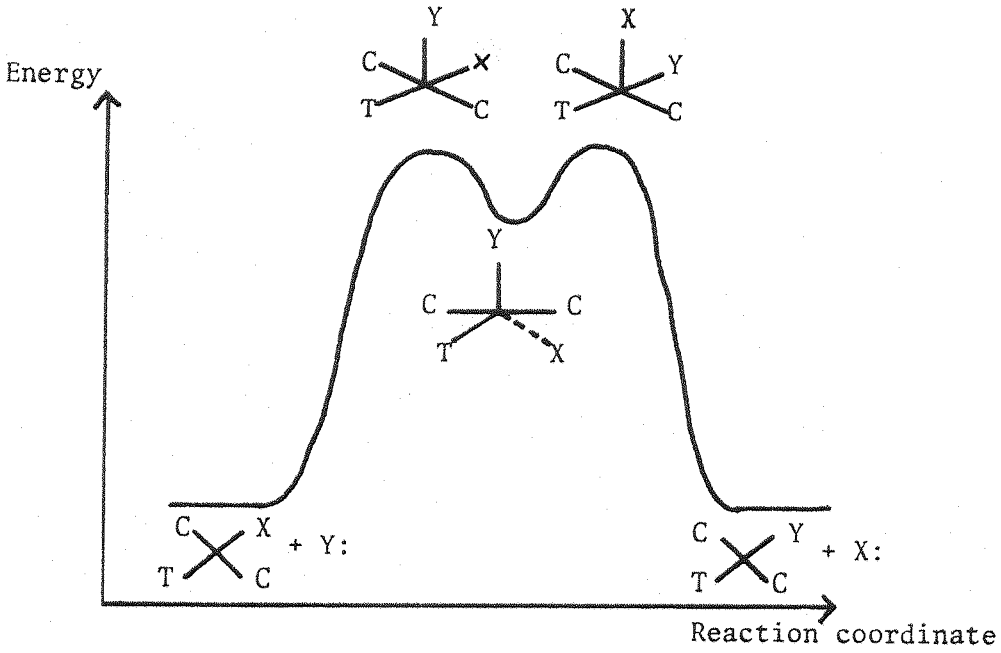


Figure 1.2
The consecutive displacement mechanism

In Figure 1.2 the trans ligand T and cis ligands C retain their relationship. The reaction proceeds through a trigonal bipyramidal intermediate with T, X and Y in the trigonal plane [11]. This is achieved through the trans effect of T, which either weakens the bond, M-X, (a trans influence) or stabilises the trigonal bipyramidal intermediate by π-acceptor properties or both [25]. Two steps are required to obtain isomerisation (i) L replaces a halide to give $[PtXL_3]^+X^-$ and (ii) attack of X^- on $[PtXL_3]^+$. Either the original or the other isomer will result depending upon which intermediate A or B forms.

(b) The pseudorotation mechanism

This process would convert A into B directly. If such a process were faster than either or both of the steps linking A and B with the ionic intermediate the isomerisation would proceed by that route. However, in the application of this mechanism there is a violation of the highly stereospecific nature of substitution reactions at square planar complexes.

An up to date consideration of the isomerisation mechanisms in Pd(II) and Pt(II) is found in reference [24].

1.12 AN INTRODUCTION TO THE GROUP VIB COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) [2,26,31,32]

Palladium(II) and platinum(II), as previously mentioned, form complexes with a wide range of donor ligands. The complexes of the group VIB donors, the thioethers, selenoethers and telluroethers have been studied to only a small extent in comparison with the group VB donors, [2,27,28,29,30]. The area of literature covered here is mainly restricted to the thioether chemistry of Pd(II) and Pt(II). However, in order to observe the trends within group VIB some selenother and telluroether complexes are also included. Some monodentate oxygen ligands are also included, again for comparative purposes.

Palladium(II) and platinum(II) are 'soft' acceptors or class 'b' metals and as a result will form stronger bonds with sulphur, selenium and tellurium ligands than with the corresponding oxygen ligand. The stabilities of the complexes of the first three are similar. The stability of a complex will also depend upon the total effective electronegativity of the donor atom and also on the total dipole moment, i.e. the stability depends upon the other substituents on the metal and also to the other groups attached to the donor atom.

A comparison of stabilities of some oxygen and sulphur ligands:

$\left.\begin{array}{l}H_2O\\ ROH\end{array}\right]$ give more stable complexes than $\left[\begin{array}{l}H_2S\\ RSH\end{array}\right.$

OH^- and SH^- complexes are of similar stability

$\left.\begin{array}{l}R_2O\\ RO^-\end{array}\right]$ give much less stable complexes than $\left[\begin{array}{l}R_2S\\ RS^-\end{array}\right.$

The permanent dipole moments and coordinating abilities for the oxygen ligands decrease in the order $H_2O > ROH > R_2O$ whereas the order is reversed for the sulphur ligands $H_2S < RSH < R_2S$. The permanent dipole is augmented by an induced dipole moment which is larger for sulphur than for oxygen due to sulphur's greater polarisability. The strength of the M(II)-S bonds, (where M = Pd, Pt) has previously been thought to be due to back donation of π-electron density into relatively low energy empty d orbitals on the sulphur.

1.13 THE PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF THE MONODENTATE GROUP VIB DONOR LIGANDS WITH SPECIAL REFERENCE TO THOSE OF THE THIOETHERS

Sulphur is known to act as a good ligating atom when in the form S^{2-} or RS^- but complexes of sulphur as a thioether R_1R_2S are much less abundant.

The section 1.13 covers a range of monodentate complexes (a) H_2E, (b) HE^-, (c) E^{2-}, (d) REH, (e) RE^- and (f) R_2S (with some reference to R_2Se and R_2Te) where E = group VIB element.

(a) H_2E

H_2S and H_2Se give only the PdE compounds. H_2O is a very poor ligand for Pd(II) and Pt(II) and so these complexes are only rarely isolated.

(b) HE^-

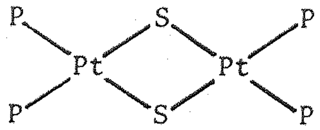
The hydroxide ion, OH^- is a 'hard' base and thus would not be expected to react readily with Pd(II) and Pt(II). However hydroxide complexes are known and will form more readily when another ligand is bound to the metal which makes it act more class 'a' in character (i.e. symbiosis).

When E=S, Se the only Pt(II) complexes are: $[(P\phi_3)_2PtH(EH)]$ [33]

(c) E^{2-}

Sulphur will act as a bridging ligand in its complexes.

e.g. $[(PMe_2\phi)_4Pt_2S_2]$



[34]

$[(PMe_2\phi)_6Pt_3S_2]X_2$ where X = ClO_4^-, $B\phi_4^-$, BF_4^- [34]

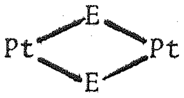
$[(P\phi_3)_4Pt_2S]$ [34]

The polysulphide ligands give:

$[(P\phi_3)_2MS_4]$ where M = Pd, Pt (this contains a MS_4 ring) [34]

When E = S and Se the polydonor complexes $[(P\phi_3)_2PtE]_n$ [33]

These contain



bridges

(d) REH

No Pd(II) and Pt(II) complexes have been isolated. RSH will only give PdS.

(e) RE^-

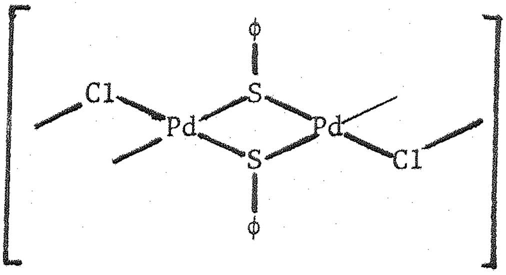
The only complexes where E = O are:

$[(PEt_3)_2Pt(Ge\phi_3)OR]$ where R = Me, Et, Pr [35]

and trans-$[(P\ Et_3)_2Pd(OMe)CN]$ [36]

The RS^- anion forms strong complexes with the M(II) ions. The complexes $[Pd(SR)_2]$ where R = Et, Pr^n, Bu^n, ϕ [37,38], C_6F_5 [39], and $[Pt(SR)_2]$ where R = ϕ [38], C_6F_5 [39] are polymeric and highly associated.

Some more examples are:



[40]

and $[(PR_3)_2Pd(S\phi)_2]$ where PR_3 = PEt_3, $PEt_2\phi$, [41]
$\frac{1}{2}\,\phi_2P(CH_2)_2P\phi_2$

and trans-$[(P\phi_3)_2M(SC_6F_5)_2]$ [42]

$[(PPr_3{}^n)M(RS)Cl]_2$ where M = Pt, cis and trans isomers
and M = Pd, only the cis isomer [43,44]

When M = Pt and R = Et then the cis and trans isomers form simultaneously. When M = Pd and R = ϕ, the complex

$[(PPr_3)ClPd(Cl)(S\phi)PdCl(PPr_3)]$ [44]

can be obtained. This complex contains both chloro and thio bridging ligands. The thio ligand has a high trans effect and as a result this complex is cis only. The halogen-bridged dimeric complexes of Pd(II) and Pt(II) are readily cleaved by monodentate ligands such as pyridine and triphenylphosphine but the corresponding thio-bridged complexes are not [40,43, 44,45].

(f) R_2S Monothioethers (with some reference to R_2Se and R_2Te)

Monomeric Complexes

The platinum group metals form monomeric complexes of the type $[ML_2X_2]$ where X = halogen, L = dialkylsulphide, diarylsulphide, alkylarylsulphide, diarylselenide and cyclic sulphides [12,15,26,32,37,46-55].

The complexes are prepared by the simple addition of the ligands to the aqueous solutions of the appropriate K_2MX_4 salts and recrystallisation from ethanol [51,52]. The separation of cis and trans-isomers is effected by utilising their different solubilities. The trans-isomer is normally insoluble in water but dissolves in benzene whereas the cis-isomer displays the reverse tendencies.

The complexes trans-$[Pt(R_2S)_2X_2]$ (X = Cl, Br and R = Me, Et, Bu^n) are stable to heat but the complex when R = n-C_5H_{11} undergoes an unusual trans to cis rearrangement [56].

The telluroether Pt(II) complexes are much less stable than their sulphur and selenium analogues. The best characterised compound is trans-$[Pt((\phi CH_2)_2Te)_2Cl_2]$ which decomposes in solution to give Pt metal, tellurium and dibenzyl [57,58].

The majority of the $[ML_2X_2]$ complexes are trans, especially in solution. An example is the set of $[ML_2X_2]$ complexes when L = SEt_2, $SeEt_2$, $TeEt_2$; M = Pd, Pt and X = Cl, Br, I [22].

The dipole moments of the monomeric $[ML_2X_2]$ complexes although not negligible are smaller than the expected values for a cis-complex and suggest a trans structure [37]. The trans structure has also been confirmed by X-ray analysis where L = $SeEt_2$, SEt_2, and M = Pd [59].

The cis-complexes $[Pd(TeEt_2)_2Cl_2]$, $[Pt(TeEt_2)_2Cl_2]$ and $[Pt(TeEt_2)_2Br_2]$ have been isolated in the solid state but in solution they rapidly isomerise to the trans form. The trend towards a trans geometry in solution increases along the series Pt < Pd; Cl < Br < I; S < Se < Te. When X = Cl, Br and L = SEt_2, Se Et_2 the cis-Pt(II) complexes have been isolated as solids but the iodo Pt(II) complex and all the Pd(II) complexes are trans. Some trans-$[ML_2X_2]$ complexes where M = Pd, Pt and X = Cl, Br, I also exist when the ligand is a cyclic sulphide, i.e. L = $S(CR_2)_n$ and n = 2-5 [32].

In addition, in the case of Pt(II) it will not only form the cis and trans-$[Pt(Me_2S)_2Cl_2]$ but also the ionic complex $[Pt(Me_2S)_4][PtCl_4]$.

A range of techniques including dipole moment determination, NMR, IR, Raman, X-ray diffraction studies and electronic spectroscopy have been used to elucidate the stereochemistry and structure of the above type complexes.

NMR Studies [22] have revealed that with the exception of $[Pt(SEt_2)_2Cl_2]$ that only the one isomer, the trans isomer, exists in solution for the series $[M(EEt_2)_2X_2]$ over a wide range of solvents. The former complex is slowly converted into the trans form at temperatures above 333K. A trans geometry is indicated by the constant value of ^1H nmr coalescence temperatures with change of halogen. These coalescence temperatures are due to inversion at the pyramidal E atom and a cis arrangement would give strongly halogen dependent values. The trans square planar $[ML_2X_2]$ complexes, where M = Pd, Pt; R = Bu^n, Bu^i, Bu^s, Pr^n; L = R_2S, Et_2Se and X = Cl, Br, [60], were studied by ^1H nmr to determine the influence of the cis-halogen upon the α-C protons of the sulphide and selenide ligands.

In the coordination of these neutral ligands to the metal the protons of the former are deshielded. There is a move to lower field, as a result, and this is larger for Pt than for Pd. This corresponds in fact to a stronger metal-ligand, σ-bond in the case of Pt. When the halogen is changed from chlorine to bromine there is a pronounced downfield shift and this may be due to bromine being more likely to be involved in metal-bromine, dπ-dπ bonding than chlorine. The metal atom then has an increased tendency to accept σ electrons from the sulphur or selenium and so deshield the α-C protons further.

Some ^1H nmr spectra of a range of Pd(II) and Pt(II) complexes where the ligand, Me_2S is terminal is given in reference [61]. The isomerism of both cis and trans-$[Pt(SMe_2)_2Cl_2]$ catalysed by SMe_2 has also been followed by ^1H nmr techniques [62].

A further section on variable temperature ^1H nmr studies is included on page 23 where chalcogen inversion and ligand exchange processes in thioether complexes are discussed.

Electronic spectroscopy studies. The trans-$[ML_2X_2]$ complexes, where M = Pd, Pt; R = Bu^n, Bu^i, Bu^s, Pr^n; L = R_2S, Et_2Se; X = Cl, Br, were studied by this technique [60].

In the palladium(II) complexes three bands (cm^{-1}) are observed:

(a) an intense band ∿ 41000 for X = Cl
and ∿ 38000 for X = Br

(b) an intense band ∿ 32000

(c) a weaker band ∿ 22000-24000.

The lowest energy band (c) probably corresponds to the ligand field type transition (i.e. d ↔ d).

i.e. $b_{1g} \rightarrow a_g^*$ where b_{1g} corresponds to the symmetry of the filled metal d_{xy} orbital and a_g^* to that of the empty metal $d_{x^2-y^2}$ orbital.

With the exception of the complex $[Pd(Et_2Se)_2Br_2]$ this band moves to lower energy from X = Cl to X = Br, i.e. with the decrease in ligand field strength.

The intense band (a) varies by as much as 4000 cm^{-1} with the change from chlorine to bromine and is probably the charge transfer transition:

$X_{nb} \rightarrow a_g^*$ (empty $d_{x^2-y^2}$ orbital on metal)
(non-bonding)

The intense band (b) moves only slightly with the halogen change but it is affected by the ligand change from R_2S to Et_2Se. (The selenide band is of lower energy). This band is probably the charge transfer transition:

S_{nb} or $Se_{nb} \rightarrow a_g^*$

These charge transfer processes are of the metal reduction variety. Metal oxidation would result in a reversal of the chloride and bromide energies.

In the platinum(II) complexes the corresponding transitions occur at higher energies and as a result the highest energy charge transfer band has not been observed.

Low frequency vibrational spectra have been recorded for the square planar $[ML_2X_2]$ complexes, where L = thio, seleno or telluro-ether and X = halogen [22,53,54,60,61,63,64,65].

The trans-complexes have D_{2h} symmetry. The metal-halogen stretching frequency is expected to be more intense than the metal-ligand stretching frequency. In addition the metal-halogen stretching frequency is largely independent of the ligand.

Metal-halogen stretching frequencies in the trans-$[ML_2X_2]$ complexes are found in references [54,66,67].

Table 1.1

Typical values of metal-halogen stretching frequency (cm^{-1}) in the trans-$[ML_2X_2]$ complexes L = group V or VIB ligand [53,66]

M-X	ν (cm^{-1})	Reference
Pd-Cl	357 ± 5	[66]
Pd-Br	275 ± 15	[66]
Pd-I	190 ± 12	[66]
Pt-Cl	340 ± 3	[66]
Pt-Br	244 ± 20	[66]
Pt-I	180	[53]

The cis-complexes have C_{2v} symmetry and have two IR active metal-halogen bands, i.e. symmetric and antisymmetric stretch. These frequencies are dependent on the trans ligand and are thus found over a much wider frequency range.

The corresponding Pt(II)-ligand and Pd(II)-ligand stretching frequencies are about the same [53]. This leads to the conclusion that the metal-ligand bonding is significantly stronger for platinum than for palladium.

Table 1.2

Some values of metal-halogen stretching frequency (cm^{-1}) for cis-[ML_2X_2] complexes [12,66,68]

M-X	ν (cm^{-1})	Reference
Pd-Cl	335-269	[66]
Pt-Cl	340-269	[12]
Pt-Br	251-184	[12]

Dimeric complexes. The complexes [$L_2M_2X_4$], where X = Cl, Br, are prepared by treating the monomeric [ML_2X_2] complex with Na_2MX_4 in ethanol (usually M = Pt). They may form unintentionally instead of the monomeric complex if excess metal salt is used, e.g. this may occur when the ligand solution is added gradually to the salt solution [53,69].

The Pt(II) complexes are in general more stable than the corresponding Pd(II) complexes. The exception is when L = R_2Se where the reverse is true. In this case the selenium orbitals used to form the σ bond and the Pd(II) orbitals may be of comparable size, the corresponding Pt(II) orbitals being larger [70].

The decreasing stability of the chloro-bridged Pt(II) complexes [$L_2Pt_2Cl_4$] [71] is

$$L = R_3P \sim R_2S > R_3As > \text{amine} > R_2Te > R_3Sb > R_2Se$$

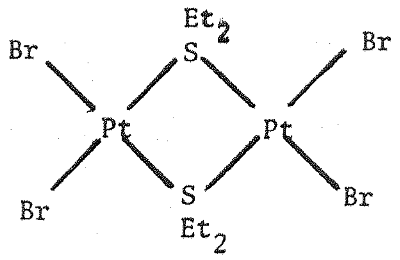
and for [$L_2Pd_2Cl_4$] [70]

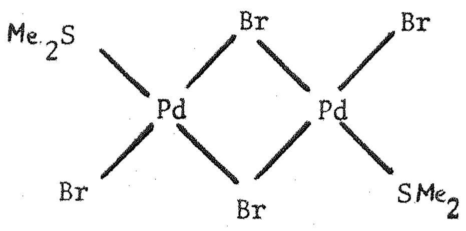
$$L = R_3P > R_3As \sim R_2S > R_2Se > R_2Te > R_3Sb$$

These chloro-bridged complexes can easily be cleaved by monodentate ligands such as amines to give the monomeric [$M(R_2E)(\text{amine})Cl_2$] type complexes (M = Pd, Pt; E = S, Se, Te) [72].

The [$(R_2S)_2Pt_2X_4$] complexes where R = Me, Et and X = Cl, Br, were found to possess different solubility properties and different infrared spectra to the other [$(R_2S)_2M_2X_4$] complexes [69]. A single crystal X-ray diffraction study on the two similarly prepared complexes [$Pd_2(SMe_2)_2Br_4$] and [$Pt_2(SEt_2)_2Br_4$]

[69,73] revealed that they both were monoclinic and possessed a centre of symmetry. They also have planar skeletons with the metals being held apart by bridging groups. However the Pd(II) complex is bromo-bridged and the Pt(II) complex was sulphur bridged. See below.





The Pt-S bond length is markedly less than that of Pd-S and this suggests that the dimethylsulphide ligand is more strongly bonded when it is bridging then when it is terminal. This is a reversal of the previous results found for metal-halogen bond lengths [53,74].

i.e. bond strengths decrease in the order $(M\text{-}X)_{terminal} > (M\text{-}X)_{bridging}$

The fact that the Pt-S bond length is shorter than the Pd-S bond length implies that the former has a significantly stronger bonding when it is bridging. In the Pd(II) complex sulphur's lone pair of electrons may act repulsively with the non-bonded d-electrons on the metal. When the sulphur is bridging in the Pt(II) complex however, all the outer sulphur electrons are used in bonding orbitals eliminating the previously mentioned repulsions and thus yielding a stronger bond.

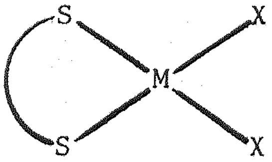
Polymeric complexes. The alkylphenyl sulphides are reported to give complexes

$[(\phi SR)Pd_2Cl_4]_n$ when R is not a straight carbon [75] chain, e.g. R = Bu^t, Me_2EtC.

1.14 THE PALLADIUM(II) AND PLATINUM(II) HALIDE COMPLEXES OF THE BIDENTATE AND MULTIDENTATE THIOETHER LIGANDS

The bidentate thioether ligand complexes

The dithioether ligands most commonly form four-coordinate square planar complexes of the type:



where X = halogen
$\overset{\frown}{S\,S}$ = dithioether
M = Pd(II), Pt(II)

Several reports concerning the dithioether complexes of the type $RS(CH_2)_nSR$ exist (R = alkyl, aryl). [26,76-80]. Palladium(II) chloride is known to form some of the most stable of these complexes, e.g. when R = ϕ, *o*-tolyl, ϕCH_2, Me and Et [78].

The 1,2-bis(alkylthio)ethanes are generally known to form stable complexes but the 1,2-bis(arylthio)ethane complexes are somewhat less stable, e.g. 1,2-bis(phenylthio)ethane does not form stable complexes with nickel, copper or mercury salts [81].

Platinum(II) chloride gives products of the following types:

(i) $[(SR)_2(CH_2)_2PtCl_2]$

(ii) $[[(SR)_2(CH_2)_2]_2Pt][PtCl_4]$

These M(II) complexes are prepared by mixing the K_2MCl_4 salt (M = Pd, Pt) in ethanol and the dithioether in dichloromethane in a 1:1 ratio. The bromide, iodide and nitrate are obtained by double decomposition, (e.g. NaBr and K_2MCl_4 solutions are mixed prior to the addition of ligand solution). [79,80].

The 1,2-bis(alkylthio)ethane, $RS(CH_2)_2SR$, ligands form five-membered rings with Pd(II) and Pt(II). This is the most stable ring size. Six-membered rings are also fairly stable for Pd(II) and Pt(II), (no examples with nickel or copper however) [82].

Previously in a study on palladium diamines and platinum diamines it was observed that the former existed in one form and the latter in two.

If the amine ligand was chelating then only one form, the ionic form, was seen for the latter [83], (see below). Thioethers (mono- and bidentate) exhibit a similar chemistry [84]. However, unlike the amines the two platinum complexes are interconvertible. The following equilibrium applies to both Pd(II) and Pt(II) but generally all the Pd(II) dimeric forms and a few of the Pt(II) are too rapidly converted to the monomeric to be isolated.

$$2[MLX_2] \rightleftharpoons [ML_2][MX_4] \qquad (1)$$

$$\text{yellow} \xleftarrow[\text{exothermic}]{} \text{pink}$$

M = Pd(II), Pt(II)
L = dithioether

Tschugaev [84] prepared the dimeric complexes by the method mentioned in 1.14. The pink, ionic complexes instantaneously precipitated out but when the solution is heated the yellow monomeric form resulted with an evolution of energy. The initial $[PtL_2][PtCl_4]$ complexes are analogous to the Magnus' green salt $[Pt(NH_3)_4][PtCl_4]$ in which the planar ionic $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ ions are situated one above the other, [85, 1 and references therein]. In this case however the mechanism of the thermal change of the dimeric to monomeric compounds can be represented as a synchronous shift of the ligands along one of the sides of a storey.

The reaction

$$2[PtCl_4]^{2-} + 2L \rightarrow [PtL_2][PtCl_4] + 4Cl^- \qquad (2)$$

is thermodynamically less favourable than

$$[PtCl_4]^{2-} + L \rightarrow [PtLCl_2] + 2Cl^- \qquad (3)$$

The reason for reaction (2) rather than reaction (3) taking place is probably due to the high trans effect of the thioether type ligands. It must be concluded that the rate of introduction of the thioether molecules into the $[PtLCl_2]$ complex is much higher than that into the $[PtCl_4]^{2-}$ ion and so after the first molecule, a second will enter leaving some unreacted

$[PtCl_4]^{2-}$ ions.

The thermal conversion (1) above is a general characteristic seen in metal halide thioether complexes.

Palladium(II) and platinum(II) have been reported to exhibit five-coordination in the nitrate complexes of the ligands $\phi E(CH_2)_3E\phi$; E = S, Se [86]. Previously Pd(II) and Pt(II) have shown this coordination number in non-aqueous media provided that certain types of ligands are present, e.g. 2,2'-bipyridyl [87] and tertiary phosphines and arsines [87-91]. Halide ions will readily replace thioether and selenoether ligands and so it was found impossible to prepare the $[Pt(\overset{\frown}{E\ E})_2X_2]$ complexes (X = Cl, Br, I) [86]. The nitrates however showed their greatest association in nitromethane, this being studied by carrying out conductivity measurements over a range of concentrations.

The following equilibrium was thought to exist:

$$[L_2M^{2+}][2NO_3{}^{2-}] \rightleftharpoons LM(NO_3)_2 \quad + \quad L$$

Association of the ions, perchlorate, fluoroborate and hexafluorophosphate with Pd(II) and Pt(II) dithioether ions has also been observed, e.g. some $[\phi SC_3H_6S\phi]_2M^{2+}$ ions [92]. In nitromethane these are extensively associated as 1:1 electrolytes and this association is preceded by loss of one of the ligand molecules.

The perchlorate and the two fluoro anions are well known for their poor donor ability. As a result the perchlorate entity occurs as a ligand in the solid complex but it is dissociated as an ion when the complex is dissolved. Electrostatic interaction in the solid state between the perchlorate and the metal ion can lead to the deformation of the former. The lifting of degeneracy in the vibrational spectra of such coordinated ions does not necessarily indicate the occurrence of covalent bonding. Sometimes there may be outer sphere ion-pairing in the case of these poorer donors (i.e. solvent molecules in the way).

The complex $ML_2(ClO_4)_2$ where M = Pd, Pt; L = $\phi S(CH_2)_3S\phi$, is a weak electrolyte but such behaviour is in fact due to the mono-chelated compound. One of the ligands has been lost.

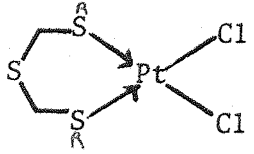
i.e. $L_2M^{2+} \rightleftharpoons LM^{2+} \quad + \quad L$

The tridentate thioether ligand complexes

The complexes [$MLCl_2$] have been reported for the following tridentate thioether ligands (L) [93].

L = $(MeSCH_2)_2S$, $(EtSCH_2)_2S$, $(Bu^nSCH_2)_2S$,
$(\phi CH_2SCH_2)_2S$, $(\phi SCH_2)_2S$.

These complexes are prepared by mixing the aqueous K_2MCl_4 (M = Pd, Pt) solution with the ligand in a 1:1 molar ratio.

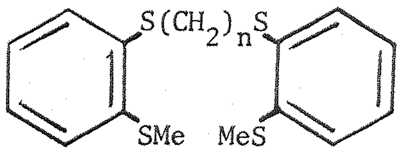
i.e. $RSCH_2SCH_2SR + K_2MCl_4$  + 2KCl

R = Me, Et, Bu^n, ϕCH_2, ϕ.

The ligands behave as bidentate trithioethers.

The tetradentate thioether ligand complexes

Complexes have been reported for the following tetradentate ligands.



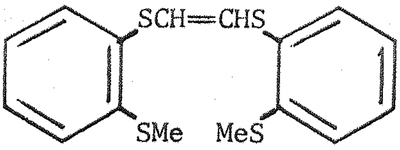
where n = 2,3,4

I Bis(o-methylthiophenylthio)alkanes [31,94]

$MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$

II Bis(methylthioalkylthio)alkanes [95] where (1) n = 2, m = 2
(2) n = 2, m = 3
(3) n = 3, m = 2
(4) n = 3, m = 3

and also

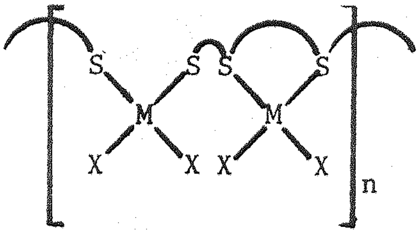


III cis-1,2-bis(o-methylthiophenylthio)ethylene [96]

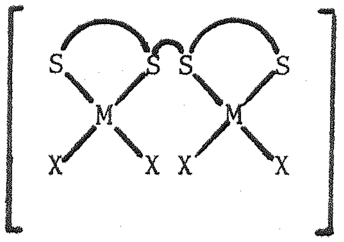
Only dimeric complexes are produced with Pd(II) and Pt(II) ions. The metals are four-coordinate and the ligands act as bridging quadridentates.

i.e. $[M_2LX_4]$ where M = Pd, Pt
X = Cl, Br, I
L = I, II, III

Possible structures for the complexes are:



or



The complexes are prepared by mixing the K_2MCl_4 salt and the ligand in ethanol in a 2:1 molar ratio. The bromides and iodides are obtained by double decomposition, i.e. by stirring NaX with the K_2MCl_4 solution (X = Br, I) prior to the addition of ligand.

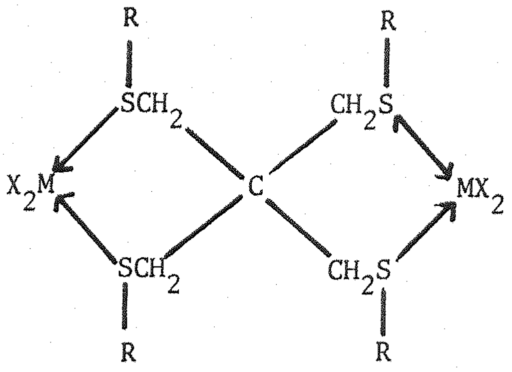
As a result of halogen coordination being dominant over thioether coordination complexes such as $[ML]X_2$ are not obtained. In order to achieve full binding of all the donors the ligands are forced to bridge rather than either displace coordinated halide or increase the coordination number to six.

Far infrared spectral data are found in references [52,54,60].

The dimeric complexes underwent S-dealkylation reactions. These reactions are almost invariably catalysed by heavy transition metals under forcing conditions [97]. In this case the metal complex, M_2LX_4 is suspended in a N,N-dimethylformamide/n-butanol mixture and heated under reflux (4-6 hours) until all the solid dissolves. The ease of S-dealkylation [98] increases in the orders Pt < Pd and $n = 2 \ll n = 3 \sim n = 4$.

In contrast, recently the ligand 1,2-bis(o-diphenylarsinophenylthio) ethane and its analogues have undergone bis(S-dealkylation) on reaction with Ni(II) salts under only mild conditions [99].

Another ligand containing four sulphur donor atoms is tetrakis-(n-alkylthiomethyl)methane [81] (alkyl = n-butyl, phenyl). This gives the dimeric complexes $[M_2X_4L]$, where M = Pd, Pt and X = Cl, Br, I, the ligand acting as a bimetallic-tetradentate chelate.



i.e. $S(CH_2SR)_4$

$R = I = Bu^n$

$R = II = \phi$

This ligand could also act as a unidentate and terdentate ligand simultaneously so producing octahedral, trigonal bipyramidal or square pyramidal structures.

Earlier investigations have revealed that the stability of the above complexes depend strongly on the nature of the groups attached to the sulphur and also on the size of the chelate ring formed [78,100], (a 5-membered ring being the most stable).

1.15 VARIABLE TEMPERATURE ^1H NMR STUDIES

Variable temperature ^1H nmr studies have been carried out on a variety of systems containing group VIII metals and thio, seleno or telluroether ligands. (See Table 1.3).

These studies have been used as a means of investigating barriers to chalcogen inversion as well as the fast exchange between free and coordinated ligands. Quantitative results have been obtained by total nmr band-shape fitting methods, computer programs being utilised [117]. A set of ^1H nmr spectra at different temperatures are obtained.

The nmr technique is limited to the measurement of barrier energies in the approximate range 20-80 $kJmol^{-1}$. Inversion rates at sulphur and selenium are often too slow for nmr detection, e.g. sulphoxides [118] and sulphonium ions [119]. However in 1966 Abel et al [110] and subsequently, Haake and Turley [105] detected sulphur inversion in a sulphur chelate complex of Pt(II) by this technique. This may be due to a stabilisation of the transition state by the π-acceptor capacity of

Table 1.3 Some ^{1}H NMR Studies on Some Group VIII - Group VIB Ligand Systems

	Monodentate ligand complexes		References
1.	$[M(EEt_2)_2X_2]$	E=S,Se,Te;X=Cl,Br,I;M=Pd,Pt	[101-104]
2.	trans-$[Pt(R_2S)_2X_2]$	R_2=Bz_2,Et_2,MeBz,Me_2	[62,104,105]
3.	$[M[ER(CH_2SiMe_3)]_2X_2]$	E=S,Se;M=Pd,Pt X=Cl,Br;R=Me,ϕ	[76]
4.	$[M[E(CH_2SiMe_3)_2]_2Cl_2]$	E=S,Se;M=Pd,Pt	[77,106]
	and mer-$[M[S(CH_2SiMe_3)_2]_3Cl_3]$	M=Rh,Ir	[108]
5.	trans-$[M[S(CR_2)_n]_2X_2]$	M=Pd,Pt;X=Cl,Br,I; R=H and/or Me; n=2-5	[107]
	Bidentate ligand complexes		
6.	$[M(RS(CH_2)_2SR)X_2]$	M=Pd,Pt;X=Cl,Br,I; R=Me,Et,Pr^n,Pr^i,Bu^n	[109,110]
7.	$[Pd(Pr^iSe(CH_2)_2SePr^i)X_2]$	X = halide	[111]
8.	$[M(RSe(CH_2)_2SeR)X_2]$	M=Pd,Pt;X=halide R=Et R=Pr^i	[103,112,113]
	Some Pt(IV) systems		
9.	$[PtXMe_3[MeE(CH_2)_nEMe]]$	E=S,Se;X=Cl,Br,I n=2,3	[114-116]

the metal atoms in the latter case. The barriers to inversion of chalcogen decrease in the order: [101,103,120,121]

Te > Se > S and Pt > Pd.

The inversion barriers are also sensitive to the trans influence of the trans ligand. Generally it is observed that the trans complexes invert considerably more rapidly than the cis.

The $[M(EEt_2)_2X_2]$ system is now taken as an example to show the general features observed in the variable temperature ^1H nmr spectra. At low temperatures the ^1H nmr spectrum analyses as ABM_3 and $ABM_3 + ABM_3Y$ for the palladium and platinum systems respectively. ($Y = {}^{195}Pt$, 33% abundant, $I = \frac{1}{2}$). As the temperature is increased the methylene regions of the spectra coalesce and at high temperature the systems A_2M_3 or $A_2M_3 + A_2M_3Y$ emerge.

There are only two dynamic processes which can bring about equivalence of the AB protons, inversion or rotation. Rotation about the C-E bonds is likely to be fast on the nmr time scale at all temperatures, and so the coalescences are regarded as reflecting the barriers to inversion of configuration.

The $^{195}Pt-^1H$ coupling is retained above the coalescence point for the Pt-S and Pt-Se systems and indicates that ligand dissociation-recombination is not occurring. The intramolecular process, pyramidal inversion at sulphur or selenium is thus operating. The sulphur atom retains a distorted tetrahedral configuration with the platinum atoms forming σ bonds alternately with the two sulphur lone pairs [105]. An averaging of these two positions is seen as a planar sulphur configuration. See Figure 1.3.

This mechanism should be sensitive to the nature of the trans ligand at the M(II) centre. Ligands can exert a trans effect in two ways, i.e. either a strong σ donor exerting a weakening effect on the M-S bond or by a π-acceptor ligand removing electron density from the metal thus encouraging nucleophilic attack. Both these processes would enhance inversion at the chalcogen. The fact that inversion is more rapid in the trans-$[(R_2S)_2PtCl_2]$ complexes than in the cis complexes is taken as evidence for either or both of these processes occurring [105].

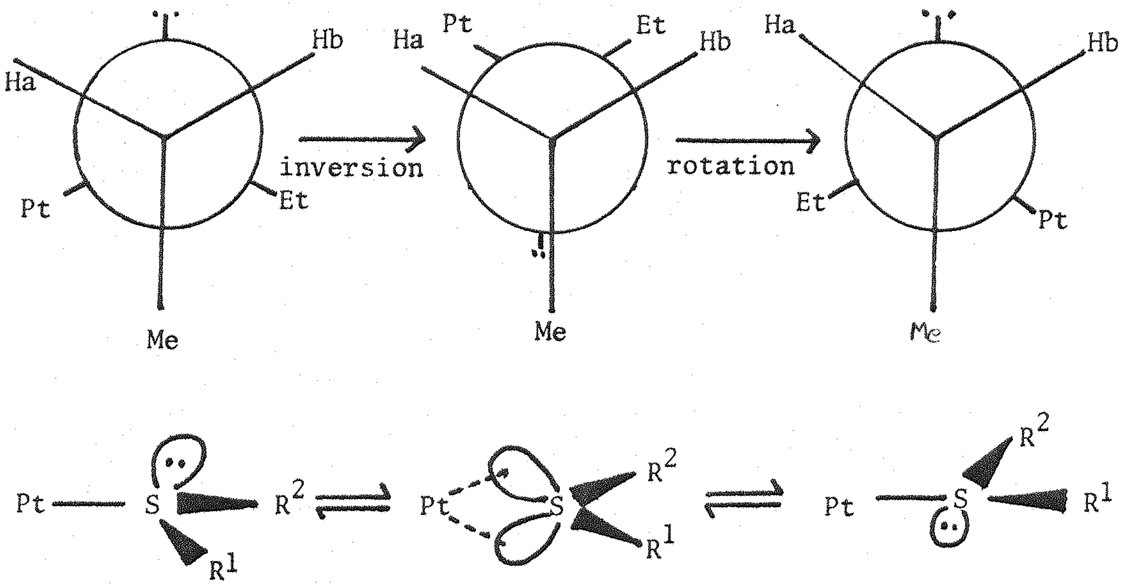


Figure 1.3

Sulphur inversion in thioether Pt(II) complexes

The probability of a synchronous inversion of both the chalcogen atoms in these complexes is very low.

The palladium(II) complexes give similar spectra to the platinum(II) complexes. However, since there is no suitable magnetic isotope of the former a dissociation-recombination mechanism could not definitely be ruled out.

Cross et al [101,104] however showed in a study on exchange between free and coordinated ligands in bis(diethylchalcogen)dihalogenopalladium(II) and platinum(II) complexes that coalescences due to chalcogen inversion are quite distinct from the exchange coalescences. This indicated for the first time that sulphur inversion in the palladium(II) complexes is not an association-dissociation process.

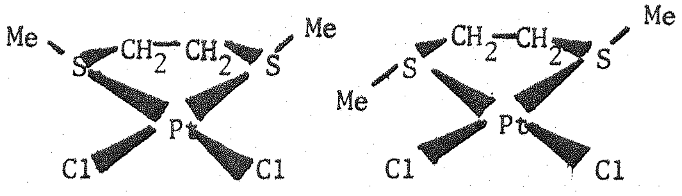
The exchange processes between the free and coordinated ligands in the EEt_2-$M(EEt_2)_2X_2$ systems are fast in each case except for SEt_2 and $[Pt(SEt_2)_2X_2]$ [101]. The rate of ligand exchange decreases in the order:

$TeEt_2 >> SeEt_2 > SEt_2$ and Pd > Pt.

The faster rates here may reflect stabilisation of the 5-coordinate intermediates. This could be due to the lower basicity of the ligand atoms or to better π-back bonding. The ligand exchange at Pd(II) being faster than at Pt(II) is in accord with the general increased lability of the lighter metal atom in associative processes of this type.

Two coalescence temperatures may be observed, one due to ligand exchange which is concentration dependent and one due to chalcogen inversion which is concentration independent.

Chelating ligands are often used in sulphur-inversion studies in order to eliminate any possible complications due to cis/trans isomerism [109,111]. However, the pyramidal conformation at the sulphur atoms leads to it being a centre of chirality which generally results in various enantiomeric forms being present at low temperatures. See Figure 1.4.



Meso DL

$[Pt(MeSCH_2CH_2SMe)Cl_2]$

Figure 1.4

At higher temperatures there is rapid interconversion of these isomers and averaged spectra result. In these cis-type complexes the rate of inversion will increase as the trans influence of X in $[M(\overset{\frown}{S\,S})X_2]$, where X = halogen and M = Pd, Pt, increases.

Cross et al [103] and Hunter et al [111-113] have considered the possibility of the coalescence phenomena being due to ring reversal but the final conclusion of the latter was that it was due to configurational inversion at the chalcogen atoms.

Abel et al [108] has considered the effects of varying the ligand ring size upon the inversion barrier at sulphur in the complexes trans-$[MX_2\{S(CR_2)_n\}_2]$. The pyramidal inversion energies are very dependent upon the ligand ring size. Five and six-membered rings give values comparable to complexes of linear sulphides whereas four-membered rings show considerable heightening of the sulphur inversion barrier. The three-membered rings show no inversion up to the temperature where decomposition commences.

In open-chain dialkyl sulphides the CSC angle is approximately tetrahedral, but in the inversion transition state this angle becomes ideally 120°. Approach to such a CSC transition geometry will be severely restricted for three-membered ring sulphides (ground state CSC angle $\sim$ 66°) and difficult for four-membered rings (CSC angle $\sim$ 80°). Five and six-membered are much more able to accommodate the changes required in going from the ground to the transition state however.

The barrier energies also show a gradual decrease in the order:

$Cl > Br > I$

A more pronounced effect would be expected to be seen in the analogous cis-complexes where the trans influence would be operating [105,107,109,122].

The corresponding Pd(II) and Pt(II) complexes give higher barrier energies for the latter which is probably due to the greater Pt-sulphur bond strength.

1.16 THIOETHER COMPLEXES OF THE OTHER TRANSITION METAL IONS

A review by S E Livingstone [123] gives an outline of some of the thioether, selenoether and telluroether complexes of the transition metal ions. A further set of references cover most of the other work achieved in this area apart from the group VII transition metal ions [94-96,124-135].

It is generally the more class 'b' metal ions which will form the greatest range of thioether complexes.

Table 1.4 displays some of the thioether complexes of the group VIII transition metal ions apart from palladium(II) and platinum(II).

Table 1.4 Some Ruthenium, Osmium, Rhodium, Iridium and Platinum IV Thioether Complexes

Metal Ion	Complexes	Ligand	Comments	Ref
Ru(III)	mer[RuL_3X_3] X = halogen	S(monodentate)	The thioethers are not strongly bound and are completely displaced by pyridine, aniline or acetonitrile	[98, 136, 137]
	[$RuL_{1.5}Cl_3$]	SS(bidentate)		
Ru(II)	trans-[RuL_2X_2]			
	[$RuLCl_3$]	SSS(tridentate)		
Ru(III)	[$RuLCl_3$] (R=Me,ϕ) [$RuL_{1.5}Cl_3$] (R=Me,Et) [RuL_2Cl_3] (R=ϕ)	$RS(CH_2)_2SR$; R=Me, ϕ	These ligands usually adopt the gauche ie chelating form, although some bridging trans examples are known when R=Me	[138, 139]
	[NMe_4][$RuLCl_4$] [$As\phi_4$][$RuLCl_4$].Me_2CO	$MeS(CH_2)_2SMe$		[140]
Os(IV)	[$OsLCl_4$]	(i) $RS(CH_2)_2SR$ (ii) RSCH=CHSR (iii) o-$C_6H_4(SR)_2$; R = Me, ϕ		[140]
	[$OsLBr_4$]	(i) $MeS(CH_2)_2SMe$ (ii) MeSCH=CHSMe		
Rh(III)	[$RhLCl_3$]$_n$	(i) $MeS(CH_2)_2SMe$ (ii) $\phi S(CH_2)_2S\phi$	Complexes of (i) probably consist of halogen-bridged dimers and (ii) trans pseudooctahedral structures. The Rh-S bonds can readily be broken by tertiary amines.	[141]
	[RhL_2X_2]$^+Y^-$ X=Cl,Br;Y=Cl,ClO_4, ½S_2O_8,PF_6,$B\phi_4$			
	[NEt_4][$RhLCl_4$]	(i) $MeS(CH_2)_2SMe$		[140]
	mer-[RhL_3Cl_3] R=Me,Et,Pr^n, Bu^n	SR(ϕ)		[142]
	fac-[RhL_3Cl_3] R=Et.Pr^n.Bu^n			
	[RhL_3X_3] X=Cl,Br,I	(i) SEt_2 (ii) SMe_2	In hot ethanol complexes of (i) lose one molecule of SEt_2 ligand to give [$Rh(SEt_2)_2X_3$] NMR studies are given in reference [145]	[50, 143, 144]

/continued.....

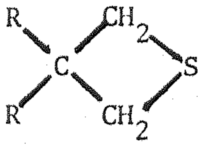
Table 1.4 continued.....

	$Rh_4L_3X_{12}$	L_I	[146]
	Rh_3LCl_9	L_I; n=3	
Ir(III)	*fac*-[IrL_3Cl_3]	SEt_2	[146]
	[IrL_4Cl_2][IrL_2Cl_4]		
	cis/*trans*-[IrL_2Cl_4]	SMe_2	[140]
Ir(IV)	[$IrLCl_4$]	(i) $RS(CH_2)_nSR$(n=2,3) (ii) *o*-$C_6H_4(SR)_2$ (iii) *cis*-RSCH=CHSR; R = Me, ϕ	[140]
Ir(III)	[$IrLCl_3$]$_n$	$MeS(CH_2)_2SMe$	[140]
	[NMe_4][$IrLCl_4$]	$MeS(CH_2)_2SMe$ $\phi S(CH_2)_3S\phi$	
	[NMe_4][$IrLBr_4$]	$MeS(CH_2)_2SMe$	
Ir(III)	[NMe_4]*cis*/*trans*-[IrL_2Cl_4]	SMe_2	
	[NMe_4]*cis*-[IrL_2Cl_4]	$S\phi_2$	
	[NMe_4]$_2$[$IrLCl_5$]	$S\phi_2$	
Pt(IV)	[$PtLX_4$] X=Cl,Br	$RS(CH_2)_2SR$ $MeS(CH_2)_3SR$ *cis*-RSCH=CHSR *o*-$C_6H_4(SR)_2$; R=Me,ϕ	[140]
	[$PtLX_4$].CH_2Cl_2 X=Cl,Br	$\phi S(CH_2)_3S\phi$	
	[$PtLI_4$]	$MeS(CH_2)_nSMe$ n=2,3	

1.17 THE SYNTHESIS OF SOME THIOETHER LIGANDS

Monodentate Thioethers [147,148]

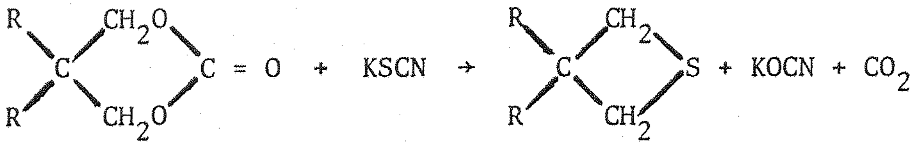
1. Thietanes



[147]

These are prepared by heating 1,3-dioxan-2-ones with dry potassium thiocyanate in the absence of solvent.

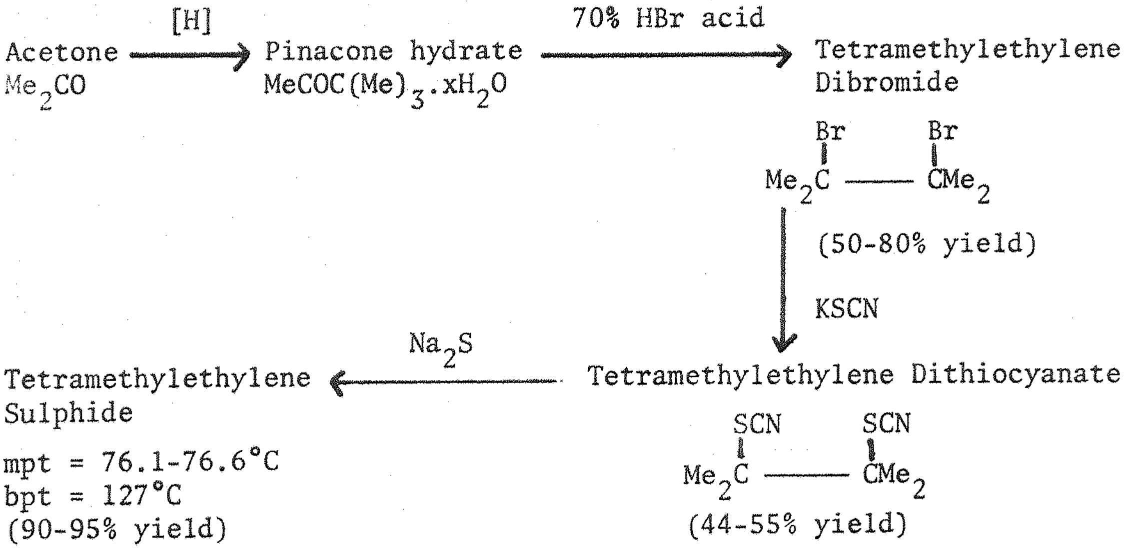
i.e.



2. Tetramethylethylene sulphide

[148]

This ligand is prepared by the following steps:



Acetone Me_2CO $\xrightarrow{[H]}$ Pinacone hydrate $MeCOC(Me)_3.xH_2O$ $\xrightarrow{70\%\ HBr\ acid}$ Tetramethylethylene Dibromide

$Me_2C(Br)-C(Br)Me_2$

(50-80% yield)

$\downarrow$ KSCN

Tetramethylethylene Dithiocyanate

$Me_2C(SCN)-C(SCN)Me_2$

(44-55% yield)

$\xrightarrow{Na_2S}$ Tetramethylethylene Sulphide

mpt = 76.1-76.6°C
bpt = 127°C
(90-95% yield)

Other cyclic ligands of this type have been prepared similarly.

Bidentate Thioethers

The general principle adopted in the preparation of these bidentate and also multidentate thioether ligands is shown in the following reaction scheme:

$$\mathrm{RSH} \xrightarrow[\mathrm{M(Na,Cu)}]{} \mathrm{RSM} \xrightarrow[\substack{\mathrm{X(CH_2)_nX;} \\ \mathrm{X\ =\ Cl,Br}}]{} \mathrm{RS(CH_2)_nSR}$$

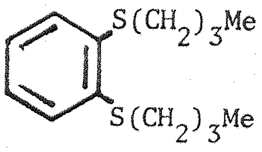
These reactions are carried out under a nitrogen atmosphere. The thioether products are generally air-stable and possess unpleasant odours. Some examples are now quoted:

3. 1,2-Bis(methylthio)ethane [97]

$$\underset{\text{(methanethiol)}}{\mathrm{MeSH}} \xrightarrow{\mathrm{NaOEt}} \mathrm{MeSNa} \xrightarrow{\mathrm{Br(CH_2)_2Br}} \mathrm{MeS(CH_2)_2SMe}$$

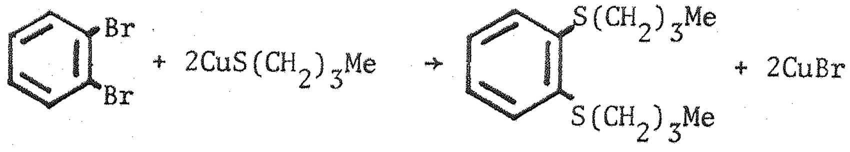
bpt = 181.5-183.5°C
(Yield = 83%)

4. 1,2-Bis(n-butylthio)benzene [149]



This is prepared in two steps:

(i) $\mathrm{2Me(CH_2)_3SH + Cu_2O \rightarrow 2Me(CH_2)_3SCu + H_2O}$

(ii)


(i) The butanethiol and cuprous oxide mixture are refluxed in 95% ethanol until the white cuprous product is obtained. The latter is washed with 95% ethanol and vacuum dried. The yield is quantitative.

(ii) Cuprous-n-butylsulphide (0.55 mol) is added to a solution of 1,2-dibromobenzene (0.25 mol) in quinoline (250 cm^3) and pyridine (80 cm^3). The mixture is stirred, heated under reflux (a 150-170°C pot temperature is required for the maximum yield) for 3.5 hours. A homogeneous solution in fact forms after only ten minutes. The resulting mixture is hydrolysed using hydrochloric acid and stirred. The organic layer is separated from the aqueous and the aqueous layer further extracted using diethyl ether. The combined diethyl ether extract is washed twice with 100 cm^3 of 10% hydrochloric acid and twice with 100 cm^3 of concentrated ammonia. The total organic layer is then dried over potassium carbonate. The diethyl ether is distilled off leaving a brown oil. A pale orange oil results upon vacuum distillation. Bpt = 123-124°C/0.3 mm Hg. Yield = 73-87%.

This procedure has been used to synthesise the following ligands also:

5. 1,4-Bis(n-butylthio)benzene [149] is prepared from p-dibromobenzene and cuprous-n-butylsulphide. The product is a pale yellow oil. Bpt = 142°C/0.5 mm Hg. Yield = 68-74%.

6. 1,2-Bis(phenylthio)benzene [149] is prepared from o-dibromobenzene and cuprous phenylsulphide. The product is a white crystalline solid. Mpt = 42.5-44.5°C. Bpt = 190°C/1 mm Hg. Yield = 83-89%. This ligand can also be prepared from o-dichlorobenzene and cuprous phenylsulphide. Yield = 58-71%.

Cuprous phenylsulphide is prepared in a similar manner to the n-butyl compound.

i.e.

$$\underset{\text{(freshly prepared)}}{Cu_2O} + \underset{\text{benzenethiol}}{\phi SH} \xrightarrow{\text{reflux 2 hours in 95\% ethanol}} \underset{\text{yellow cuprous phenylsulphide}}{CuS\phi}$$

Chloro-compounds can be used in place of bromo-compounds for the reaction with cuprous phenylsulphide but if so a higher reaction time is required, ca 24 hours. In addition the necessary pot temperature would be achieved by using a mixture of quinoline (350 cm^3) and pyridine (8 cm^3) as solvents. A large excess of cuprous phenylsulphide may also be advantageous.

Unfortunately the aromatic chloro compounds cannot be used for reactions with aliphatic cuprous sulphides.

7. 1,4-Bis(phenylthio)benzene [149] is also prepared from the p-dibromo or p-dichlorobenzene and cuprous phenylsulphide using a mixture of quinoline and pyridine as solvent. This has also been prepared from p-dibromobenzene or p-bromophenyl phenyl sulphide and lead phenylsulphide and from diazotised 4-aminophenyl phenyl sulphide and sodium phenylsulphide.

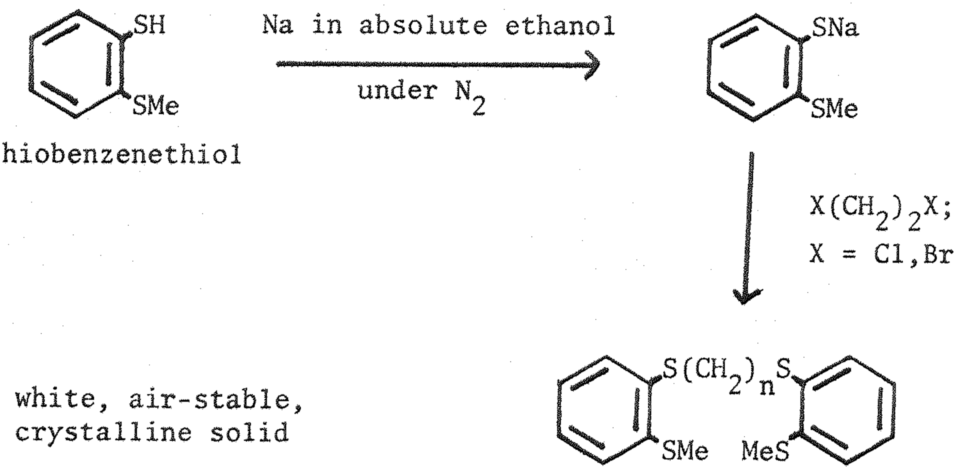
Tridentate Thioethers [93]

8. 2,4,6-Trithio-n-heptane $(MeSCH_2)_2S$ is prepared from a solution of sodium methoxide, methanethiol and 1,3-bis(bromomethylene)sulphide. The ligand is then vacuum distilled. Bpt = 41-44°C/0.3 mm Hg. Yield = 82%.

This general method has been applied to the preparation of the other ligands $(RSCH_2)_2S$ where R = Et, Bu^n, ϕ, ϕCH_2.

Tetradentate Ligands

9. Bis(o-methylthiophenyl)alkanes [150]



o-methylthiobenzenethiol

white, air-stable,
crystalline solid

When n = 2, i.e. 1,2-bis(*o*-methylthiophenylthio)ethane, mpt = 99.5°C
n = 3, i.e. 1,3-bis(*o*-methylthiophenylthio)propane, mpt = 78°C
n = 4, i.e. 1,4-bis(*o*-methylthiophenylthio)butane, mpt = 108°C

Nmr data for these three ligands is found in reference [95] and mass spectral data in reference [151].

The ligands containing a double bond, e.g. cis-1,2-bis(*o*-methylthiophenylthio)ethylene are prepared similarly using cis-XCH=CHX instead of $X(CH_2)_nX$ [96][151].

10. Bis(*o*-methylthioalkylthio)alkanes [95]

i.e. $MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$

Sodium methylsulphide is reacted with the chloroalcohol in absolute ethanol, and the resulting hydroxyalkylmethylsulphide is chlorinated using thionyl chloride in dry chloroform, yielding the toxic chloroalkylmethylsulphide. The disodium salt of the alkanedithiol is prepared in absolute ethanol, and to this is added the chloroalkylmethylsulphide.

i.e.

$$\begin{tikzcd}
MeSNa + Cl(CH_2)_nOH \arrow[r] & MeS(CH_2)_nOH \arrow[d, "SOCl_2"] \\
 & MeS(CH_2)_nCl \arrow[d, "NaS(CH_2)_mSNa"] \\
 & MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe
\end{tikzcd}$$

When n = 2 and m = 3, i.e. 1,3-bis(2-methylthioethylthio)propane, the yield is 87% and when n = 2 and m = 2, i.e. 1,2-bis(2-methylthioethylthio)ethane the yield is 70%.

The nmr data for some of these ligands is found in reference [95] and the mass spectral data in reference [151]. The synthesis of the analogous 1,3-bis(methylselenoethylseleno)propane is found in reference [152].

Some other thioether ligand syntheses and mass spectral data are found in references [153] and [154].

1.2 EXPERIMENTAL SECTION

1.21 THE PREPARATION OF A SERIES OF DITHIOETHER LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES

1.211 Dithioether Ligands

The following ligands were synthesised:

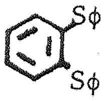
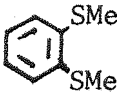
1. 1,2-Bis(phenylthio)ethane, $\phi S(CH_2)_2S\phi$.
2. 1,3-Bis(phenylthio)propane, $\phi S(CH_2)_3S\phi$.
3. 1,6-Bis(phenylthio)hexane, $\phi S(CH_2)_6S\phi$.
4. 1,8-Bis(phenylthio)octane, $\phi S(CH_2)_8S\phi$.
5. 1,12-Bis(phenylthio)dodecane, $\phi S(CH_2)_{12}S\phi$.
6. 1,2-Bis(methylthio)ethane, $MeS(CH_2)_2SMe$.
7. 1,3-Bis(methylthio)propane, $MeS(CH_2)_3SMe$.
8. Cis-1,2-bis(phenylthio)ethylene, cis-$\phi SCH{=}CHS\phi$.
9. Cis-1,2-bis(methylthio)ethylene, cis-$MeSCH{=}CHSMe$.
10. 1,2-Bis(phenylthio)benzene, 
11. 1,2-Bis(methylthio)benzene, 
12. Bis(phenylthio)methane, $\phi SCH_2S\phi$.
13. Bis(methylthio)methane, $MeSCH_2SMe$.

Table 1.5 gives yields, melting points, carbon and hydrogen analyses, and ^1H nmr data for the ligands.

1. 1,2-Bis(phenylthio)ethane

The apparatus that was used in this preparation and in all the others consisted of a one litre, three-necked, round-bottomed quickfit flask fitted with a nitrogen inlet, a mechanical stirrer and a reflux condenser.

Sodium (4.6 g; 0.2 g atom) was dissolved in absolute ethanol (500 cm^3) under a dry dinitrogen atmosphere. To this solution of sodium ethoxide, benzenethiol (22.0 g, 0.2 mol) was added and the mixture stirred for thirty minutes. 1,2-dichloroethane (9.9 g, 0.1 mol) was added dropwise and the solution refluxed for two hours. (The reflux mixture had a pale yellow colouration). The ethanol was then removed on a rotary evaporator and the residue extracted with dichloromethane (2 x 200 cm^3). The sodium chloride was then removed by filtration and the filtrate evaporated nearly to dryness. The resulting oil was dissolved in ethanol (100 cm^3) and on standing at 0°C deposited the ligand as white needles. This product had a sickly irritating odour. The reaction sequence is:

(i) $EtOH + Na \rightarrow NaOEt + \frac{1}{2}H_2$
(ii) $NaOEt + \phi SH \rightarrow NaS\phi + EtOH$
(iii) $2NaS\phi + Cl(CH_2)_2Cl \rightarrow \phi S(CH_2)_2S\phi + 2NaCl$

The following ligands were all prepared by the same method as ligand 1. The products all being white solids except for ligand number two which is an oil.

2. 1,3-Bis(phenylthio)propane
3. 1,6-Bis(phenylthio)hexane
4. 1,8-Bis(phenylthio)octane
5. 1,12-Bis(phenylthio)dodecane
12. Bis(phenylthio)methane.

6. <u>1,2-Bis(methylthio)ethane</u> (2,5-dithiahexane) [79]

Ethane-1,2-dithiol (25.0 g, 0.26 mol) was dissolved in ethanol (250 cm^3) under nitrogen, and sodium (12.0 g, 0.52 mol) added. When the sodium had dissolved the mixture was heated to reflux and iodomethane (74.0 g, 0.52 mol) was added dropwise. The ethanol was distilled off and the residue fractionated in vacuo.

Reaction sequence is:

$$\begin{tikzcd}
HS(CH_2)_2SH + 2Na \arrow[r, "\text{ethanol}/N_2"'] & NaS(CH_2)_2SNa \arrow[d, "2MeI"] \\
& MeS(CH_2)_2SMe + 2NaI
\end{tikzcd}$$

The ligand 1,3-bis(methylthio)propane was similarly prepared.

13. Bis(methylthio)methane [155]

This ligand was prepared by the method of Brandsma [155] from methanethiol and formaldehyde in aqueous hydrochloric acid.

$$HCHO + MeSH \xrightarrow[25\%\ HCl]{40\text{-}50^\circ C} MeSCH_2SMe$$

8. Cis-1,2-bis(phenylthio)ethylene [124]

A solution of sodium phenylsulphide was prepared from sodium (8.0 g, 0.35 g atom), benzenethiol (22.0 g, 0.2 mol) and ethanol (500 cm^3). The solution was heated to reflux and treated with cis-1,2-dichloroethylene (10.4 g, 0.1 mol) and refluxed for a further six hours. The ethanol was distilled off under a water pump vacuum and the residue then treated with water (200 cm^3) and diethylether (3 x 100 cm^3). The ether extract was then dried over anhydrous sodium sulphate. The latter was filtered off and the ether solution evaporated. An oil resulted and this was recrystallised from ethanol at 0°C giving yellowish crystals.

9. Cis-1,2-bis(methylthio)ethylene

Sodium (14.0 g, 0.62 g atom) was dissolved in ethanol (200 cm^3) under nitrogen and the solution cooled to -10°C. Methanethiol (24.0 g, 0.5 mol) was added and the mixture stirred at this temperature for one hour. It was then treated with cis-1,2-dichloroethene (24.0 g, 0.25 mol) and heated under reflux for seven hours. The ethanol was distilled off and the residue fractionated *in vacuo*.

10. 1,2-Bis(phenylthio)benzene

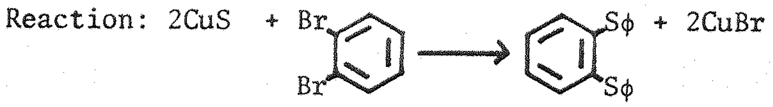
This synthesis involves two stages.

(a) The synthesis of copper phenylsulphide, $CuS\phi$.

Benzenethiol (50 g, 0.46 mol) was dissolved in ethanol (700 cm^3) under a dry nitrogen atmosphere and freshly prepared copper(I) oxide (36 g, 0.25 mol) added [149]. The mixture was refluxed and stirred until the orange-red colour of the copper(I) oxide had been replaced by the yellow colour of copper phenylsulphide. This reaction proceeded rapidly and two hours were sufficient to ensure complete reaction. The solution was cooled, the yellow precipitate filtered off, washed with ethanol and vacuum dried. The yield was essentially quantitative.

Reaction: $2\phi SH + Cu_2O \longrightarrow \underset{\text{yellow}}{2CuS\phi} + H_2O$

(b) Copper phenylsulphide (70.0 g, 0.4 mol) was suspended in a mixture of quinoline (300 cm^3) and pyridine (20 cm^3) and treated with o-dibromobenzene (42.0 g, 0.18 mol) in a dry nitrogen atmosphere. The mixture was then heated under reflux for 16 hours. The pot temperature was maintained between 130 and 150°C to ensure a maximum yield. The mixture was cooled to 100°C and slowly poured into a mixture of ice (1500 g) and concentrated hydrochloric acid (400 cm^3). Two layers separated and the upper aqueous layer was decanted off to leave a dark brown sticky solid. The aqueous layer was extracted with diethyl ether (2 x 200 cm^3), the extract added to the residue and the latter mixture stirred vigorously. The combined ether extracts were washed successively with 10% aqueous HCl, water, 10% aqueous ammonia, water and then dried over potassium carbonate. (The acid was used to remove the quinoline and pyridine, the ammonia to remove excess copper salt and the water to remove all the ionic species present). The diethyl ether was distilled off and the residual oil heated to 175°C/2 mm Hg until all the volatiles were distilled (mainly ϕ_2S impurity). The residue was dissolved in ethanol (20 cm^3) and on standing white crystals were deposited. (If there was any contamination with o-dibromobenzene starting material then crystals were difficult to obtain).



1,2-bis(phenylthio)benzene

11. 1,2-Bis(methylthio)benzene [150]

O-methylthiobenzenethiol (78.0 g, 0.5 mol) [150] was dissolved in ethanol (250cm^3) and sodium (12.0 g, 0.52 g atom) added. The mixture was heated to reflux and iodomethane (71.0 g, 0.5 mol) added dropwise. After a further one hour under reflux the solvent was distilled off and the residue fractionated.

1.212 THE PALLADIUM(II) AND PLATINUM(II) HALIDE COMPLEXES OF THE DITHIOETHER LIGANDS

1. Dichloro[1,2-bis(phenylthio)ethane]palladium(II)

i.e. $[Pd[\phi S(CH_2)_2S\phi]Cl_2]$

Sodium tetrachloropalladate(II) (0.3 g, 1 mmol) was dissolved in ethanol (15 cm^3) and the solution filtered. The ligand (0.24 g, 1 mmol) in dichloromethane (5 cm^3) was added and the mixture refluxed for three hours during which any initial precipitate redissolved. The resulting deep orange solution was concentrated and yielded an orange solid which was filtered off, washed with ethanol and ether and dried in vacuo. The yield was 78%.

The corresponding bromo and iodo palladium(II) complexes were similarly prepared except that the Na_2PdCl_4 solution was stirred with a five-fold excess of LiX (X = Br, I) for three hours prior to the addition of the ligand. The yields were 70-85%.

2. Dichloro[1,2-bis(phenylthio)ethane]platinum(II)

i.e. $[Pt(\phi S(CH_2)_2S\phi)Cl_2]$

Potassium tetrachloroplatinate(II) (0.4 g, 1 mmol) in water (10cm^3) and the ligand (0.24 g, 1 mmol) in dichloromethane (10 cm^3) were mixed and sufficient ethanol added to produce a homogeneous solution. The mixture was heated for four hours, resulting in an initial pink precipitate which slowly redissolved to give a pale yellow solution. Concentration of the solution gave a yellow solid. The yield was 65%.

The $[PtLX_2]$ (X = Br, I; L = $\phi S(CH_2)_2S\phi$) complexes were prepared similarly to the above palladium(II) complexes.

The palladium(II) and platinum(II) complexes of the ligands 1,3-bis(phenylthio)propane, 1,2-bis(methylthio)ethane, 1,3-bis(methylthio) propane, 1,2-bis(phenylthio)benzene, 1,2-bis(methylthio)benzene, cis-1,2-bis(phenylthio)ethylene and cis-1,2-bis(methylthio)ethylene were prepared by the above methods.

3. Dichloro[1,6-bis(phenylthio)hexane]palladium(II)

Sodium tetrachloropalladate(II) (0.3 g, 1 mmol) was dissolved in ethanol (20 cm^3) and the solution filtered into a vigorously stirred solution of the ligand (0.3 g, 1 mmol) in ethanol (50 cm^3). After one hour the orange precipitate was filtered off, washed with ethanol and diethyl ether and dried in vacuo. The yield was 90%.

The other Pd(II) complexes of $\phi S(CH_2)_nS\phi$ (n = 6,8) were prepared similarly.

4. Dichloro[1,12-bis(phenylthio)dodecane]palladium(II)

Sodium tetrachloropalladate(II) (0.3 g, 1 mmol) was dissolved in ethanol (20 cm^3), filtered and added dropwise to a solution of the ligand (0.38 g, 1 mmol) in dichloromethane (50 cm^3). The resulting solution was heated to reflux, filtered from the small amount of yellow precipitate and evaporated to dryness. The remaining orange oil was dissolved in dichloromethane, filtered and concentrated to ∿ 10 cm^3. On standing for two days at 0°C an orange solid precipitated. The yield was 80%.

The above isolated complexes and their colours are listed in Table 1.6. This table also gives molecular weight and infrared spectral data.

5. Dichlorodi(bis(phenylthio)methane)palladium(II)

A solution of the ligand (0.46 g, 2mmol) in dichloromethane (20 cm^3) was treated dropwise with a solution of sodium tetrachloropalladate(II) (0.3 g, 1 mmol) in ethanol (15 cm^3) and the mixture stirred at room temperature for two hours. The solution was evaporated to dryness, extracted with chloroform, filtered and concentrated to a small volume. A yellow solid resulted which was then filtered and dried in vacuo. The yield was 0.38 g, (i.e. 60%).

The other $Pd(\phi SCH_2S\phi)_2X_2$ (X = Br, I), and $Pt(\phi SCH_2S\phi)_2X_2$ (X = Cl, Br, I) complexes were prepared similarly. In the case of the platinum complexes potassium tetrachloroplatinate(II) in aqueous ethanol was used as starting material.

6. Dichloro(bis(phenylthio)methane)palladium(II)

A solution of the ligand (0.23 g, 1 mmol) in ethanol (10 cm^3) was added slowly to a vigorously stirred solution of sodium tetrachloropalladate(II) (0.3 g, 1 mmol) in ethanol (20 cm^3), and the mixture stirred for one hour. A brown-orange precipitate was collected, washed with ethanol and diethyl ether, and then dried in vacuo. The yield was 0.37 g (i.e. 90%). The same material was also obtained from $[PdCl_2(\phi CN)_2]$ and the ligand in a 1:1 mole ratio in chloroform.

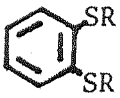
1.22 THE DITHIOETHER LIGANDS

A series of dithioether ligands have been synthesised. The systematic changes in the ligand structure take the form of (i) alkane, alkene or phenyl-backbone; (ii) differing R terminal groups.

The ligands synthesised were of the following types:

(a) $RS(CH_2)_nSR$ ($R = \phi$, Me; $n = 2,3,6,8,12$)

(b) cis-RSCH=CHSR ($R = \phi$, Me)

(c)  ($R =$ Me, ϕ)

(d) $RSCH_2SR$ ($R = \phi$, Me)

The alkane-backboned ligands (a), when $R = \phi$, were prepared from sodium phenylsulphide, $NaS\phi$, and the appropriate α,ω-dihaloalkane with subsequent recrystallisation from ethanol. When R = Me, the ligands were prepared from the appropriate dithiol and iodomethane via the sodium salt. The product was obtained by fractionation in vacuo.

The ligands (b), i.e. the cis-dithioalkenes, [157,158] were obtained stereospecifically from the reaction of cis-1,2-dichloroethylene with sodium alkyl(aryl)sulphide, NaSR, in the presence of sodium ethoxide. The trans-1,2-dichloroethylene however did not react under these conditions. When copper phenylsulphide, $CuS\phi$, was used then the major product was diphenyldisulphide. Although trans-ϕSCH=CHSϕ [157] has been reported to form by distillation under reduced pressure, only a mixture of ϕ_2S, $\phi SS\phi$ and the starting material could be obtained.

The ligand (c), when $R = \phi$, i.e. 1,2-bis(phenylthio)benzene could be obtained in good yield from copper phenylsulphide and o-dibromobenzene in a quinoline/pyridine (20:1) solution [149]. When o-dichlorobenzene was used in place of the bromo-compound a much lower yield was obtained [149]. The product was also contaminated with substantial amounts of (o-chlorophenyl)phenylthioether, o-ϕSC_6H_4Cl, as was shown by the former's microanalysis and mass spectrum. In addition when o-dichlorobenzene was used, a higher pot temperature was required (210-220°C) and a longer reaction time also (24 hours) [149].

The ligand (c), when R = Me, i.e. 1,2-bis(methylthio)benzene was obtained easily from o-methylthiobenzenethiol, i.e. o-$C_6H_4(SMe)(SH)$ [149], sodium ethoxide and iodomethane in ethanol.

The ligand (d) when R = ϕ, was prepared in the same way as the ligands (a). However, when R = Me the ligand was prepared from methanethiol and formaldehyde in aqueous hydrochloric acid [155].

The phenyl-substituted ligands are generally white or yellow solids at room temperature whereas the methyl-substituted ligands are liquids. They are all air-stable and have irritating, unpleasant odours. They are obtained in fairly good yields, their purity being corroborated by their elemental analyses and their mass spectra. Reference [159] contains the mass spectral data of the ligands $\phi S(CH_2)_nS\phi$ (n = 2,3,6,8), cis-$\phi SCH{=}CHS\phi$, o-$C_6H_4(S\phi)_2$, $\phi SCH_2S\phi$ and some of their methyl analogues. The bis(phenylthio)methane ligand and its methyl analogue will be referred to in the following section, 1.25.

Some mass spectral data of the ligand, 1,2-bis(phenylthio)ethane is reported here:

Table 1.7

Mass spectral data of 1,2-bis(phenylthio)ethane

Nominal Mass	Ions
246	$\phi S(CH_2)_2S\phi$ Parent ion M^+
137	$\phi S(CH_2)_2$
123	ϕSCH_2
110	ϕSH
109	ϕS
77	ϕ
65	C_5H_5
28	CH_2CH_2

The values of nominal mass reported here are those which possess the highest intensity peaks, and these could be represented by the fragments given.

The ^1H nmr spectra of the ligands in $CDCl_3$ with a tetramethylsilane (TMS) reference are as expected for the proposed formulae. The ligands containing phenyl groups show a characteristic multiplet at about 7.2 ppm representing the five protons on the ring. The 1,2-bis(phenylthio)ethane ligand, for example, also shows a singlet at 3.1 ppm representing two protons, i.e. the methylene group. The ratio of phenyl protons to methylene protons is $^5/_2$ as would be expected for the $\phi SCH_2CH_2S\phi$ formula. The chemical shifts for the methylene protons which are not directly adjacent to the sulphur atoms are all approximately the same and as a result a complex multiplet is observed in the region 1.2-1.9 δ, e.g. ligands 3-5, see Table 1.5.

1.23 THE PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF THE DITHIOETHERS

The dithioether ligands (L), $\phi S(CH_2)_nS\phi$ (n = 2,3,6,8,12), $MeS(CH_2)_nSMe$ (n = 1,2,3), cis-RSCH=CHSR (R = Me, ϕ) and $\underset{=}{o}$-$C_6H_4(SR)_2$ (R = Me, ϕ) gave halide complexes whose carbon, hydrogen and halogen elemental analyses corresponded to the formulation $[MLX_2]$ (M = Pd(II), Pt(II); L = dithioether; X = halogen). It was not found possible to produce 2:1 (ligand:Pd(Pt)) complexes for the above ligands when X = halide. The lowering of vapour pressure of a 1,2-dichloroethane solution at fixed temperature by the addition of a 1,2-dichloroethane solution of these complexes gave values of molecular weight which corresponded to the latter being monomers [Table 1.6].

Conductivity measurements of 10^{-3} M solutions of the complexes in nitromethane and 1,2-dichloroethane gave molar conductivity values (Λ_M) which were too low for 1:1 electrolytes, i.e. ∿ 10 and ∿ $4\Omega^{-1}cm^{-1}$ mol^{-1} respectively [161].

The above results confirmed the presence therefore of the monomeric $[MLX_2]$ species rather than the ionic $[ML_2][MX_4]$ species with the aforementioned ligands.

In this study complexes of a 2:1 (ligand:Pd(Pt)) ratio were however prepared for the single ligand $\phi SCH_2S\phi$. Previously some 2:1 (ligand:Pd(Pt)) perchlorate complexes, $[ML_2](ClO_4)_2$ have been obtained [162].

A. The complexes of the ligands $RS(CH_2)_2SR$ (n = 2,3; R = Me, ϕ), cis-RSCH=CHSR (R = Me, ϕ) and o-$C_6H_4(SR)_2$ (R = Me, ϕ)

The reaction of the above ligands with potassium chloroplatinate (II) in water, K_2PtCl_4, initially produces pink precipitates. These have previously been observed in the platinum(II) chemistry of other thioether ligands and also of the group VB ligands [83,84,161,163,164]. They are 'Magnus' type salts, i.e. $[PtL_2][PtX_4]$ (X = halogen; L = dithioether) [1,85,165]. This result could be rationalised in terms of the sulphur in the dithioether having a greater trans effect than the chloride (i.e. X = Cl) and so the dithioether attacks the first formed $[PtLCl_2]$ faster than the $[PtCl_4]^{2-}$ anions. The $[PtL_2][PtCl_4]$ salt is insoluble and thus precipitates out.

When these complexes are heated the solids redissolve to give pale yellow solutions from which the $[PtLCl_2]$ complexes can be obtained by evaporation. The bromo- and iodo- complexes are similarly formed from $[PtX_4]^{2-}$ (X = Br, I).

The reactions of the dithioethers with $[PdX_4]^{2-}$ (X = Cl, Br, I) also proceed via $[PdL_2][PdX_4]$ but these intermediates are much less stable than their platinum(II) analogues and easily rearrange to the monomeric $[PdLX_2]$ complexes.

The ligands in this section possess short backbones and because of this a trans configuration in the $[MLX_2]$ complexes is not possible. The gauche, i.e. cis, conformation of dithioethers has been previously observed in complexes containing the ligand $MeS(CH_2)_2SMe$ (dithiahexane) [142,166].

The far infrared spectra (i.e. the range 400-150 cm^{-1}) for these complexes show two intense and well defined bands which have been assigned as metal-halogen stretches. The fact that there are two metal halide stretching frequencies and also that these occur over a wide range, the frequencies varying with the ligand for each cis-$[MLX_2]$

complex, seems consistent with previous observations in cis-complexes.

e.g. <u>cis</u>-$[PdLCl_2]$ $\nu(Pd-Cl) = 269-335\ cm^{-1}$ [66]

and for comparison <u>trans</u>-$[PdLCl_2]$ $\nu(Pd-Cl) = 353-359\ cm^{-1}$ [66]

A cis structure would have C_{2v} symmetry and this would imply that there were two $\nu(M-X)$, $A_1 + B_1$, and two $\nu(M-S)$, $A_1 + B_1$, infrared active vibrations. A trans complex would possess D_{2h} symmetry and only one infrared active metal-halogen vibration and one infrared active metal-sulphur vibration. The infrared active vibrations in the cis-complexes would also be expected to be affected by the ligands which were in the trans positions and this would therefore lead to a range of frequencies.

The following table shows the metal-halogen vibrational modes of some cis-complexes of the palladium(II) and platinum(II) halides with some group VB and VIB ligands.

<u>Table 1.8</u>

<u>Metal-halogen vibrational modes of some cis-palladium(II) halide complexes</u>

Complex	$\nu(M-X)$ (cm^{-1})	Reference
$[Pd(C_2H_4(NH_2)_2)Cl_2]$	306s 272m	[66]
$[Pd(Me_2N(CH_2)_2NHMe)Cl_2]$	331s 321s	[66]
$[Pt(PEt_3)_2Cl_2]$	305s 283s	[66]
$[Pd(\underline{o}-C_6H_4(P\phi_2)_2)Cl_2]$	312 288	[167]
$[Pd(AsMe_3)_2Cl_2]$	316s 298.5s	[66]
$[Pt(AsMe_3)_2Cl_2]$	312.5s 293s	[66]
$[Pd(MeS(CH_2)_2SMe)Cl_2]$	314.5s 296s	[66]
$[Pd(EtS(CH_2)_2SEt)Cl_2]$	322.6 309.6	[66]
$[Pt(SEt_2)_2Cl_2]$	330vs 318.2s	[12]
$[Pt(SEt_2)_2Br_2]$	254s 226.2s	[12]
$[Pd(EtS(CH_2)_2SEt)Cl_2]$	323s 303sh 308m	[68]

Values for metal-halogen stretching frequencies in dithioether complexes are found in references [12,53,54,66,68]. The values of metal-halogen stretching frequencies obtained in this study fall into the ranges for cis-MX_2 groups given in the above table and on page 16.

The metal-chlorine stretching frequencies of $[Pd(MeS(CH_2)_2SMe)Cl_2)$ shown in Table 1.6 agree closely with the literature values given in Table 1.8 [66].

The complexes of the ligand, $\phi S(CH_2)_nS\phi$ (n = 2,3) in this study had metal-halogen stretching frequencies which correspond well with the other complexes in section A (see Table 1.6) but which differ considerably from the literature values shown in Table 1.9 [86]. Reference [168] quotes bands at 324(s) and 308(s) for $[Pd(\phi S(CH_2)_2S\phi)Cl_2]$ which are intermediate between these two. Such non-coincidence can occur when different synthetic methods and different solvents of crystallisation are employed. Three forms of cis-$[Pt(SMe_2)_2Cl_2]$ are known to exist with distinctly different vibrational spectra [61].

Table 1.9

The infrared spectral data of some Pd(II) and Pt(II) halide complexes containing the $\phi S(CH_2)_nS\phi$ (n=2,3) ligands

Complex	ν(M-X) (cm^{-1})	Reference
$[Pd(\phi S(CH_2)_2S\phi)Cl_2]$	277vs	[86]
$[Pd(\phi S(CH_2)_3S\phi)Cl_2]$	278s 262s	[86]
$[Pt(\phi S(CH_2)_3S\phi)Cl_2]$	317vs, 312.5vs	[86]
$[Pt(\phi S(CH_2)_3S\phi)Br_2]$	266.5m	[86]

The metal-halogen stretching frequencies of the $[MLX_2]$ complexes in this section show only small and irregular changes when the metal or ligand is varied. These vibrations are probably coupled with others and as a result there is no discernable trend.

A comparison of the data given in Table 1.8 for the corresponding ditertiary amine, phosphine, arsine and thioether complexes shows the trend in ν(M-X) with trans donor as $P < As < S < N$. This is consistent with the trans influence series [2].

Generally it has been observed that metal-halogen bands are more well defined and more intense than the metal-ligand bands. In these complexes the bands which have been allocated to the metal-sulphur bonds appeared as moderately intense absorptions in the range 290-350 cm^{-1}. The bands were often broad and had ill-defined maxima. They were probably extensively coupled to other vibrational modes and as a result of which how they varied with metal, ligand and halogen was difficult to interpret. They are therefore not quoted in Table 1.6.

It was noticed that the ν(Pt-S) had similar values to the ν(Pd-S) for the same ligands. The former would have been expected to be lower due to the greater mass of the platinum. This result supported previous observations that the bond strengths of Pt-S > Pd-S [53].

The electronic spectra were recorded in chloroform and/or N,N-dimethylformamide and were characteristic of planar d^8 systems.

The $[MX_4]^{2-}$ ions have previously been much studied [169-171] but the $[MLX_2]$ species have received limited study.

In the $[MLX_2]$ complexes the lower energy moderately intense band was assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition (in D_{4h} symmetry) and the second band at higher energy to $^1A_{1g} \rightarrow {}^1E_g$. The intense absorptions >30,000 cm^{-1}, were thought to be predominantly $S \rightarrow M$ and $X \rightarrow M$ charge transfer transitions.

Weak shoulders were also observed in a few cases on the low energy side of the first 'd-d' band and these were probably transitions to the spin forbidden triplet states.

The solid reflectance spectra were similar generally to the solution spectra. The spin forbidden transitions were more readily observable in the solid state.

The following expected increase in energy of the band maxima was observed:

$I < Br < Cl$ and $\phi S < MeS$ and $Pd(II) < Pt(II)$

The spectrochemical effect of changing the ligand backbone was small. However, the order of increasing energy was o-C_6H_4 < -CH=CH- < $(CH_2)_3$ < $(CH_2)_2$. This order differed from that previously obtained with some group VB donors [172], i.e. o-C_6H_4 < $(CH_2)_2$ < -CH=CH-.

The ligand field of the dithioethers has been compared with the corresponding group VB donors and has been shown to be rather weaker [53,167,172-181].

Table 1.10

Some solid state electronic spectral data for some group VB Palladium(II) and Platinum(II) halide complexes [174,182]

Complex	E_{max} $(cm^{-1}) \times 10^{-3}$
$[Pd(\phi_2P(CH_2)_2P\phi_2)Cl_2]$	28.9, 28.2sh
$[Pd(\phi_2P(CH_2)_2P\phi_2)Br_2]$	28.0
$[Pd(\phi_2As(CH_2)_2As\phi_2)Cl_2]$	27.2
$[Pd(\phi_2As(CH_2)_2As\phi_2)Br_2]$	25.8
$[Pd(\phi_2Sb(CH_2)_3Sb\phi_2)Cl_2]$	32.5, 26.0
$[Pd(\phi_2Sb(CH_2)_3Sb\phi_2)Br_2]$	31.8, 24.5
$[Pd(\phi_2Sb(CH_2)_3Sb\phi_2)I_2]$	31.1, 21.9
$[Pt(\phi_2Sb(CH_2)_3Sb\phi_2)Cl_2]$	∿31.0sh
$[Pt(\phi_2Sb(CH_2)_3Sb\phi_2)Br_2]$	30.0
$[Pt(\phi_2Sb(CH_2)_3Sb\phi_2)I_2]$	25.5
$[Pd(Me_2N(CH_2)_2NMe_2)Cl_2]$	25.1, 21.0sh

The order of increasing ligand strength deduced from the data in Table 1.10 and the analogous group VIB complexes in this study (Table 1.11) can be seen to be:

N < S < Sb < As < P

Venanzi et al [176] deduced a similar order for monodentate ligands but here the positions of antimony and sulphur were reversed.

B. The complexes of the ligands $\phi S(CH_2)_nS\phi$ (n = 6,8)

The longer backboned ligands $\phi S(CH_2)_nS\phi$ (n = 6,8) gave the $[PdLX_2]$ complexes by the reaction of the former with either $Na_2[PdX_4]$ or $[Pd(\phi CN)_2X_2]$ (X = Cl, Br, I). The complexes were insoluble in all solvents examined.

The far infrared spectra of these complexes differed considerably from the $[MLX_2]$ complexes in Section A.

For the two chloro-complexes there were broad absorptions at 320-340 cm^{-1} and single sharp bands at 343 cm^{-1} (n = 6), and 346 cm^{-1} (n = 8). These were assigned as 'ν(Pd-L)' and 'ν(Pd-Cl)' respectively. The single metal-halogen stretching frequency is consistent with a trans structure with D_{2h} symmetry at the metal. Single 'ν(Pd-Cl)', B_{3u}, and 'ν(Pd-L)', B_{2u} vibrations would be expected for this symmetry, [53,61,177]. The bromo and iodo complexes were similarly assigned. (See Table 1.12).

Table 1.12

The palladium(II)-halogen stretching frequencies for the bromo and iodo complexes of the $\phi S(CH_2)_nS\phi$ (n = 6,8) ligands

Complex	ν(Pd-X) cm^{-1}
$[Pd(\phi S(CH_2)_6S\phi)Br_2]$	280
$[Pd(\phi S(CH_2)_6S\phi)I_2]$	205
$[Pd(\phi S(CH_2)_8S\phi)Br_2]$	263
$[Pd(\phi S(CH_2)_8S\phi)I_2]$	218

The $[Pd(\phi S(CH_2)_6S\phi)I_2]$ complex however yielded only weak absorptions in the range 190-230 cm^{-1}. It has previously been shown by Duddel et al [177] that the as ymmetric M-I vibrations may be weak in trans-

$[ML_2I_2]$ complexes (L = monodentate ligand). On the basis of this a weak band at 205 cm^{-1} was assigned as ν(M-I).

The far infrared data implied a trans-MX_2 arrangement in these complexes. This and their insolubility suggested a polymeric structure with bridging dithioether. The other possibility, that of trans chelation by the dithioether, was ruled out by the relatively short interdonor linkage and by the fact that trans-chelated complexes have been found to be highly soluble.

Repeated attempts were made to prepare the platinum(II) analogues. These proved unsuccessful and only produced intractable yellow oils which were moderately soluble in halocarbon solvents. Thin layer chromatography studies suggested that more than one species were present. Cyclic oligomers may in fact be present [178].

The electronic spectra of the solids contained a number of broad intense bands with shoulders at low energy (Table 1.11).

This work on the $[Pd(\phi S(CH_2)_nS\phi)X_2]$ (n = 6,8) complexes has recently been confirmed by Sanger et al [168]. Sanger et al [168] have also prepared the complexes where n = 4 and n = 5 and have concluded that these also are trans structures which are polymeric with bridging dithioether ligands.

C. The complexes of 1,12-bis(phenylthio)dodecane

The $[PdLX_2]$ complexes were prepared by the reaction of the appropriate sodium tetrahalopalladate(II), Na_2PdX_4 (X = Cl, Br) with the ligand in a 1:1 molar ratio in an ethanol/dichloromethane solution.

Initially small quantities of yellow solid precipitated (5% by weight). These were filtered off and the remaining mother liquor evaporated to yield orange-brown complexes in a 70-80% yield (see Table 1.6). Identical products were obtained when $[Pd(\phi CN)_2X_2]$ were used as starting materials.

The $[PtLCl_2]$ complex was prepared similarly. Repeated attempts were made to prepare $[PdLI_2]$ but these produced only black insoluble powders of low (and variable) carbon and hydrogen content. The majority of the ligand was recoverable from the mother liquor.

In the preparation of the $[PdLX_2]$ complexes some insoluble by-products resulted which analysed as $[PdLX_2]$. They are probably oligomeric with bridging dithioether, but this could not be confirmed due to their insolubility.

It was noticed that these dithioether complexes did not sublime in high vacuum unlike the $[Pt(Bu^t{}_2P(CH_2)_{12}PBu^t_2)Cl_2]$ complex [179].

The $[MLX_2]$ complexes were very soluble in halocarbon solvents. Conductivity measurements in 10^{-3} M 1,2-dichloroethane solutions gave values of $\Lambda_M \sim 4\ \Omega^{-1}cm^{-1}mol^{-1}$ indicating that the complexes were non-electrolytes.

The molecular weight determinations of these complexes (see Table 1.6) gave values very close to what would be expected for monomers.

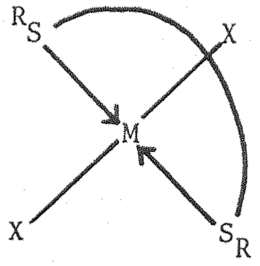
Mass spectra were recorded in an attempt to provide an independent check of the molecular weights. However these only exhibited fragments of low M/e values. This was probably due to S-dealkylation of the ligand.

The far infrared spectra show single 'ν(M-X)' vibrations and these were in the range expected for trans complexes (see page 15). [53,54, 177].

In dichloromethane the electronic spectra of the complexes consisted of very broad intense absorptions at 28000-29000 cm^{-1} with distinct low energy shoulders.

The high solubility and single far infrared metal-halogen stretching frequency indicated a trans configuration. The fact that these complexes were also monomeric implied that the complexes were trans chelated.

i.e.



These complexes were in fact the <u>first</u> reported complexes which contain a trans-chelating bidentate ligand involving sulphur donors.

Several recent studies have reported that bidentate phosphines and arsines with suitably long backbones can chelate trans to square planar

Rh(I), Ir(I), Pd(II) and Pt(II) [178,179,183,184]. Examples of these are the 13 atom ring of $[PtCl_2Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]$ [183], the 12-membered ring of $[PtCl_2(Bu^t{}_2P(CH_2)_9PBu^t{}_2)]$ [183], the 15-membered ring of $[PtCl_2(Bu^t{}_2P(CH_2)_{12}PBu^t{}_2)]$ [184], and the 13-membered ring of $[IrCl(CO)(Bu^t{}_2P(CH_2)_{10}PBu^t{}_2)]$ [184].

The bulky t-butyl group has previously been thought to produce favourable conformational effects which favour the formation of these trans chelating complexes. However, although the presence of bulky substituents, in this case the t-butyl group, may well aid in the isolation of the trans chelates [179] they are not absolutely necessary for the formation of the complexes. Complexes containing ligands with methyl or phenyl groups have been produced providing the backbone length is correct [184]. In addition to the dithioether complexes described in this section the complex [Pd(1,12-bis(dimethylarsino)dodecane)Cl_2] [178,185] is an example of this. The latter trans-chelating complex is prepared in high yield by the reaction of the Na_2PdCl_4 salt with the ligand in an ethanol/dichloromethane mixture.

The fact that such trans chelation occurs suggests that complexes containing trans chelating ligands can be obtained without the presence of any bulky terminal groups.

Attempts have been made to grow crystals of the complexes of the 1,12-bis(phenylthio)dodecane ligand for X-ray studies but these have proved unsuccessful. The fact that it was difficult to isolate solid complexes of this type may well account for the scarcity, until recently, of these trans spanning chelates [178].

D. The complexes of the ligands $RSCH_2SR$ ($R = Me, \phi$)

The reaction of the ligand bis(phenylthio)methane, $\phi SCH_2S\phi$, with sodium tetrahalopalladates(II), Na_2PdX_4 ($X = Cl, Br, I$), in a dichloromethane/ethanol mixture gave complexes of a 2:1 (ligand:metal) stoichiometry, PdL_2X_2 [168]. These complexes were only slightly soluble in chlorocarbons, but in these they were shown to be non-electrolytes and monomers (by molecular weight determinations). The data obtained for all the complexes in Section D is found in Tables 1.13a and b.

The far infrared spectra exhibited only one medium intensity band which was attributed to a palladium-halogen stretching frequency, ν(Pd-X). These bands were identified as the antisymmetric stretches of trans-PdX_2 groups (B_{2u}) [66]. The solid and solution electronic spectra were similar and implied a planar structure.

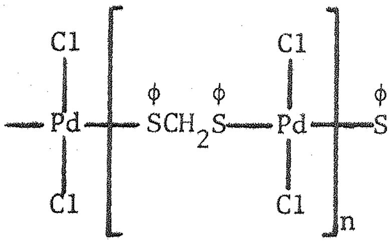
The proton nuclear magnetic resonance spectra in deuterated dimethylsulphoxide displayed only resonances identical with those of the free dithioether ligand. Obviously the solvent must have displaced the ligand from the complexes.

In deuterated chloroform the complexes were not very soluble. However saturated solutions gave proton nuclear magnetic resonance spectra showing only a single methylene resonance which was downfield from that of the free ligand at 4.26δ. It was thought therefore that probably only one isomer was present in solution. It is possible however that a small quantity of a second isomer went undetected due to the poor solubility of the complexes and hence the poor quality spectra obtained.

The above data shows that the complexes PdL_2X_2 (X = Cl, Br, I), are monomeric, contained monodentate dithioether, and were of a trans planar geometry.

Several attempts were made to obtain 1:1 complexes but only one pure sample of the complex of stoichiometry, $Pd(\phi SCH_2S\phi)Cl_2$, resulted. This is an orange-brown powder and was prepared by the reaction of sodium tetrachloropalladate(II) and bis(phenylthio)methane in ethanol in a metal:ligand ratio of 1:∿0.9. The complex however was insoluble in or decomposed by every solvent tried.

The far infrared spectrum of this 1:1 complex displayed a single band at 355 cm^{-1}, assigned as a palladium-chlorine stretching frequency, ν(Pd-Cl). This band is in the range expected for trans-$PdCl_2$ groups [66] (see page 15) which suggested that the structure was similar to that found with the dithioethers of intermediate chain length. A possible structure is shown in Figure 1.3 below.



$$-\overset{Cl}{\underset{Cl}{Pd}}-\left[\overset{\phi}{S}CH_2\overset{\phi}{S}-\overset{Cl}{\underset{Cl}{Pd}}-\right]_n\overset{\phi}{S}$$

Figure 1.4

In the attempts to prepare these 1:1 complexes a number of orange materials were obtained under the various conditions adopted. Their elemental analyses seemed to indicate a variable composition, $Pd(\phi SCH_2S\phi)_nCl_2$ (n = 1-∿1.3) but their infrared spectra were effectively the same. Characterisation of these complexes was prevented by their insolubility but it seems probable that they are oligomers of varying chain length related to that in Figure 1.4 with bis(phenylthio)methane end groups.

The reaction of sodium tetrachloropalladate(II) and $[Pd(\phi SCH_2S\phi)_2Cl_2]$ provided orange materials similar to those above, and a crimson insoluble material $[Pd_2Cl_4(\phi SCH_2S\phi)]$.

Potassium tetrachloroplatinate(II) and bis(phenylthio)methane in 1,2-dichloroethane reacted to give only the 2:1 complexes $[Pt(\phi SCH_2S\phi)_2X_2]$ (X = Cl, Br, I) regardless of the ligand:metal ratio used. These complexes were like the corresponding palladium(II) ones except for the fact that they were rather less soluble in deuterated chloroform.

The above palladium(II) halide complexes could also be prepared from the nitrile complexes $Pd(MeCN)_2X_2$ or $Pd(\phi CN)_2X_2$ [168]. This method offered no advantages over the use of sodium chloropalladate(II) whilst use of platinum(II) nitriles produced impure compounds containing much unreacted starting material.

The reaction of the tetrahalopalladates(II) and tetrahaloplatinates (II) with bis(methylthio)methane produced complexes of a 1:1 (ligand: metal) stoichiometry $[M(MeSCH_2SMe)X_2]$ (X = Cl,Br,I; M = Pd,Pt) irrespective of the ligand:metal ratio adopted. All attempts to prepare the 2:1 complexes failed.

These complexes were insoluble in ethanol or acetone and only very slightly soluble in chlorocarbons. This very low solubility prevented molecular weight and solution electronic spectral measurements.

The proton nuclear magnetic resonance spectra could not be observed in the weakly coordinating solvents, e.g. $CDCl_3$ and CD_3NO_2. However these spectra in deuterated dimethylsulphoxide showed only a large resonance attributable to the free ligand at 2.05 ppm. The solutions used in fact smelled strongly of the ligand. However, when freshly prepared deuterated dimethylsulphoxide solutions of the complexes were used, weak bands could be seen at 2.4-2.6 ppm, (^{195}Pt satellites were sometimes observed). These resonances decreased rapidly in intensity with time eventually showing free ligand as being the major species present.

The solid state electronic spectra were typical of those expected for square planar complexes with S_2X_2 donor sets (see Table 1.11) and the far infrared spectra contained medium intensity bands in the ranges expected for cis-MX_2 (X = Cl, Br, I; M = Pd, Pt) groups where X is trans to SMe [12,66] (see Sections 1.13f and 1.25A).

The properties of the bis(methylthio)methane complexes were generally similar to those of the dithioethers with longer backbones, e.g. $MeS(CH_2)_nSMe$ and n = 2 or 3, which are monomeric complexes containing chelating dithioether, apart from the fact that the latter are not appreciably decomposed in dimethylsulphoxide. The greater ring strain involved in chelation of the bis(methylthio)methane compared with these latter complexes probably accounts for the ready displacement of the ligand by dimethylsulphoxide.

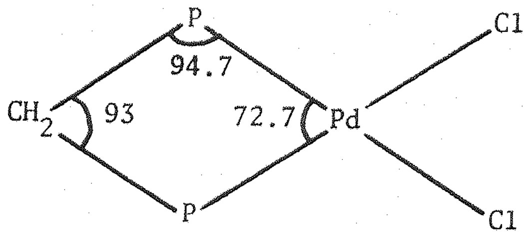
These 1:1 complexes were thought to be monomeric cis-$[M(MeSCH_2SMe)X_2]$ complexes, the dithioether ligand acting as a bidentate, although a di or polymeric structure could not be definitely ruled out.

Previously it has been shown that ligands where the donor atoms are separated by a single methylene group can bond to metal ions in a variety of ways whereas ligands with longer backbones, for example di and trimethylene, usually bind as cis-chelates. Chelation, in the case of the former type ligands, leads to a strained ring. These single methylene backboned ligands may well, as a result, prefer to act as either monodentate or bridging bidentates.

The bis(phenylthio)methane complexes prepared in this study can be compared with corresponding bis(diphenylphosphino)methane complexes [186].

Sanger [186] has prepared the complexes $[MCl_2(\phi_2PCH_2P\phi_2)]$ (M = Pd, Pt) and has shown them to be monomeric, in the solid and solution states. The structure of the $[PdCl_2(\phi_2PCH_2P\phi_2)]$ complex has been confirmed by X-ray analysis [188].

The $[PdCl_2(\phi_2PCH_2P\phi_2)]$ complex [188] exhibits, as would be expected, large deviations of its internal angles in the chelate ring from the expected values of 109.28° for the P-$\hat{C}$-P and C-$\hat{P}$-Pd and 90° for P-$\hat{Pd}$-P, (see Figure below) showing a strained ring.



The bis(phenylthio)methane ligand has been shown to bind predominantly in a monodentate fashion to palladium(II) and platinum(II) ions. The ϕS-group is in fact a poor donor and the energy gain in binding a second ϕS-group, to make a chelating ligand, to the same metal ion is not sufficiently favourable to overcome the strain in this case.

A few complexes containing bis(phenylthio)methane acting as a bridging bidentate have also been obtained in this study. The above diphosphine ligand has similarly been observed to act as a bridging ligand in for example $[PtCl(\phi_2PCH_2P\phi_2)]_2$ [187] as well as a monodentate in a complex such as $[Ni(\phi_2PCH_2P\phi_2)_2Br_2]$ [188].

The studies of the coordination chemistry of this ligand are hindered by the ease of displacement of the ligand by moderately strong donor solvents.

The bis(methylthio)methane ligand has formed only complexes where the ligand is acting as a chelating bidentate. The greater σ donor power of the MeS-group is presumably the reason for such behaviour.

The poor solubility of the bis(methylthio)methane complexes has prevented molecular weight determinations and hence definite proof of their monomeric structures. However since no species where the ligand acted as a monodentate could be obtained it seems likely no bridging bidentate species existed either.

E. A variable temperature ^1H nmr study

A variable temperature ^1H nmr study has been carried out on the methyl substituted dithioethers $\overset{\frown}{\text{MeS SMe}}$, ($\frown$ = $-(CH_2)_2-$, $-(CH_2)_3-$, $\underline{o}-C_6H_4$ and cis-CH=CH-) in order to identify any effects due to the chelate backbone.

Cross et al [109] have previously examined the $[MLX_2]$ complexes where $L = RS(CH_2)_2SR$; R = Me, Et, Pr^n, Pr^i, Bu^n; M = Pd, Pt. A summary of past work in this area is given on pages 23-28.

Table 1.14 lists the resonance positions of the methyl groups (δ), their shift on coordination (Δ) and for the platinum complexes, $^3J_{Pt-H}$.

On coordination the methyl resonance shifts downfield, the extent of the shift increasing with the trans ligand in the order Cl < Br < I.

The $^3J_{Pt-H}$ coupling constant is virtually insensitive to the X group or to the backbone of the ligand and lies in the range, 45-50 Hz.

The downfield shift for the vinyl protons of the cis-MeSCH=CHSMe complexes give the reverse order to the methyl protons (see Table 1.15) i.e. Cl > Br > I. This can be rationalised in terms of the trans influence of the X group in that as the trans influence increases, Cl < Br < I, the electron density on the sulphur increases and this is partially delocalised onto the unsaturated backbone. The vinyl protons, as a result, experience more shielding in the order I > Br > Cl and so now it is the chloride complex which has the greatest shift and the iodide the least.

The $^3J_{Pt-H}$ coupling to the vinyl protons is much larger than to the methyl protons and this is probably due to the vinyl carbon having more "s" character than the saturated methyl carbon. The values are 77-80 Hz.

The complexes of cis-ϕSCH=CHSϕ give vinyl proton resonances which are insensitive to changes in the X group. This may reflect the ability of the phenyl substituent to compensate for electronic effects in the system.

As previous studies have shown [76,110] the temperature dependence of the ^1H nmr spectra of coordinated thioethers is due to inversion at the sulphur atom and not, in the case of bidentate ligands, to conformational changes in their backbones. At low temperatures the spectra show resonances due to meso and DL forms of the ligand, (see page 27). As the temperature rises a complicated second order spectrum results, which then broadens until finally there is coalescence and only one "form" appears to be present. At the coalescence temperature the inversion process is sufficiently fast compared with the nmr time scale that only the time-averaged signals of the isomers are visible. The latter is equivalent to a planar intermediate. The coalescence temperatures thus tell us the relative rates of inversion at sulphur.

The methyl-substituted complexes used in this study have poor solubility in the usual nmr solvents and only $(CD_3)_2SO$ can be used. However due to the latter's relatively high melting point (18.5°C) coalescence temperatures can only be obtained for one of the Pd(II) and seven of the Pt(II) complexes. All the other complexes (Table 1.15) are already above their coalescence temperatures at the melting point of the solvent.

Various trends have been deduced by looking at the data obtained:

(i) Inversion is easier for palladium(II) than for platinum(II).

(ii) Coalescence temperatures fall in the order Cl > Br > I which is consistent with the trans influence of the X group [11].

(iii) The coalescence temperatures decrease with ligand backbone in the order $-(CH_2)_2- > \underline{o}-C_6H_4 > cis-CH=CH- > -(CH_2)_3-$.

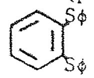
The observations (i) and (ii) have previously been noted [76,102,108,109, 115,122] but (iii) has not.

A more detailed analysis of the spectra, as in reference [76] has not been possible since the spectra have been of insufficient quality due to the solubility problems. However the coalescence temperatures, accurate to ±5°C, demonstrate the above trends unequivocally.

Inversion has been considered to be a function of the strength of the metal-sulphur bond [102]. This explains the ease of inversion being Pd > Pt since the bond strengths are in the order Pt-S > Pd-S, and also the series reflecting the trans influence of the halide.

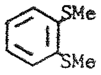
The effect of ligand backbone demonstrates the greater stability of five over six-membered chelate rings, [82,108] with the inversion process being easiest for the $MeS(CH_2)_3SMe$ complexes. For the three C_2 backboned ligands inversion is easier with the unsaturated systems. This suggests that delocalisation of the sulphur lone pair onto the backbone may be occurring in the transition state.

Table 1.5 Dithioether ligand data

	Ligand	Yield (%)	M.pt.[b] (°C)	Elemental Analyses[d]		^{1}H NMR[a,c]		
				C	H			
1.	1,2-bis(phenylthio)ethane $\phi S(CH_2)_2S\phi$	73	61	68.1(68.3)	5.9(5.7)	7.25(m)[5H]	3.1(s)[2H]	
2.	1,3-bis(phenylthio)propane $\phi S(CH_2)_3S\phi$	83	viscous oil at 25	70.2(69.3)	6.4(6.2)	7.2(m)[5H]	2.9(t)[2H]	1.9(q)[1H]
3.	1,6-bis(phenylthio)hexane $\phi S(CH_2)_6S\phi$	85	74-75	71.2(71.6)	7.0(7.3)	7.2(m)[5H]	2.85(t)[2H]	1.5(m)[4H]
4.	1,8-bis(phenylthio)octane $\phi S(CH_2)_8S\phi$	85	78-80	72.6(72.8)	7.6(7.9)	7.2(m)[5H]	2.8(t)[2H]	1.3(m)[6H]
5.	1,12-bis(phenylthio)dodecane $\phi S(CH_2)_{12}S\phi$	80	85-87	76.2(75.5)	8.5(8.4)	7.2(m)[5H]	2.8(t)[2H]	1.25(m)[10H]
6.	Cis-1,2-bis(phenylthio)ethylene cis-$\phi SCH=CHS\phi$	75	30	69.0(69.0)	5.3(4.9)	7.22(m)[5H]	6.48(s)[1H]	
7.	1,2-bis(phenylthio)benzene 	55	42	73.1(73.4)	5.3(5.45)			
8.	1,2-bis(methylthio)ethane $MeS(CH_2)_2SMe$	67	B.pt. 63-64/ 20mm Hg	-		2.67(s)[2H]	2.09(s)[3H]	
9.	1,3-bis(methylthio)propane $MeS(CH_2)_3SMe$	78	-	-		2.55(t)[2H]	2.05(s)[2H]	1.80(q)[1H]
10.	cis-1,2-bis(methylthio)ethylene Cis-MeSCH=CHSMe	70	B.pt 52/6mm Hg	-		6.10(s)[1H]	2.28(s)[3H]	

/continued.....

Table 1.5 continued.....

11.	1,2-bis(methylthio)benzene 	65	B.pt. 78/1mm Hg		-	7.2(m)[2H]	2.45(s)[3H]
12.	bis(phenylthio)methane $\phi SCH_2S\phi$	80	-	68.0(67.8)	5.1(5.2)	7.3(m)[5H]	4.21(s)[H]
13.	bis(methylthio)methane $MeSCH_2SMe$	76	B.pt. 150		-	3.55(s)[H]	2.06(s)[3H]

---

[a] s = singlet; m = multiplet; q = quintet; t = triplet.

[b] b.pt. = boiling point and m.pt. = melting point in degrees centigrade.

[c] in deuterochloroform with tetramethylsilane as internal standard; scale is in δ(ppm).

[d] Found (calculated).

Table 1.6 Analytical and physical data of the palladium(II) and platinum(II) halide complexes of some dithioether ligands

Complexes	Colour	C%[a]	H%[a]	X%[a]	M.W.[a,b]	ν(M–X) cm^{-1} [c]
$PhSCH_2CH_2SPh$ (L)						
$PdLCl_2$	orange	39.9(39.9)	3.4(3.2)	16.8(16.8)	–	315, 296
$PdLBr_2$	brown	32.8(32.8)	2.8(2.7)	31.3(31.2)	–	258, 245
$PdLI_2$	purple	27.8(27.7)	2.5(2.3)	42.4(41.8)	–	158, 148
$PtLCl_2$	pale yellow	32.9(32.9)	2.8(2.6)	14.0(13.9)	–	315, 302 sh
$PtLBr_2$	yellow	28.5(28.5)	2.4(2.3)	26.0(26.6)	–	245, 226
$PtLI_2$	yellow	24.6(24.2)	2.0(2.0)	36.5(36.5)	695(695)	165, 158 sh
$PhSCH_2CH_2CH_2SPh$						
$PdLCl_2$	yellow	40.2(41.2)	3.8(3.7)	16.5(16.3)	–	324, 308
$PdLBr_2$	orange-yellow	33.8(34.2)	3.0(3.0)	30.3(30.4)	–	254, 240 sh
$PdLI_2$	purple	28.7(29.0)	2.4(2.5)	40.2(40.8)	–	163, 149
$PtLCl_2$	pale yellow	34.1(34.1)	3.0(3.4)	13.9(13.5)	–	328, 312
$PtLBr_2$	fawn	29.4(29.0)	2.7(2.9)	25.5(26.0)	–	242, 228
$PtLI_2$	yellow	25.4(25.4)	2.4(2.5)	35.8(35.8)	692(709)	168, 154
o-$C_6H_4(SPh)_2$						
$PdLCl_2$	orange-brown	46.0(45.8)	3.2(3.0)	15.6(15.1)	–	322, 308
$PdLBr_2$	deep orange	38.5(38.6)	2.4(2.5)	28.4(28.6)	–	260, 248
$PdLI_2$	purple	33.0(33.0)	2.2(2.2)	38.8(38.8)	652(654)	158, 142
$PtLCl_2$	yellow	37.6(38.5)	2.7(2.5)	13.5(12.8)	–	326, 308
$PtLBr_2$	yellow	33.2(33.2)	2.4(2.2)	25.6(24.7)	–	244, 232
$PtLI_2$	yellow	29.5(29.1)	2.0(1.9)	33.2(34.2)	720(739)	165, 150
cis-$PhSCH=CHSPh$						
$PdLCl_2$	yellow	40.0(39.9)	2.7(2.8)	17.0(16.8)	–	318, 298
$PdLBr_2$	orange	33.4(32.9)	2.6(2.3)	29.8(30.2)	523(510)	246, 228
$PdLI_2$	purple-red	27.6(27.7)	2.0(2.0)	41.8(41.8)	–	164, 162
$PtLCl_2$	yellow	34.0(33.0)	2.1(2.3)	14.4(13.9)	–	316, 300 sh
$PtLBr_2$	yellow	28.4(28.0)	2.3(2.0)	26.9(26.9)	–	248, 232
$PtLI_2$	orange	24.4(24.2)	1.9(1.7)	35.6(36.5)	–	165, 146
$PhS(CH_2)_6SPh$						
$PdLCl_2 \cdot \frac{1}{2}CH_2Cl_2$	yellow	41.7(42.6)	4.5(4.4)	19.7(20.2)	–	343
$PdLBr_2$	orange	39.5(39.0)	4.5(4.0)	28.5(28.3)	–	280
$PdLI_2$	black	32.4(32.0)	3.3(3.1)	37.8(37.6)	–	205
$PhS(CH_2)_8SPh$						
$PdLCl_2 \cdot \frac{1}{2}CH_2Cl_2$	yellow-orange	45.8(44.5)	5.0(5.0)	19.8(19.5)	–	346
$PdLBr_2$	deep orange	40.2(40.3)	4.3(4.3)	27.0(26.8)	–	263
$PdLI_2$	black	34.2(34.7)	3.8(3.7)	37.1(36.8)	–	218
$PhS(CH_2)_{12}SPh$						
$PdLCl_2$	orange	51.7(51.6)	6.1(6.3)	13.0(12.7)	587(564)	352
$PdLBr_2$	orange	44.1(44.2)	5.4(5.3)	24.6(24.8)	665(652)	275
$PtLCl_2$	buff	44.8(44.2)	4.7(5.2)	10.7(10.8)	640(653)	346
$MeSCH_2CH_2SMe$						
$PdLCl_2$	orange-yellow	16.2(16.0)	3.6(3.3)	–	–	314, 298
$PdLBr_2$	orange	12.35(12.4)	2.6(2.6)	–	340(388)	252, 234
$PdLI_2$	red-brown	9.7(9.9)	2.3(2.1)	–	470(482)	162, 141
$PtLCl_2$	pale yellow	12.0(12.4)	2.6(2.6)	–	–	322, 308
$PtLBr_2$	yellow	10.4(10.1)	2.3(2.1)	–	–	248, 222
$PtLI_2$	brown	8.5(8.5)	2.0(1.8)	–	576(571)	168

/continued.....

Table 1.6 continued.....

$MeSCH_2CH_2CH_2SMe$						
$PdLCl_2$	yellow-brown	19.7(19.1)	3.9(3.8)	22.6(22.6)	–	326, 314
$PdLBr_2$	orange	14.4(14.8)	3.1(3.2)	39.7(31.8)	–	240, 232 sh
$PdLI_2$	red	12.3(12.1)	2.4(2.4)	50.7(50.2)	–	160. 155
$PtLCl_2$	pale yellow	14.6(14.8)	2.9(3.0)	19.7(19.5)	–	323, 305
$PtLBr_2$	yellow	12.2(12.2)	2.7(2.4)	32.0(32.5)	–	238, 228
$PtLI_2$	yellow	10.5(10.3)	2.1(2.1)	42.4(42.6)	–	162, 154 sh
o-$C_6H_4(SMe)_2$						
$PdLCl_2$	orange	27.4(27.6)	2.7(2.9)	20.8(20.4)	328(347)	322, 308
$PdLBr_2$	orange	22.3(22.0)	2.4(2.3)	35.8(36.5)	407(446)	260
$PdLI_2$	red	18.1(18.0)	1.9(1.9)	47.9(47.4)	–	164, 140
$PtLCl_2$	yellow	22.6(22.2)	2.7(2.3)	15.9(16.3)	–	322, 310
$PtLBr_2$	yellow	18.0(18.3)	1.9(1.9)	30.0(30.3)	–	258, 244
$PtLI_2$	yellow	15.9(15.4)	1.6(1.6)	40.1(40.0)	607(619)	165, 154
cis-MeSCH=CHSMe						
$PdLCl_2$	orange	17.0(16.3)	2.3(2.7)	23.6(24.0)	367(386)	315, 294
$PdLBr_2$	orange	13.2(12.6)	2.1(2.1)	40.8(41.5)	–	264, 224
$PdLI_2$	red-brown	10.1(10.0)	1.8(1.7)	53.4(53.0)	465(480)	168, 156
$PtLCl_2$	yellow	13.0(12.6)	2.2(2.1)	18.2(18.4)	–	308, 298
$PtLBr_2$	yellow	10.2(9.7)	2.0(1.7)	31.8(32.3)	–	252, 228
$PtLI_2$	deep yellow	8.5(8.2)	1.6(1.4)	42.6(43.1)	–	168, 145

[a] Found (calc), X = halide. [b] $10^{-3}M$ CH_2ClCH_2Cl. [c] Nujol mull.

Table 1.11 Electronic spectra of the palladium(II) and platinum(II) halide complexes of some dithioether ligands

Complex	$F_{max}(\epsilon_{mol}) \times 10^{-3}$ cm$^{-1\,a,b}$	$E_{max} \times 10^{-3}$ cm$^{-1\,c}$
$PhSCH_2CH_2SPh$[a]		
	24.00(2150), 34.00sh(7370)	23.70, 33.30sh, 37.31
$PdLBr_2$	23.00(2720), 25.20(2440), 2955(6100)	22.50, 31.30sh, 36.60
$PdLI_2$	19.47(3870), 33.77(4500)	17.40sh, 20.40, 36.60
$PtLCl_2$	27.00(1550), 30.60(2255), 36.40sh(3820)	25.64, 31.90, 37.20
$PtLBr_2$	26.72(1880), 29.53(2600), 33.45(1905)	24.71, 29.58, 37.04
$PtLI_2$	25.25(3667), 30.82(2010)	21.74sh, 24.31, 33.00sh, 36.90
$PhSCH_2CH_2CH_2SPh$[b]		
$PdLCl_2$	23.02(450), 26.32(2770), 30.80(7300)	24.10, 26.30sh, 31.25sh
$PdLBr_2$	21.80sh(570), 24.30(1260), 30.30sh(4430)	23.55, 30.60
$PdLI_2$	19.40(810), 21.65(1080), 29.40(3100), 32.00(3675)	19.61, 22.22, 32.00sh
$PtLCl_2$	27.02sh(3690), 30.25(4030), 33.35(5020)	25.65, 30.32, 37.20
$PtLBr_2$	25.20(1320), 29.20(870), 33.40(1510), 35.50(3100)	24.35, 30.32sh, 33.90
$PtLI_2$	24.80(2100), 33.80sh(5180)	24.70, 33.00sh, 36.00
o-$C_6H_4(SPh)_2$[a]		
$PdLCl_2$	24.00(4365), 33.00(3912), 35.30(4048)	23.25, 31.25sh, 36.80
$PdLBr_2$	23.50(810), 29.87(3565), 34.30(2440)	22.71, 29.85sh, 34.25
$PdLI_2$	19.27(2975), 23.00(1210), 28.94(9630), 34.67sh	19.60sh, 23.25, 30.30, 37.00
$PtLCl_2$	26.80(1260), 30.95(3480), 34.60(9370)	23.64, 31.06, 35.09
$PtLBr_2$	25.40(1107), 29.33(2076), 34.80(7960)	23.30, 29.41, 36.23
$PtLI_2$	24.20(4880), 33.50(9354), 36.70(19260)	21.28sh, 24.21, 33.44, 35.97
cis-$PhSCH{=}CHSPh$[b]		
$PdLCl_2$	24.40sh(2010), 29.67(2675), 33.50(6380)	23.25, 33.00sh
$PdLBr_2$	22.80(2375), 25.30(2410), 29.50(3580)	22.62, 26.32, 33.90
$PdLI_2$	19.05(2557), 23.70(1586), 28.80(6990), 33.70(10970)	18.87, 20.83, 33.33
$PtLCl_2$	25.40sh(2068), 31.00(9700)	23.80, 32.00sh, 36.76
$PtLBr_2$	25.30sh(755), 29.00(2075), 33.20sh(3768)	23.11, 31.05, 37.45
$PtLI_2$	23.50(2700), 28.35(13820), 33.75(5280)	21.97sh, 23.36, 33.56
$PhS(CH_2)_6SPh$		
$PdLCl_2$	–	22.23, 29.85, 31.34
$PdLBr_2$	–	21.46, 23.64, 33.00sh, 36.90
$PdLI_2$	–	16.40sh, 19.60, 22.24, 34.48
$PhS(CH_2)_8SPh$		
$PdLCl_2$	–	22.22, 29.41, 35.34
$PdLBr_2$	–	20.83sh, 22.26, 33.78sh, 36.90
$PdLI_2$	–	15.6sh, 17.54sh, 21.37, 28.98, 37.45
$PhS(CH_2)_{12}SPh$[a]		
$PdLCl_2$	22.80(1080)sh, 29.15(10000)	22.48, 29.90
$PdLBr_2$	21.50(1107)sh, 28.30(9590)	21.62sh, 22.47, 35.54
$PtLCl_2$	28.50sh, 30.80(9030)	28.00, 34.00

/continued...

Table 1.11 continued...

$MeSCH_2CH_2SMe$[b]		
$PdLCl_2$	25.23(1165), 31.75(1710), 35.40sh(8390)	23.54, 29.00sh, 37.45
$PdLBr_2$	24.45(1370), 27.50(1250), 33.30(8100)	22.73, 29.40sh, 37.07
$PdLI_2$	20.75(3055), 24.75(810), 34.10(18240)	20.84, 23.80sh, 35.70
$PtLCl_2$	27.00(910), 31.55(760), 36.00(11900)	21.30sh, 26.74, 31.75, 35.08
$PtLBr_2$	26.80(900), 31.00(510), 35.60(8600)	24.10, 31.45sh, 35.97
$PtLI_2$	26.20(1190), 30.80(315), 34.50(7600)	23.26, 25.97sh, 35.40
$MeSCH_2CH_2CH_2SMe$[b]		
$PdLCl_2$	25.46(2837), 28.90(3270), 33.15(7745)	24.20sh, 32.36sh
$PdLBr_2$	25.18(780), 33.80(8100), 36.70(11250)	23.36, 31.45, 36.42
$PdLI_2$	20.60(1430), 30.20(7450), 35.15(10450)	20.40sh, 21.51, 31.05sh, 36.75
$PtLCl_2$	27.10(385), 32.10(1370)	25.13, 34.84sh
$PtLBr_2$	26.20(900), 30.70(4600), 33.20(4650)	24.27, 31.55, 37.31
$PtLI_2$	25.60(1195), 30.75sh(2440), 35.00(5016)	23.72, 31.85sh, 36.49
$o\text{-}C_6H_4(SMe)_2$[b]		
$PdLCl_2$	25.80(770), 35.07(1740)	23.70, 32.26sh, 35.08
$PdLBr_2$	21.80(645), 26.80(1310), 32.50(5380)	20.83sh, 22.63, 33.00
$PdLI_2$	20.90(3660), 27.00sh(6840), 30.20(2160)	19.25sh, 21.05, 30.4sh, 36.76
$PtLCl_2$	26.40(1430), 32.20sh(2557)	25.00, 32.25sh, 37.20
$PtLBr_2$	25.60(445), 29.75sh(1730), 33.40(3100)	24.51, 31.05sh, 37.04
$PtLI_2$	23.60(3565), 30.67(1740)	21.97sh, 24.50, 36.00
$MeSCH{=}CHSMe$[b]		
$PdLCl_2$	26.00(1135), 30.90sh(2010), 34.33(4685)	23.25, 34.12sh, 37.31
$PdLBr_2$	23.50(890), 26.60(1190), 34.00(5600)	22.73, 30.00sh, 37.04
$PdLI_2$	20.75(1135), 23.30(835), 25.30sh(970), 30.40(4010)	18.50sh, 21.28, 31.25sh, 36.90
$PtLCl_2$	25.90(760), 29.80(1550), 30.65(2076), 31.80 (2080)	23.64, 34.01sh
$PtLBr_2$	25.40(550), 30.60(1675), 35.35(2440)	23.80, 31.05, 37.45
$PtLI_2$	23.90(2366), 30.75(1367)	22.47sh, 23.97, 30.00sh

---

[a] 10^{-3} *M* solutions in CH_2Cl_2. [b] In N,N-dimethylformamide range 36,000–12,000 cm^{-1}. [c] Diffuse reflectance range 38,000–12,000 cm^{-1}.

Table 1.13a The $RSCH_2SR$ (R=Me,ϕ) complexes of **Palladium(II)** and **Platinum(II)** halides, their elemental analysis, molecular weights, infrared and proton nmr data

Complex	Colour	Elemental Analyses[a] C%	H%	X%	M.wt[b]	(M-X)[f]	^{1}H NMR (δ)[e]
$[PdCl_2(\phi SCH_2S\phi)_2]\frac{1}{3}CH_2Cl_2$	yellow	45.4(45.3)	3.5(3.5)	17.3(17.8)	645(640)	360	4.65(s)
$[PdBr_2(\phi SCH_2S\phi)_2]$	orange	42.6(42.2)	2.9(3.2)	21.8(21.8)	696(730)	248	4.75(s)
$[PdI_2(\phi SCH_2S\phi)_2]$	dark-brown	37.3(37.9)	2.0(2.9)	30.7(30.8)	-	218	4.35(s)
$[PtCl_2(\phi SCH_2S\phi)_2]$	yellow	42.6(42.4)	2.9(3.2)	9.4(9.6)	-	356	4.70(34)
$[PtBr_2(\phi SCH_2S\phi)_2]$	buff	38.9(38.2)	2.9(2.7)	19.5(19.5)	783(819)	256	4.80(28)
$[PtI_2(\phi SCH_2S\phi)_2]$	yellow-brown	33.8(34.1)	2.6(2.6)	27.4(27.8)	940(920)	204	4.68(30)
$[PdCl_2(\phi SCH_2S\phi)]_n$[g]	orange-brown	39.6(38.2)	3.1(2.9)	16.8(17.5)	insoluble	355	-
$[PdCl_2(\phi SCH_2S\phi)]_n$[h]	orange-brown	38.9(38.2)	3.1(2.9)	17.0(17.5)	insoluble	355	-
$[Pd_2Cl_4(\phi SCH_2S\phi)]$	brick-red	26.5(26.6)	1.8(2.0)	23.7(24.2)	insoluble	-	insoluble
$[PdCl_2(MeSCH_2SMe)]$	yellow	12.8(12.7)	2.8(2.8)	24.6(25.0)	-	332 308	-
$PdBr_2(MeSCH_2SMe)$	brown	9.5(9.6)	2.2(2.15)	42.9(43.0)	-	262 -	-
$PdI_2(MeSCH_2SMe)$	brown-black	7.5(7.7)	1.5(1.7)	55.3(54.5)	-	163 144	-
$PtCl_2(MeSCH_2SMe)$	yellow	10.0(9.7)	2.2(2.15)	18.4(19.0)	-	328 306sh	-

/continued.....

Table 1.13a continued.....

$PtBr_2(MeSCH_2SMe)$	yellow	7.6(7.8)	1.7(1.7)	34.0(34.7)	-	269	246	-
$PtI_2(MeSCH_2SMe)$	brown-yellow	6.5(6.5)	1.4(1.45)	46.0(45.8)	-	163	146	-

[a] found (calculated)

[b] osmometric 10^{-3} M 1,2-dichloroethane.

[c] solutions in dichloromethane; ϵ_m in $dm^3\ mol^{-1}\ cm^{-1}$.

[d] diffuse reflectance (diluted with barium sulphate).

[e] in deuterated chloroform relative to tetramethylsilane. The $^3J(Pt\text{-}H)$ coupling constants are in parentheses.

[f] metal-halogen stretching frequencies.

[g] from Na_2PdCl_4.

[h] from $PdCl_2(\phi CN)_2$.

Table 1.13b Electronic spectral data of the $RSCH_2SR$ ($R=Me,\phi$) complexes of Palladium(II) and Platinum(II) halides

Complex	E_{max} (ε_{mol}) x 10^{-3} cm^{-1} [c]	E_{max} x 10^{-3} cm^{-1} [d]
$[PdCl_2(\phi SCH_2S\phi)_2]\frac{1}{3}CH_2Cl_2$	27.5(1430), 28.2(8700)	23.0, 28.6
$[PdBr_2(\phi SCH_2S\phi)_2]$	23.50(8290), 28.8(17390), 31.35(15900)	23.9, 36.5
$[PdI_2(\phi SCH_2S\phi)_2]$	20.4(1177), 30.2(1940)	20.0sh, 22.5, 33.5
$[PtCl_2(\phi SCH_2S\phi)_2]$	25.3sh(2760), 27.9(8600)	25.32, 31.75
$[PtBr_2(\phi SCH_2S\phi)_2]$	23.8(210), 32.8(9340)	20.7sh, 24.3, 31.5
$[PtI_2(\phi SCH_2S\phi)_2]$	21.25(727), 28.75(9940), 30.75(4787)	21.9sh, 24.5, 27.8
$[PdCl_2(\phi SCH_2S\phi)]_n$[g]	-	20.0sh, 23.8, 27.6sh
$[PdCl_2(\phi SCH_2S\phi)]_n$[h]	-	-
$[Pd_2Cl_4(\phi SCH_2S\phi)]$	-	19.6, 24.3, 27.2sh
$[PdCl_2(MeSCH_2SMe)]$	-	23.0, 26.6, 30.0sh
$PdBr_2(MeSCH_2SMe)$	-	22.0, 26.7, 31.3sh
$PdI_2(MeSCH_2SMe)$	-	20.6sh, 24.0, 27.0sh
$PtCl_2(MeSCH_2SMe)$	-	24.8sh, 26.45
$PtBr_2(MeSCH_2SMe)$	-	24.0, 27.3
$PtI_2(MeSCH_2SMe)$	-	21.0sh, 24.0

** For footnotes see Table 1.13a.

Table 1.14 PMR Data for some dithioether complexes containing methyl substituted ligands (the methyl protons)(a)

	Complex	δ(ppm)(b)	Δ(ppm)(c)	$^3J_{Pt-H}$(Hz)	Coalescence Temp(°C)
$MeS(CH_2)_2SMe$	$PdLCl_2$	2.63	0.54	-	+40
2.09ppm(d)	$PdLBr_2$	2.69	0.60	-	(e)
	$PdLI_2$	2.81	0.72	-	(e)
	$PtLCl_2$	2.62	0.53	46.8	+102
	$PtLBr_2$	2.66	0.57	46.8	+92
	$PtLI_2$	2.68	0.59	48.6	+88
$MeS(CH_2)_3SMe$	$PdLCl_2$	2.55	0.50	-	(e)
2.05ppm(d)	$PdLBr_2$	2.61	0.56	-	(e)
	$PdLI_2$	2.67	0.62	-	(e)
	$PtLCl_2$	2.62	0.57	46.8	+30
	$PtLBr_2$	2.70	0.65	48.6	(e)
	$PtLI_2$	2.75	0.70	46.8	(e)
cis MeSCH = CHSMe	$PdLCl_2$	2.78	0.50	-	(e)
2.28ppm(d)	$PdLBr_2$	2.86	0.58	-	(e)
	$PdLI_2$	2.99	0.71	-	(e)
	$PtLCl_2$	2.82	0.54	45.0	+35
	$PtLBr_2$	2.89	0.61	45.0	(e)
	$PtLI_2$	2.99	0.71	48.6	(e)
$\underline{o}$-$C_6H_4(SMe)_2$	$PdLCl_2$	3.00	0.55	-	(e)
2.45ppm(d)	$PdLBr_2$	3.07	0.62	-	(e)
	$PdLI_2$	3.16	0.71	-	(e)
	$PtLCl_2$	3.03	0.58	44.1	+50
	$PtLBr_2$	3.11	0.66	46.8	+39
	$PtLI_2$	3.18	0.73	49.5	(e)

(a) In $(CD_3)_2SO$ solution referenced with tms.

(b) CH_3- signal above coalescence temp referred to tms.

(c) Shift of CH_3- signal between complex and free ligand.

(d) Free ligand in $(CD_3)_2SO$.

(e) Below m.pt. of $(CD_3)_2SO$.

Table 1.15 PMR Data for the MeSCH=CHSMe complexes (the vinyl protons)[a]

Complex	δ(ppm)[b]	Δ(ppm)[b]	$^3J_{Pt-H}$(Hz)
$PdLCl_2$	6.90	0.80	
$PdLBr_2$	6.84	0.74	
$PdLI_2$	6.75	0.65	
$PtLCl_2$	6.98	0.88	77.4
$PtLBr_2$	6.90	0.80	79.2
$PtLI_2$	6.76	0.66	79.2

[a] Complexes run in $(CD_3)_2SO$ with internal TMS standard, free ligand 6.10 ppm.

[b] See Table 1.14.

CHAPTER TWO

THE IRON(III) BROMIDE COMPLEXES OF SOME MONODENTATE AND BIDENTATE GROUP VB LIGANDS

2.1 LITERATURE SURVEY

2.11 INTRODUCTION TO THE CHEMISTRY OF IRON WITH SPECIAL REFERENCE TO THAT OF GROUP VB LIGANDS

Iron belongs to the first transition series and has an electronic configuration (Ar)$3d^6 4s^2$ [1].

It is the second most abundant metal and is by far the most widespread and important transition metal functioning in living systems. Examples of the latter are seen in (a) iron-containing proteins where it is important in oxygen transport and in electron transfer processes, or (b) in conjunction with molybdenum in enzymes that catalyse nitrogen fixation.

Iron exists in the following oxidation states -2, 0, +1, +2, +3, +4 and +6. The most commonly found of these are the +2 and +3 oxidation states. Table 2.1 shows some examples of the more common coordination numbers found for iron(III).

Table 2.1

The more common coordination numbers found for Fe(III)

d^n	coordination number	stereochemistry	Examples[a]
d^5	4	td	$[FeCl_4]^-$
	5	SP	$[FeCl(dtc)_2]$
	5	TBP	$[Fe(N_3)_5]^{2-}$
	6*	oct	$[FeCl_6]^{3-}$

[a] dtc = dithiocarbamate

* most commonly found coordination number and stereochemistry

In the first transition series when the metal atoms are positively charged the 3d orbitals become stabilised relative to the 4s orbital. As a result of this the predominant oxidation state in the ionic compounds and in the compounds containing non-π bonding ligands would be expected to be +2 or higher. However in general the stability of a particular oxidation state will depend substantially on the conditions. An oxidation state may be particularly stable for example in the absence of air or in the solid state but non-existent in air or in aqueous solution.

When the iron(II) and iron(III) cations are considered several factors seem to determine their relative stabilities:

(i) their ionisation potentials (IP)

i.e. Fe(metal) → Fe(I) IP = 7.9 eV
Fe(I) → Fe(II) IP = 16.18 eV
Fe(II) → Fe(III) IP = 30.64 eV

(ii) their ionic radii

Fe(II)	0.74 Å
Fe(III)	0.64 Å

(iii) the nature of the anions or ligands involved with respect to their polarisability

(iv) the electronic structure of the metal ions

(v) the stereochemistry of the metal ions in a complex ion or a crystalline lattice

(vi) the nature of the solvents and other media used.

Iron(II) and iron(III) form a large number of complexes most of which are octahedral. Iron(II) is readily oxidised to iron(III) by molecular oxygen particularly in basic solutions.

Iron is a first row transition metal and thus the crystal field splittings observed for its complexes are less than if it belonged to the second or third transition metal series. As a result of this with iron(II) quite strong ligand fields are required for spin pairing to occur. Some low spin iron(II) ions are known however, e.g. $Fe(CN)_6^{4-}$, $Fe(CNR)_6^{2+}$ and $[Fe(phen)_3]^{2+}$ [189].

As with the iron(II) cation, the iron(III) cation occurs in salts with most anions, the exceptions being those with which it is incompatible for example, iodide ions due to the fact that the former is a strong oxidising agent and the latter a strong reducing agent. In aqueous solutions Fe^{3+} and I^- react quantitatively:

$$Fe^{3+} + I^- \rightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

In general most of the work with iron(II) and iron(III) involves complexes containing oxygen and nitrogen donor ligands [1]. Iron(II) appears to have a greater affinity for nitrogen donor ligands and iron(III) for oxygen donor ligands. These are 'hard' donor ligands and in this study we are mainly concerned with 'soft' donor ligands of group VB.

The complexes of the 'soft' group VB donor ligands with the earlier first row transition elements are in general experimentally difficult to obtain and are often air and/or moisture sensitive. The ability however of these metal ions to bond to 'soft'donors can be increased by the presence of other substituents on the metal which have 'symbiotic effects'. (E.g. an iodide would be more likely to be stable than a chloride complex).

The solvents which are commonly used in the preparation of complexes, e.g. water, ethanol and acetone, are 'hard' oxygen donors which will preferentially bond to the metal ion and thus it is necessary to use solvents which are suitably inert and dry.

Various techniques have been used to elucidate the structure and stereochemistry of the iron(III) complexes prepared [190].

The infrared technique utilises symmetry arguments to determine the stereochemistry of the molecule. For example, for complex $[FeL_2Cl_2]ClO_4$ (L = bidentate ligand), if there is a cis octahedral distribution (C_{2v}) around the metal then there should be two infrared active ($A_1 + B_1$) metal-chlorine stretching frequencies whereas if it is trans (i.e. D_{2h}) then only one such frequency would be expected (B_{1u}) [191].

The position of the absorption bands will depend upon the atomic weight, the oxidation state, the electron configuration and the nature of the ligands bonded to the metal.

The ground state of the high spin iron(III) cation is ^6S which then becomes $^6A_1$ in a weak crystal field. There are no other sextuplet states, all the excited states of the d^5 ion have a different multiplicity to the ground state. As a result all the electronic transitions to the excited states are spin forbidden and are extremely weak. In fact they are frequently obscured by charge-transfer bands which tail into the visible region of the spectrum [190].

The low spin, d^5, iron(III) cation with a $^2T_{2g}$ ground state is expected to exhibit some spin-allowed transitions. Some examples are found in References [192-195].

Iron(III), like iron(II), is high spin in nearly all its complexes only those containing strong field ligands being low spin.

In the high spin complexes where the electronic configuration of the iron(III) is $t_{2g}^3e_g^2$ and the total spin is $\frac{5}{2}$, the magnetic moments are always very close to the spin only value of 5.9 BM. This is due to the fact that the ground state derived from the ^6S state of the free ion has no orbital angular momentum and there is no effective mechanism for introducing any by coupling with excited states.

Iron(III) systems where $S = \frac{3}{2}$ are rare and generally occur where there is a strong tetragonal field [196,197].

The low spin iron(III) complexes, possessing a t_{2g}^5 electronic configuration, generally exhibit considerable orbital contribution. A room temperature magnetic moment of 2.3 BM may be obtained. However these magnetic moments are intrinsically temperature dependent and at 77K they decrease to 1.9 BM [198,199].

The magnetic moments of all the iron complexes are seriously affected by the presence of impurities.

Hydrolysis readily occurs in the iron complexes resulting in the formation of iron-oxo species. Ferromagnetic behaviour then occurs due to subsequent interionic interaction in the complexes.

In ferromagnetic substances the moments of the separate ions tend to align themselves parallel and thus reinforce one another.

Significant deviations from the magnetic moment therefore result from the minutest quantity of a ferromagnetic impurity.

Low magnetic moments can also arise when the moments of the ions in the crystal lattice align themselves so as to cancel one another out and this is known as an antiferromagnetic interaction.

The Mössbauer technique [200] involves the decay of ^{57}Co to ^{57}Fe, γ rays being emitted, and then reabsorption of the γ rays. The ^{57}Fe nucleus possesses an excited state with a half life of 10^{-7} s which is 14.4 keV above the ground state.

For a resonant absorption the iron nuclei in the absorber (the iron complex under study) must be identical with the source. A velocity generally has to be applied to the absorber relative to the source in order to attain this.

The spectra can only be obtained from nuclei bound in a rigid solid environment or sometimes from solutions that have been frozen to glasses.

Two parameters can be extracted, the isomer shift (δ) and the quadrupole splitting (ΔE). The former is a linear function of the electron density at the nucleus and the latter occurs when the environment of the iron atom is unsymmetrical.

In low spin compounds the isomer shift is near to 0 mms^{-1} and is independent of the oxidation state. For example $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ possess almost identical isomer shifts.

In the high spin compounds the isomer shift values are higher and two different ranges for the iron(II) and iron(III) cations have been observed.

It has been noticed also that an inverse relationship exists between the isomer shifts and the positions of the ligands in the spectrochemical series [189].

The isomer shifts also depend linearly on the magnetic moment , increasing with increasing magnetic moment [195,201].

The following Table shows some typical isomer shifts and quadrupole splittings for iron(II) and iron(III).

Table 2.2
Isomer shifts and quadrupole splittings for iron(II) and iron(III)

	δ (mms^{-1})	ΔE (mms^{-1})
HS,oct,iron(II)	1.09-1.75 [202,203]	varies considerably [204,205]
LS,oct,iron(II)	0.20-0.40 [200]	0.20-0.40 [200]
HS,td,iron(III)	∿0.50-0.80 [206]	0.00-0.50 (nearer 0.00) [206]
LS,oct,iron(III)	0.10-0.30	$\lesssim$ 2.50

2.12 THE SYNTHESIS OF THE GROUP VB (P,As) LIGANDS AND THEIR PRECURSORS

This section is restricted, mainly, to the types of precursors and group VB ligands mentioned later in the experimental section. The ligand types mentioned are the monodentate phosphines and arsines and the bidentates, the diphosphines and diarsines. The mixed donor bidentates are referred to in the next chapter.

Tables are included showing other similar ligands and their references.

A series of reviews containing methods for the formation of carbon-group VB element bonds can be found in references [207-212].

2.121 Precursors

There are two types generally used (i) R_nEX_{3-n}, and (ii) MER_2 (M = alkali metal; R = alkyl, aryl; χ = Cl, Br).

Several of the type (i) precursors can be obtained commercially, e.g. dichlorophenylphosphine, chlorodiphenylphosphine, dichlorophenylarsine, triphenylphosphine and arsine, and trihalophosphine and arsine.

The type (i) arsenic containing precursors are more easily prepared than the phosphorus ones. This is due to the arsenic(V) in the arsonic or arsinic acids being readily reduced to arsenic(III) in aqueous acid. The haloarsines are also more corrosive and air-stable than the halophosphines.

Table 2.3 gives a list of commonly used type (i) precursors with references to their preparations and properties.

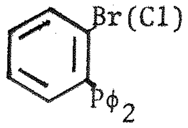
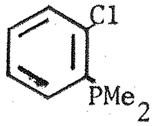
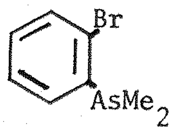
The type (ii) precursors $ME\phi_2$ are readily prepared by the cleavage of a phenyl group from $E\phi_3$ by lithium in tetrahydrofuran [227,228], sodium in liquid ammonia [229] or potassium in dioxan [230-233].

$$\text{i.e.}\quad 2M + E\phi_3 \xrightarrow[\text{dry } N_2]{} ME\phi_2 + M\phi$$

The metal phenyl can then be destroyed by the addition of a calculated ammount of either tertiary butyl chloride or ammonium chloride.

These precursors are normally prepared <u>in situ</u> and are used without isolation.

Table 2.3
Some commonly used precursors

Precursor		Reference
$RPCl_2$	R=ϕ,aryl,o-C_6H_4(Br),Me	[213-216]
R_2PCl	R=ϕ,Me	[217-218]
		[215,219,220]
		[219,220]
$RAsX_2$	X = I	[221]
	X=Cl,R=ϕ,o-C_6H_4(Br)	[222-224]
R_2AsX	X=Cl,R=ϕ	[222]
		[225,226]

The tertiary alkyl and cycloaliphatic phosphines are not cleaved by alkali metals [211] but compounds such as dimethylphenylphosphine can be cleaved by lithium in tetrahydrofuran under dry dinitrogen to give lithium dimethylphosphide in 70% yield [220,234,235].

The dimethylphosphide and arsenide anions are readily obtained in ether (as lithium salts) or in ammonia (as sodium salts) by alkali metal cleavage of the E-E bond in Me_2EEMe_2 (yields $\sim$45%). The other dialkylphosphide or arsenide nucleophiles (R = Et, Pr^n, Bu^n, $\frac{1}{2}Me\phi$) can also be prepared by this route [236].

The dimethylarsenide however is preferably prepared by the reaction of sodium and dimethyliodoarsine or dimethylarsine in tetrahydrofuran [237,238].

The type(ii) precursors generally possess a deep colour and are soluble in ether, tetrahydrofuran, dioxan and liquid ammonia. They are readily hydrolysed and oxidised and handling under dry dinitrogen is essential. Their strong nucleophilic character results in their reacting with many functional groups. The tetrahydrofuran used in many of their preparations is in fact slowly ring opened by PR_2^- under reflux to yield $M^+O(CH_2)_4PR_2^-$ compounds.

2.122 The monodentate phosphines and arsines

The majority of the monodentate phosphines and arsines had been prepared prior to the bidentate and multidentate ligands due to their previous use in organophosphorus chemistry. A great number of these are known and many can be commercially obtained.

The general synthetic routes to these monodentate ligands are as follows:

(a) EX_3, REX_2 or R_2EX + Grignard or Organolithium reagent → ER_3', RER_2', R_2ER' respectively.

(b) $R'X$ + alkaliphosphides → $R'PR_2$

The products from reactions (a) and (b) are readily obtained and are purified by distillation under nitrogen or in vacuo.

The lower alkyl and branched-chain alkylphosphines are exceedingly malodorous compounds which are highly toxic, and very air-sensitive. They are sometimes spontaneously inflammable. The tertiary arylphosphines by contrast are air-stable solids [239].

The mixed alkylphosphines have been only rarely used as ligands but the alkylarylphosphines where aryl is usually phenyl, have been extensively studied. These are less air-sensitive than the trialkyls and better donors than the triaryls [207,239].

The trialkylarsines are highly toxic liquids with an unpleasant odour and like the phosphines are readily oxidised in air. (Trimethylarsine is spontaneously inflammable).

The phenylalkylarsines are also air-sensitive but triphenylarsine is air-stable.

Some examples of monodentate phosphines and arsines and their preparation and properties are found in the following references: Et_3P [37], $Pr_3{}^nP$ [37], $Bu_3{}^n$ [240], Cy_3P [240], ϕ_3P [239], $Me_2\phi P$ [241], $Me\phi_2P$ [242], $Et_2\phi P$ [241], and ϕ_3As [243].

2.123 The bidentate ligands containing phosphorus donors only

The most general synthesis for these ligands is by the following reaction:

$$2MPR_2 + X\frown X \rightarrow R_2P\frown PR_2 + 2MX \qquad (1)$$

where M = alkali metal; X = Cl, Br; $\frown$ = alkyl, alkenyl or aryl backbone.

The yields for the majority of these reactions is high and the pure products can be obtained provided an excess of the dihaloorganic compound is not used. (Phosphonium salts will result otherwise). The products are purified by either recrystallisation or distillation. [229,244-247].

The phenyl-substituted ligands are generally air-stable solids whereas the alkyl-substituted ones are usually air-sensitive and often pyrophoric liquids. The phenyl ligands also have weaker ligand field strengths than the corresponding methyl ones.

Some of the more relevant diphosphine ligands are now discussed in parts (i)-(v).

(i) α,ω-Bis(diphenylphosphino)alkanes. $\phi_2P(CH_2)_nP\phi_2$ (n=2,3) (dpe, n=2)

These are commonly prepared by route (1) with M = Li, X = Cl, Br and $\frown$ = $(CH_2)_n$. The n = 3 ligand is also often prepared using sodium in liquid ammonia.

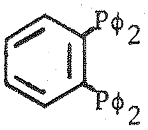
When n = 2, the ligand can also be obtained by the base catalysed addition of diphenylphosphine ($P\phi_2H$) to $\phi_2PCH{=}CH_2$. However the latter is difficult to prepare and this method is more usually applied to multidentate ligand synthesis [248].

The n = 2 and n = 3 ligands are air-stable solids. Their preparations and properties are found in references [229,245,249,250].

(ii) Cis-1,2-bis(diphenylphosphino)ethylene. cis-$\phi_2PCH{=}CHP\phi_2$ (vpp)

This ligand is prepared in excellent yield by route (1) with M = Li, X = Cl and $\frown$ = cis-CH=CH-. The reaction is stereospecific [251].

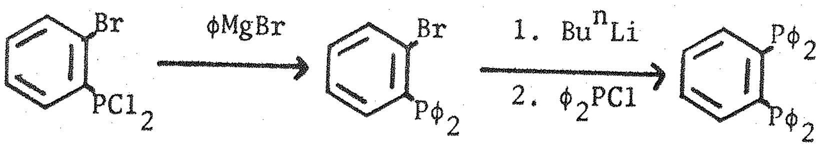
(iii) 1,2-Bis(diphenylphosphino)benzene.



(PPφ)

This ligand is prepared by the

following route:



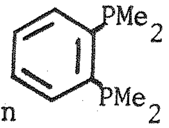
[215]

The ligand is a white solid with a melting point of 185°C [218].

(iv) α,ω-Bis(dimethylphosphino)alkanes. $Me_2P(CH_2)_nPMe_2$ (n=2,3) (n=3,dppm)

These ligands are prepared by route (1) using sodium in liquid ammonia. They are colourless, very air-sensitive liquids [217,252].

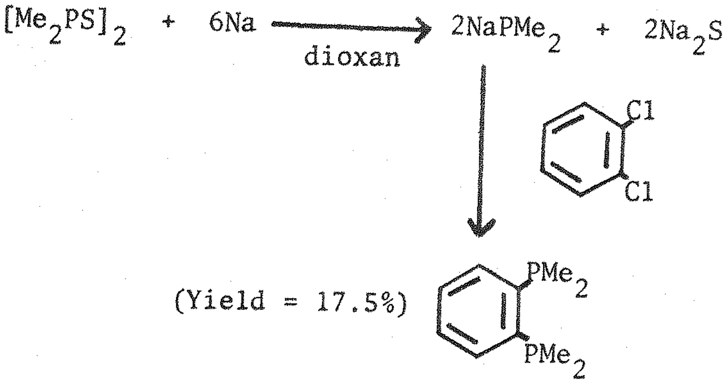
(v) 1,2-Bis(dimethylphosphino)benzene [220]



(PP_{me})

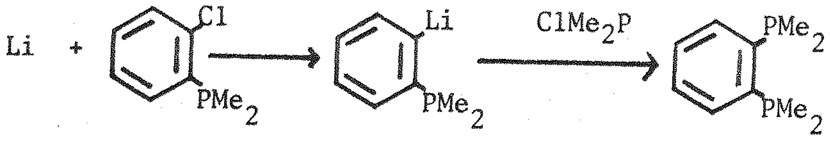
This ligand has been prepared by route (1) [220]. This involves the dropwise addition of o-dichlorobenzene to lithium dimethylphosphide in a 1:2 molar ratio. The yield is ∿40%.

Warren and Bennet [253] and Clark et al [254] have also prepared the ligand by the following route:



As with route (1) a colourless, air-sensitive, oily, foul-smelling liquid results, which is slightly impure. The impurities could not be easily removed by vacuum distillation.

Chatt et al [120] have used a similar route to (1) but here the yield is only 11%:



2.124 Bidentate ligands containing arsenic donors only

The general method of synthesis is similar to the diphosphines:

$$R_2AsM \; + \; \underset{(X\frown X)}{\text{Organohalogen compound}} \rightarrow R_2As\frown AsR_2 \qquad (2)$$

The more relevant diarsines are now discussed in parts (A) and (B).

(A) The phenyl-substituted diarsine ligands

(i) α,ω-Bis(diphenylarsino)alkanes. $\phi_2As(CH_2)_nAs\phi_2$ (n=1-3)

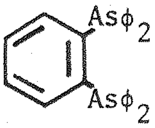
The n = 1 [255] and n = 3 [232] ligands are prepared by route (2) using lithium diphenylarsenide and dichloromethane or 1,3-dichloropropane respectively. The n = 1 ligand is however difficult to crystallise [255].

The n = 2 ligand is similarly obtained using 1,2-dichloroethane. In this case, unlike the other two, using the bromoalkane leads only to elimination products [232,256].

(ii) Cis-1,2-bis(diphenylarsino)ethylene. $\phi_2AsCH{=}CHAs\phi_2$ (vaa)

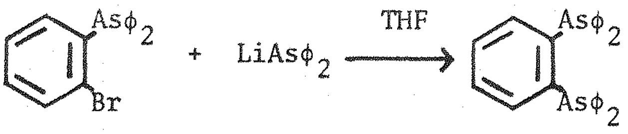
This ligand is prepared by route (2) using cis-1,2-dichloroethylene [236,255,257] and lithium diphenylarsenide in tetrahydrofuran. This is a stereospecific reaction.

(iii) 1,2-Bis(diphenylarsino)benzene.



(AAϕ)

This ligand is prepared as follows:



(54% yield) [181]

(B) Methyl-substituted diarsine ligands

Many of these are prepared by route (2) but using sodium dimethylarsenide in tetrahydrofuran.

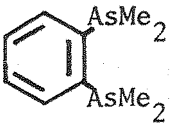
(i) α,ω-Bis(dimethylarsino)alkanes. $Me_2As(CH)_nAsMe_2$ (n=3, dapm)

When n ⩾ 3 a reasonable reaction yield results when route (2) is used [258,259]. However when n = 2, the products are tetramethyldiarsine and ethylene. A low yield of n = 2 ligand has been claimed from sodium dimethylarsenide and 1,2-dichloroethane in liquid ammonia at -78°C [256], but this has not been confirmed.

(ii) Cis and trans-bis(dimethylarsino)ethylene. cis and trans-$Me_2AsCH=CHAsMe_2$ (edas)

These ligands are obtained in a racemic mixture when sodium dimethylarsenide is reacted with cis-1,2-dichloroethylene [194,236,260,261].

(iii) 1,2-Bis(dimethylarsino)benzene. (dias)



This ligand was originally prepared by a six-stage synthesis from o-nitroaniline [262] but is now prepared by route (2) using sodium dimethylarsenide and 1,2-dichlorobenzene [237,238,261]. The latter process gives a 45% yield. The preparation and properties of the ligand can be found in reference [220].

2.13 MONODENTATE TERTIARY PHOSPHINE AND ARSINE HALIDE COMPLEXES OF IRON(II) AND IRON(III)

Iron(II)

Iron(II) phosphine complexes are somewhat unstable and dissociate readily in solution, especially in hydroxylic solvents.

The $[Fe(PR_3)_2X_2]$ complexes (X = halide; $R_3 = \phi_3$, ϕ_2Et, ϕEt_2, Et_3 and X = Br; R_3 = p-tolyl) are prepared by refluxing the ligand and the anhydrous iron(II) halide in benzene [263,264]. The most stable of this set are the cream diphenylethylphosphine complexes $[Fe(PEt_2\phi)_2X_2]$.

The preparation of the triethylphosphine complex in ethanol [265] has been attempted but this failed and it was necessary to use the above solvent. However, the complexes which have been obtained are still too unstable for accurate analysis.

The $[Fe(PR_3)_2X_2]$ complexes have been found to possess magnetic moments in the range 4.77-5.25 BM, although for the same complex differing values have been obtained by different workers [263,264,266,267]. This range is consistent with four unpaired electrons and thus a high spin tetrahedral configuration.

The structure has been given additional support by the visible and ultraviolet spectrum of $[Fe(P\phi_3)_2Br_2]$ [264]. The "d-d" band at 6410 cm^{-1} is in the expected region for distorted tetrahedral iron(II) complexes [268] when the relative position of phosphine ligands in the spectrochemical series is taken into account [269].

Iron(III)

Iron(III) halide phosphine complexes are generally less stable than the corresponding iron(II) complexes and as a result fewer of these have been prepared.

Triphenylphosphine produces iron(III) chloride complexes by the following methods:

(i) $$\underset{\text{anhydrous}}{FeCl_3} + P\phi_3 \xrightarrow[\text{ether}]{} [Fe(P\phi_3)_2Cl_3]_2 \qquad \mu_{eff} = 5.94\ BM$$
(possibly halogen-bridged dimers) [267]

(ii) $$Fe_3(CO)_{12} + P\phi_3 \xrightarrow[CHCl_3]{\text{reflux}} Fe(P\phi_3)Cl_3 \qquad [270]$$

The chloroform here acts as both a solvent and a chlorinating agent.
The $[Fe(P\phi_3)Cl_3]$ complex has been assigned a tetrahedral configuration [206].
The complex $[Fe(PCy_3)Cl_3]$ has also been reported [240].

2.14 BIDENTATE TERTIARY PHOSPHINE AND ARSINE COMPLEXES OF IRON(II) AND IRON(III) HALIDES

The complexes of the ligands in sections 2.123 and 2.124 are now discussed in a ligand by ligand manner.

1. 1,2-Bis(diphenylphosphino)ethane. $\phi_2P(CH_2)_2P\phi_2$ (dpe)

1,2-Bis(diphenylphosphino)ethane gives $[FeLX_2]$ (X = Cl, Br) and also the pseudohalide complex $[FeL_2(NCS)_2]$ when the iron(II) salt and the ligand are mixed in alcoholic solution [271]. The X-ray powder pattern of $[FeLCl_2]$ is identical with that of $[ZnLCl_2]$ which is known to be a distorted tetrahedron [271].

The electronic spectra of the $[FeLX_2]$ complexes both show a single band in the near infrared region. This probably results from a splitting of the $^5T_2$ state due to a distortion from tetrahedral symmetry in these complexes [268].

Their magnetic moments are ∿5.5 BM implying a high spin tetrahedral structure.

The isomer shifts obtained from the Mössbauer spectra are rather lower than what would be expected for a high spin iron(II) cation but this is known to occur in species where the coordination number of the iron is low [204]. Also there is a lack of temperature dependence of the quadrupole splitting and this is probably indicative of a large distortion from the cubic, tetrahedral symmetry.

The $[FeL_2(NCS)_2]$ complex is six-coordinate and diamagnetic.

Iron(III) chloride will react with dpe to give the complex trans-$[FeL_2Cl_2][FeCl_4]$ which possesses a low spin d^5 cation [272].

2. 1,2-Bis(dialkylphosphino)ethane [273] $R_2P(CH_2)_2PR_2$ (R = Me, Et, ie dme and dee resp)

The iron(II) chloride complexes, trans-$[FeL_2Cl_2]$ are prepared by reacting the ligand and anhydrous iron(II) chloride in benzene/petroleum solutions. The complexes are green crystalline solids which are soluble in non-polar solvents but decompose rapidly in water or alcohol and slowly in moist air.

The trans configuration was confirmed by the low dipole moment (1.3D) of the $[FeL_2Cl_2]$ (R = Et) complex [273].

The chlorine in trans-$[Fe(dee)_2Cl_2]$ is readily replaced on treatment with LiX (X = NCO, NCS, N_3, Br, I) to give trans-$[Fe(dee)_2X_2]$. A series of these octahedral $[Fe(dee)_2X_2]$ complexes have been studied by Mössbauer spectroscopy [273].

The iron(III) complexes, $[FeL_2Cl_2][FeCl_4]$, are stable, dark red or green crystalline solids which are prepared from iron(III) chloride in benzene/ethanol solutions. The complexes are soluble in polar organic solvents, in which they are ionised, but insoluble in water and hydrocarbons.

The iron(III) chloro-complexes have been used to prepare mono- and dihydrides by reduction with lithium aluminium hydride [273].

3. <u>Cis-1,2-bis(diphenylphosphino)ethylene</u> [274] cis-ϕ_2PCH=CHPϕ_2 (vpp)

The iron(II) complexes, FeL_2X_2 (X = Cl, Br, NCS, N_3) are prepared by the addition of the appropriate iron(II) salt to (usually) an excess of vpp in ethanol or ethanol/acetone solution under oxygen-free conditions. The use of different molar ratios have resulted only in the 1:2 (iron: ligand) stoichiometry with the exception of a 1:1, $[FeLBr_2]$ complex.

These complexes are stable in the solid state in a dry atmosphere except for $[FeL_2(N_3)_2]$ and $[FeLBr_2]$ which darken slowly upon storage.

The $[FeL_2X_2]$ (X = Cl, Br) are high spin and trans six-coordinate on the basis of their electronic spectra, magnetic moments and their conductivity.

The $[FeL_2(NCS)_2]$ and $[FeL_2(N_3)_2]$ however are low spin i.e. $t_{2g}^6e_g^0$ systems and the $[FeLBr_2]$ high spin tetrahedral.

In solution the electronic spectrum of $[FeL_2Br_2]$ appears to be identical to that of $[FeLBr_2]$ and as a result the following equilibrium is thought to occur in solution:

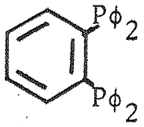
$$\underset{\text{6-coordinate}}{[FeL_2X_2]} \rightleftharpoons \underset{\text{tetrahedral}}{[FeLX_2]} + L \qquad (X = Cl, Br)$$

The iron(III) complex, $[FeL_2Cl_2][FeCl_4]$ [274] has been obtained as a byproduct in the preparation of the iron(II) complex. It can also be prepared from anhydrous iron(III) chloride and the ligand in absolute ethanol solution [272]. It consists of a low spin iron(III) cation and a high spin tetrahedral tetrachloroferrate(III), $[FeCl_4]^-$, anion. The magnetic moment per iron atom is 4.45 BM which is consistent with the expected moment of 5.92 BM (five unpaired electrons) for the anion and 2.14 BM (one unpaired electron for the cation).

The far infrared spectrum contains a band at 380 cm^{-1} which is characteristic of the iron-chlorine stretch in $[FeCl_4]^-$ [65].

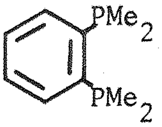
The complex is a 1:1 electrolyte in nitromethane and the Mössbauer spectrum at 293K proves the presence of two different iron environments [274].

4. 1,2-Bis(diphenylphosphino)benzene [272] (PP_{ϕ})



The green iron(III) complex, $[FeL_2Cl_2][FeCl_4]$ is prepared similarly to the vpp complex. Its conductivity, far infrared and magnetic moments all also agree closely with the vpp complex [272].

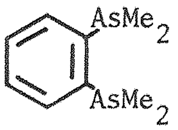
5. 1,2-Bis(dimethylphosphino)benzene [253] (PP_{me})



This ligand forms light-green, low spin diamagnetic iron(II) complexes, trans-$[FeL_2Cl_2]$ when reacted with iron(II) chloride in alcohol in the absence of air [275]. These can then be oxidised by iron(III) chloride to give the deep red cation $[FeL_2Cl_2]^+$ which can be isolated as a perchlorate salt. This iron(III) complex can undergo a reversible electrochemical oxidation in acetonitrile to produce an iron(IV) cation isolated as a deep purple-brown perrhenate salt, $[FeL_2Cl_2][ReO_4]_2$. The latter possesses a low spin d^4 cation and is highly oxidising and unstable [276]. This iron(IV) cation can also be achieved by nitric acid oxidation of $[FeL_2Cl_2]^+$.

The single metal-halide stretching frequency in the iron(II), (III) and (IV) complexes indicates a trans structure. [277,278].

6. 1,2-Bis(dimethylarsino)benzene (dias)



Iron(II) chloride gives the octahedral trans-$[FeL_2X_2]$ (X = Cl) in 75% yield on reaction with the ligand in alcohol under dry nitrogen [191, 279]. The corresponding complexes where X = Br, I, N_3, NCS, NCO are readily made by metathesis in alcoholic solution but ligands such as nitrite or tin(II) chloride will only yield the monosubstituted derivatives, $[FeL_2Cl(NO_2)]$ and $[FeL_2Cl(SnCl_3)]$ [280].

The $[FeL_2Cl_2]$ is stable under nitrogen or under vacuum. The odour of the ligand is noticeable over samples of these complexes but the extent of decomposition is minor.

The diamagnetic $[FeL_2I_2]$ has also been prepared by oxidation of $[Fe(CO)L_2]$ with iodine in ether [281].

The iron(II) complexes are readily oxidised to the octahedral iron(III) cations $[FeL_2X_2]^+$ [279,282].

A number of iron(II) and iron(III) complexes containing the fragment FeL_2^{n+} and small molecules such as NO, CO, MeCN, N_3, NCS have been prepared from $[FeL_2Cl_2]$ [282,283,284].

The chemistry of the $[FeL_2Cl_2]^+$ cation has been studied using mainly complexes with counter anions such as tetrafluoroborate or perrhenate. The perchlorate counter anion has been used less frequently due to its explosive tendencies.

The iron(II), (III) and (IV) halide complexes of the types $[FeL_2X_2]$, $[FeL_2X_2]Y$ and $[FeL_2X_2]Y_2$ ($Y = ClO_4$, ReO_4, BF_4) all show a single absorption band in their far infrared spectra. This indicates a trans arrangement of the halides [191].

The crystal structure of $[FeL_2Cl_2]$ has not been determined but the $[FeL_2Cl_2]^+$ ion in the perchlorate compound has been shown by X-ray powder photographs to be isostructural with the green form of $[CoL_2Cl_2]ClO_4$ [191]. The latter compound is known to possess a trans-dichloro-configuration from a single crystal X-ray study. [285].

Proton magnetic resonance has also been used to confirm a trans arrangement in these complexes [279,282].

The iron(II) halide complexes are diamagnetic whereas the magnetic moments of the spin-paired iron(III) complexes are consistent with a t_{2g}^5 configuration, where the $^2T_{2g}$ ground state has been split slightly by a tetragonal field [284]. The iron(IV) complexes have magnetic moments indicative of two unpaired electrons (t_{2g}^4) [277].

Finally the electronic spectra of the $[FeL_2X_2]^{n+}$ ($n = 0,1,2$) complexes have been reported by a number of authors [275,277,192,193,279]. The iron(II) cation shows one spin forbidden and two spin allowed "d-d" transitions and the iron(III) cation only four spin allowed ones. The intensities of these absorptions are within the range found for "d-d" transitions in metal-arsine complexes ($< 400\ mol^{-1}\ell cm^{-1}$).

7. Cis-1,2-bis(dimethylarsino)ethylene [194] cis-$Me_2AsCH{=}CHAsMe_2$

This ligand whether it is pure cis or a mixture of cis and trans forms will react with iron(III) chloride in ethanol or ether to form an insoluble red precipitate which contains only the cis chelate, $[FeL_2Cl_2][FeCl_4]$. If complexes of the trans isomer form at all they must remain in solution.

The $[FeL_3][ClO_4]_2$ complex is prepared from hydrated iron(II) perchlorate, $Fe(ClO_4)_2.6H_2O$, and the ligand in ethanol. The $[FeL_3][ClO_4]_3$ is prepared similarly and is more stable with respect to hydrolysis compared with the corresponding dias complex.

The visible spectrum of the $[FeL_3]^{2+}$ cation is typical of that obtained for octahedral spin-paired d^6 complexes and is very similar to that of the dias complex apart from the fact that the extinction coefficients of the former are much smaller.

8. <u>Cis-1,2-bis(diphenylarsino)ethylene</u> [272] cis-ϕ_2AsCH=CHAsϕ_2 (vaa)

This ligand reacts with iron(III) chloride in absolute ethanol to give the green $[FeL_2Cl_2][FeCl_4]$ complex whose conductivity, far infrared spectrum and magnetic moment closely resemble those of the vpp complex.

2.2 EXPERIMENTAL

2.21 THE SYNTHESIS OF SOME BIDENTATE LIGANDS CONTAINING PHOSPHORUS OR ARSENIC DONORS

The following ligands have been synthesised:

1. 1,2-Bis(diphenylphosphino)ethane, dpe. [229]
2. Cis-1,2-bis(diphenylphosphino)ethylene, vpp. [251]
3. Cis-1,2-bis(diphenylarsino)ethylene, vaa. [255]
4. 1,3-Bis(dimethylarsino)propane, dapm. [259]
5. 1,3-Bis(dimethylphosphino)propane, dppm. [252]
6. 1,2-Bis(dimethylarsino)benzene, dias. [237]
7. 1,2-Bis(dimethylphosphino)benzene, PP_{me}. [220]
8. 1,2-Bis(diphenylarsino)benzene, AA_ϕ. [181]
9. 1,2-Bis(diphenylphosphino)benzene, PP_ϕ. [215]

These ligands have all been prepared by literature methods.

The synthesis of these bidentate phosphine and arsine ligands normally requires well ventilated fume cupboards, dry dinitrogen atmospheres, and also adequate fire precautions, (dimethylphosphine for example is pyrophoric). The byproducts are often unpleasant and need to be chemically treated (nitric acid or bleach are often used) before release into the environment.

The methods of ligand preparation are basically the same for a number of the ligands. As a result one example will be quoted for each type.

The apparatus used in the preparation of the following 1,2-bis(diphenylphosphino)ethane ligand is common to all the other syntheses.

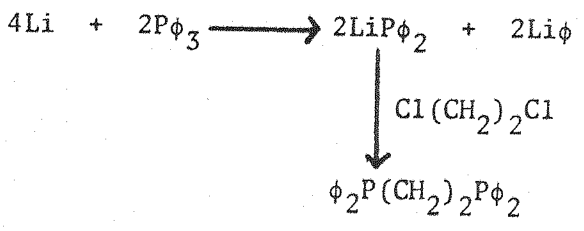
1. 1,2-Bis(diphenylphosphino)ethane

Lithium pieces (∿2 g) were suspended in freshly distilled sodium-dried tetrahydrofuran, THF, (∿250 cm^3) in a three-necked round bottomed quick fit flask fitted with a pressure equalizing funnel, a nitrogen inlet, and a water condenser, and triphenylphosphine (34.1 g, 0.13 mol) was added.

The mixture was stirred overnight with cooling (ice bath). The excess lithium was filtered off. Tertiary butyl chloride (8.33 g, 0.09 mol) was added dropwise with cooling and the mixture stirred for ∿30 minutes.

1,2-Dichloroethane (8.91 g, 0.09 mol) was added dropwise and the mixture refluxed for approximately one hour. The cooled mixture was carefully hydrolysed using deoxygenated water (150 cm^3). The white solid ligand precipitated out and was purified by recrystallisation using a dichloromethane/methanol mixture. The ligand was washed with diethyl ether and dried *in vacuo*. The yield was 25 g (49%).

The above preparation could be written as the following reaction sequence:

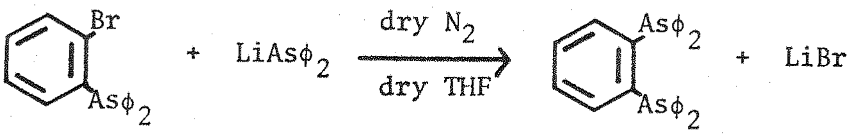


$$\begin{tikzcd}
4Li + 2P\phi_3 \arrow[r] & 2LiP\phi_2 \arrow[d, "Cl(CH_2)_2Cl"] & + \ 2Li\phi \\
& \phi_2P(CH_2)_2P\phi_2 &
\end{tikzcd}$$

and $Li\phi + Bu^tCl \longrightarrow LiCl + \phi H + Me_2C{=}CH_2$

The ligands cis-1,2-bis(diphenylphosphino)ethylene and cis-1,2-bis(diphenylarsino)ethylene were prepared similarly from lithium diphenylphosphide or arsenide and the appropriate haloorganic compound in ∿65% yields.

The 1,2-bis(diphenylarsino)benzene was prepared from the (o-bromophenyl)diphenylarsine compound and lithium diphenylarsenide in 55% yield:



All the ligands dpe, vpp, vaa and AA_ϕ are white air-stable solids.

6. 1,2-Bis(dimethylphosphino)benzene

This preparation was conducted entirely in a dry dinitrogen atmosphere.

Lithium pieces (8-9 g) were suspended in sodium-dried THF (250 cm^3) solution. Dimethylphenylphosphine (56 cm^3, 0.4 mol) was added and the mixture stirred overnight with cooling. The excess lithium was filtered off and tertiary butylchloride (33 cm^3, 27.8 g, 0.3 mol) in dry THF (25 cm^3) was added dropwise with cooling. The mixture was then stirred for thirty minutes.

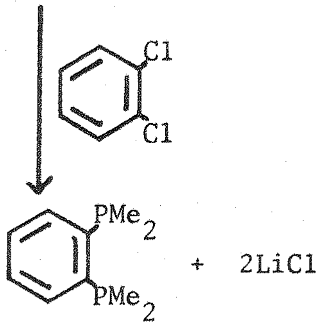
o-Dichlorobenzene (16 cm^3, 22.05 g, 0.15 mol) was added dropwise with cooling and the mixture refluxed for one hour. The cooled mixture was carefully hydrolysed using deoxygenated water (150 cm^3). Two layers then separated out. The lower aqueous layer was extracted twice using diethyl ether and the extract added to the organic layer. The total organic layer was subsequently dried over anhydrous sodium sulphate for twenty-four hours.

The diethyl ether was distilled off under nitrogen at atmospheric pressure and the residue distilled *in vacuo*. The fraction boiling at ∿82°C/1 mm Hg was the ligand. The yield was 35%.

The proton nmr spectrum in deuterochloroform with tetramethylsilane as internal standard displayed a singlet with some underlying structure at 8.68τ (12H) due to the PMe_2 groups and a complex multiplet at ∿2.65τ (4H) due to the aromatic protons.

The reaction could be written as:

$4Li + 2P\phi Me_2 \longrightarrow 2LiPMe_2 + 2Li\phi$ (removed as in (α))



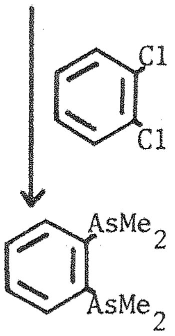
The ligands 1,3-bis(dimethylphosphino)propane and 1,3-bis(dimethylarsino)propane were prepared similarly from the appropriate bromo- or chloroorganic compound and lithium dimethylphosphide or arsenide respectively.

The ligands PP_{me}, dapm and dppm are all air-sensitive liquids which require storage under a nitrogen atmosphere.

7. 1,2-Bis(dimethylarsino)benzene

The ligand was prepared as in the literature [237] under a dry dinitrogen atmosphere. The steps of the preparation can be summarised as follows:

$2IAsMe_2 + 4Na \longrightarrow 2NaAsMe_2 + 2NaI$

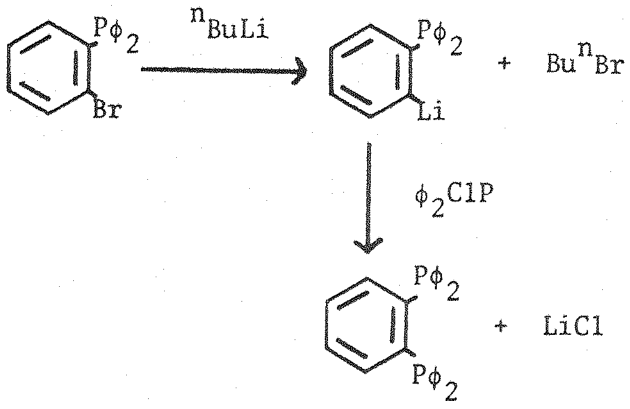


The boiling point of the ligand was 100°C/1 mm Hg. The ligand is an air-sensitive liquid and is obtained in a 45% yield.

9. 1,2-Bis(diphenylphosphino)benzene

n-Butyllithium in hexane (37 cm^3, 0.41 mol) was syringed into a dinitrogen filled reaction flask and the apparatus cooled to 0°C. A solution of (o-bromophenyl)diphenylphosphine (10 g, 0.03 mol) in dry THF (80 cm^3) was added dropwise with vigorous stirring over a one hour period. The solution was then stirred for a further hour after the addition had been completed. Diphenylchlorophosphine (6.5 g, 0.03 mol) in ether (50 cm^3) was added dropwise with stirring and the mixture stirred for five hours at room temperature. The mixture was hydrolysed by the addition of a very dilute hydrochloric acid solution ($300cm^3$). A fawn solid precipitated out and was filtered off. Separation and evaporation of the ether layer produced a further quantity of this solid. The ligand was purified by dissolution in the minimum volume of boiling N,N-dimethylformamide and on cooling the ligand separated out as white crystals. The yield was 7.5 g, i.e. 57%.

The reaction sequence is:



2.22 THE PREPARATION OF THE IRON(III) COMPLEXES OF SOME MONO- AND BIDENTATE PHOSPHINE AND ARSINE LIGANDS

The following preparations were carried out under a dry dinitrogen atmosphere in dry solvents. Anhydrous iron(III) bromide and chloride were handled carefully in order to exclude moisture.

A list of the complexes, their colours and their elemental analyses is given in Tables 2.4 and 2.5.

(a) The preparation of the iron(III) halide (halide = Cl,Br) complexes of the monodentate phosphines and arsines. General method.

Anhydrous iron(III) halide (1 mmol) in sodium dried diethyl ether

(10 cm^3) was added to the ligand (3 mmol) in dichloromethane/diethyl ether (15 cm^3). The product precipitated immediately. The precipitate was filtered off, washed with diethyl ether, recrystallised from dry dichloromethane and finally dried in vacuo. The yields were ∿55%.

In the cases where the product was an oil or a sticky solid the supernatant liquid was poured off, n-hexane added and the mixture heated almost to dryness on a hot plate.

(b) The preparation of the iron(III) halide (halide = Cl,Br) complexes of the bidentate phosphines and arsines

Anhydrous iron(III) halide (1 mmol) in absolute ethanol (10 cm^3) was added to the ligand (2 mmol) in the same solvent (10 cm^3). The product immediately precipitated and was then washed with absolute ethanol and diethyl ether and subsequently dried in vacuo. The yields were ∿75%.

(c) The preparation of the iron(III) halide (halide = Cl,Br) perchlorate, $[FeL_2X_2]ClO_4$, complexes of the bidentate phosphines and arsines

To anhydrous iron(III) halide (1 mmol) in absolute ethanol (10 cm^3) was added lithium perchlorate (5 mmol) also in absolute ethanol (10 cm^3). This solution was then added to the ligand (2 mmol) in the same solvent (10 cm^3). The product precipitated immediately and was washed with absolute ethanol and diethyl ether and subsequently dried in vacuo. The yields were ∿70%.

(d) Attempted preparation of iron(III) thiocyanate complexes of the bidentate ligands cis-1,2-bis(diphenylphosphino)ethylene and 1,2-bis(diphenylphosphino)ethane

The general procedure used was to firstly prepare an absolute ethanol solution containing iron(III) thiocyanate, "$Fe(NCS)_3$", and then react it with the ligand in the same solvent. A "$Fe(NCS)_3$" solution was achieved by displacing the chloride ions in an iron(III) chloride (0.325 g, 2 mmol) absolute ethanol solution (15 cm^3) using an excess of potassium thiocyanate (0.582 g, 6 mmol) dissolved in absolute ethanol (20 cm^3). This total solution was subsequently added dropwise to the ligands (1 mmol) in absolute ethanol. Brown and purple solids respectively were precipitated, washed with diethyl ether and dried in vacuo. The purple solid formulated (see Table 2.9) as $[Fe(dpeO_2)(H_2O)_2(NCS)_2]$ was obtained in a yield of 60%.

(d) Attempted preparation of an iron(III) iodide complex of 1,2-bis (diphenylphosphino)ethane

In this preparation an attempt was made to displace the chlorine in the complex $[Fe(dpe)_2Cl_2][FeCl_4]$ with iodine using an excess of lithium iodide.

The $[Fe(dpe)_2Cl_2][FeCl_4]$ (0.56 g, 1 mmol) complex was dissolved in dichloromethane (10 cm^3) and lithium iodide (0.67 g, 5 mmol) in absolute ethanol (15 cm^3) added dropwise. A brown solid was filtered off, washed with diethyl ether and dried in vacuo.

(e) Attempted preparation of an iron(III) nitrate complex of 1,2-bis (diphenylphosphino)ethane

Hydrated iron(III) nitrate (0.37 g, 1 mmol) in absolute ethanol (10 cm^3) was added to the ligand (0.398, 1 mmol) in dichloromethane (10 cm^3). The yellow product was filtered off, washed with diethyl ether and dried in vacuo. A 60% yield was obtained for the complex formulated as $[Fe(dpeO_2)(NO_3)_2(H_2O)_2]$.

(f) The preparation of iron(III) halide (halide = Br,Cl) complexes of 1,2-bis(dimethylamino)benzene and (o-dimethylaminophenyl)dimethylarsine

Anhydrous iron(III) halide (1 mmol) in absolute ethanol (10 cm^3) was added to the ligand (1 mmol) in the same solvent (10 cm^3). The solid product obtained was filtered off, washed with diethyl ether and dried in vacuo. The yields were ∿70%.

2.23 THE IRON(III) HALIDE COMPLEXES OF SOME MONODENTATE AND BIDENTATE GROUP VB LIGANDS

Levason et al [272] have prepared a series of complexes by the reaction of anhydrous iron(III) chloride with monodentate and bidentate phosphines and arsines. In this study the preparation of the corresponding iron(III) bromide complexes (including the bromide perchlorates) was attempted. The preparations of several iron(III) chloro-complexes were repeated in order to check the method, and some new chloro-complexes were prepared. Attempts were also made to produce nitrate, thiocyanate and iodide complexes of the bidentate ligands, as well as iron(III) halide (halide = Br, Cl) complexes of two bidentate ligands containing nitrogen donors.

The products were characterised by carbon, hydrogen, nitrogen and halogen analysis, by far infrared spectroscopy, conductivity measurements and electronic spectral measurements.

2.231 The iron(III) halide (halide = Cl,Br) monodentate phosphine and arsine complexes

The reaction of anhydrous iron(III) halide with the following ligands in sodium dried diethyl ether was investigated [207]:

(i) Triphenylphosphine, $P\phi_3$.
(ii) Triphenylarsine, $As\phi_3$.
(iii) Tricyclohexylphosphine, PCy_3.
(iv) Tri-n-propylphosphine, PPr_3^n.
(v) Triethylphosphine, PEt_3.
(vi) Tri-n-butylphosphine, PBu_3^n.
(vii) Diethylphenylphosphine, $PEt_2\phi$.
(viii) Dimethylphenylphosphine, $PMe_2\phi$.
(ix) Diphenylmethylphosphine, $PMe\phi_2$.

The products in many cases were found to be oils or sticky solids. Numerous attempts were undertaken to obtain solid crystalline products. One technique employed was to pour off the liquid above the oil or sticky solid, to add n-hexane and then to heat almost to dryness on a hot plate. The solution remaining was then left to cool and the solid to precipitate out completely.

The solid complexes, which were obtained, had a tendency to decompose in the solvents commonly used for conductivity, molecular weight determinations and ultraviolet and visible spectroscopy and this has limited the value of these methods of characterisation.

The monodentate ligands used in this study were chosen in order to show how the donor power of the ligand and the size of the substituent groups, e.g. ϕ or Me, affects the types of complexes formed and their ease of formation and isolation.

Table 2.4 gives a list of the solids obtained from the reaction of iron(III) halide with the monodentate phosphine and arsine ligands and includes their colours, elemental analyses and empirical formulae.

Levason [272] has previously reacted iron(III) chloride with all of these monodentate ligands, except for diethylphenylphosphine, in absolute ethanol yielding crystalline products most of which have been characterised. The iron(III) bromide complexes, however, were found to require rigorously anhydrous conditions and the use of sodium dried diethyl ether was necessary to prevent hydrolysis.

Anhydrous iron(III) bromide reacts with tricyclohexylphosphine and diphenylmethylphosphine to yield red-brown solids whose elemental analyses are consistent with an $FeLBr_3$ empirical formulation. Tricyclohexylphosphine also formed a yellow, 1:1, chloro-complex which has been formulated as a tetrahedral monomer $FeLCl_3$ [272].

The molar conductivities for the chloro- and bromo-cyclohexylphosphine complexes [272] are 22.0 and 29.0 $\Omega^{-1}cm^{-1}$ respectively in nitromethane and this implies that they are both non electrolytes (see Table 2.6).

The far infrared spectra of these halo-cyclohexylphosphine complexes exhibit ν(Fe-X) at 302-310 and 245 cm^{-1} for the bromide and 385 and 350 cm^{-1} for the chloride [272]. Three bands may be expected for each of the bromide and chloride. The third band however may easily be obscured by ligand bands or be too low a frequency to be detected.

Triphenylphosphine and triphenylarsine react with iron(III) bromide to give reddish-brown solids. The former gave elemental analyses which were consistent with the formulation, $Fe(P\phi_3)_2Br_3$, whereas the latter appeared to be an impure 1:1 complex, $Fe(As\phi_3)Br_3$.

Both of these solids readily decomposed in nitromethane as also did the corresponding chloro-complexes. A molar conductivity of 37.56 $\Omega^{-1}cm^{-1}$ for the $Fe(P\phi_3)_2Br_3$ complex in 10^{-3} M nitromethane served to confirm this. The latter complex however gave a molar conductivity of 4.2 $\Omega^{-1}cm^{-1}$ in 1,2-dichloroethane which indicated non-electrolyte behaviour.

The previously prepared green iron(III) chloride triphenyl arsine complex formulated by Levason et al [273] as $[Fe(As\phi_3)_2Cl_3]_2$ possessed a magnetic moment of 6.04 BM and far infrared active ν(Fe-Cl) at 370(s), 280(m) and 235m. The $[Fe(P\phi_3)_2Br_3]$ complex has a magnetic moment of 5.91 BM and this corresponds well with the above complex and implies a d^5, iron(III) cation which is high spin, (five unpaired electrons). This bromo-triphenylphosphine complex also exhibits a band of medium intensity at 299 cm^{-1} in its far infrared spectrum due to ν(Fe-Br).

Impure brown-black solids were also isolated from the reaction between iron(III) bromide and the ligands, tri-n-butyl and tri-n-propylphosphine and purple ones were from the ligands dimethylphenyl and diphenylmethylphosphine.

Previous work [272] has resulted in an orange-yellow complex of empirical formula, $Fe(PPr_3{}^n)Cl_3$ and an orange-yellow oil as the chloro-tri-n-butylphosphine complex. The latter corresponds to the yellow-brown solid obtained in this study.

It was generally found that the monodentate phosphine and arsine ligands containing phenyl-substituted groups gave complexes which were more easily isolated than those with small alkyl groups. The triethylphosphine and diethylphenylphosphine ligands gave only intractable oils upon reaction with iron(III) bromide. An orange-yellow iron(III) chloride complex has however been isolated by Levason [272] and formulated as $[FeLCl_3]$.

The conclusion from this work on the iron(III) halide complexes of the monodentate phosphines and arsines is that they are very difficult to obtain pure. A full characterisation of each of the complexes isolated, was also not always possible due to their instability in common organic solvents and ready decomposition in air.

Finally it was noticed that the iron(III) bromide complexes were generally more difficult to obtain than the chloride ones. The bromine in fact softens the iron(III) cation making it more ready to bond to soft donors such as phosphines and arsines. However, the bromo-complexes which do form are more susceptible to hydrolysis.

2.232 The iron(III) complexes (bromides, chlorides, iodide, nitrates, thiocyanates) of some bidentate group VB ligands

The reaction of anhydrous iron(III) bromide with the following ligands in absolute ethanol was investigated [28].

(i) 1,2-Bis(diphenylphosphino)ethane, dpe.
(ii) Cis-1,2-bis(diphenylphosphino)ethylene, vpp.
(iii) Cis-1,2-bis(diphenylarsino)ethylene, vaa.
(iv) 1,3-Bis(dimethylarsino)propane, dapm.
(v) 1,2-Bis(diphenylphosphino)benzene, PP$_{\phi}$.
(vi) 1,2-Bis(dimethylarsino)benzene, dias.
(vii) 1,2-Bis(diphenylarsino)benzene, AAϕ.
(viii) (*o*-Dimethylphosphinophenyl)dimethylarsine, PAs$_{me}$.
(ix) 1,2-Bis(dimethylamino)benzene, NN$_{me}$.
(x) 1,4-Bis(dimethylamino)benzene, NN$_{me}^{para}$.
(xi) (*o*-Dimethylaminophenyl)dimethylarsine, NAs$_{me}$.
(xii) 1,2-Bis(dimethylphosphino)benzene, PP$_{me}$.
(xiii) (*o*-Diphenylphosphinophenyl)diphenylarsine, PAϕ.
(xiv) (*o*-Diphenylstibinophenyl)diphenylarsine, SbAϕ.
(xv) 1,3-Bis(dimethylphosphino)propane, dppm.

A few iron(III) chloride complexes were also prepared for verification of the method. These have been compared with those of Levason [272] and also with the corresponding iron(III) bromide complexes.

The 1,2-bis(dimethylamino)benzene ligand and the other mixed donor ligands can be referred to in Chapter 3. Their iron(III) complexes are however included in this chapter.

Table 2.5 gives a list of the solid compounds for which elemental analyses were obtained and includes the postulated formulations.

Iron(III) bromide in absolute ethanol reacts with 1,2-bis(diphenylphosphine)ethane, 1,3-bis(dimethylarsino)propane, 1,2-bis(diphenylarsino) benzene and 1,2-bis(dimethylarsino)benzene to yield brown crystalline solids of stoichiometry, $FeLBr_3$ (see Table 2.5). This same stoichiometry was exhibited by cis-1,2-bis(diphenylphosphino)ethylene which gave a green complex and also 1,2-bis(diphenylphosphino)benzene, which gave a complex, brown at 298K, and bright green at 77K. The corresponding chloro-complexes were either red or green crystalline solids at room temperature [272]. The green iron(III) chloride vpp complex of stoichiometry $FeLCl_3$, first prepared by Levason, was remade in this study.

A brown solid was obtained from the reaction of iron(III) bromide and cis-1,2-bis(diphenylarsino)ethylene but this time of stoichiometry FeL_2Br_3.

The ligands 1,2-bis(dimethylphosphino)benzene [275] and (o-diphenylphosphinophenyl)diphenylarsine again gave brown solids but these were impure.

The ligand (o-diphenylstibinophenyl)diphenylarsine however appeared to form no product upon reaction with iron(III) halide (halide = Cl, Br) in absolute ethanol. Sodium dried diethyl ether was then tried as solvent but with no success. This latter method has been used previously in the case of monodentate ligands and also in the preparation of some of the iron(III) chloride complexes. For example dpe, PP_ϕ, PA_ϕ, and vaa [272]. The reason for adopting this solvent in preference to absolute ethanol is that the strong oxygen donor alcohol is able to compete successfully with the softer group VB donors for the 'hard' iron(III).

An attempt was made to prepare an iron(III) chloride complex of 1,2-bis(diphenylarsino)benzene in sodium dried diethyl ether but no reaction appeared to occur.

Previous attempts to prepare the iron(III) chloride complexes of dae, AA_ϕ, dpm and dppp also failed [272].

Some observations were made regarding the iron(III) chloride and bromide complexes:

(1) Iron(III) chloride forms complexes readily with dias but forms none with AA_ϕ.

(2) Iron(III) chloride forms complexes with dpe but not with dpm.

(3) Iron(III) bromide forms complexes with PP_ϕ, AA_ϕ and PA_ϕ but not with SbA_ϕ.

(4) Iron(III) bromide forms a complex with AA_ϕ but iron(III) chloride does not.

These results have shown the importance of both the donor properties of the ligand and chelate ring size on the formation of complexes of 'soft' donors with 'hard' acceptors. A small chelate ring size for example causes greater strain and thus such a complex is likely either not to form or to decompose readily. Also ligands containing the heavier donor atoms (for example arsenic rather than phosphorus) or those containing aryl rather than alkyl substituent groups are poorer donors and are thus less likely to form complexes. Finally since bromide softens iron(III) more than chlorine, iron(III) bromide has more chance of forming complexes with the poorer donor ligands.

The isolated complexes both in this study and in the iron(III) chloride complexes of Levason were found to be 1:1 electrolytes in 10^{-3} M nitromethane and 1,2-dichloroethane solutions. The experimental values shown in Table 2.6 in fact compare very well with two other iron(III) bromide complexes, $[Fe(dias)_2Br_2][FeBr_4]$ and $[Fe(dias)_2Br_2](BF_4)$ reported in the literature [277] which have molar conductivities of 86 and 98 Ω^{-1} mol^{-1} in 10^{-3} M nitromethane respectively.

It was noticed that the molar conductivities of the vaa and vpp complexes in nitromethane were rather high and this implied that a considerable degree of solvolysis was occurring.

This had previously been observed also for the $[FeL_2Cl_2][FeCl_4]$ (L = vaa, dpe) (123 and 113 $\Omega^{-1}cm^{-1}$ in 10^{-3} M nitromethane resp) complexes.

Table 2.8 shows the accepted ranges for the various electrolyte types in two solvents. Two different solvents were required in this iron work due to the differing degrees of solubility and decomposition of the complexes in each.

The iron(III) bromide complexes possessing the $FeLBr_3$ stoichiometry gave no evidence of phosphine or arsine oxide in their infrared spectra but did exhibit a strong band at ∿290 cm^{-1} in the far infrared region. This latter band was indicative of the presence of a tetrabromoferrate(III) anion, $FeBr_4^-$. This was established by the preparation of the reddish-brown compound triphenylmethylphosphonium tetrabromoferrate(III), $[PMe\phi_3][FeBr_4]$ which gave a very strong band at 290 cm^{-1}. This evidence together with the fact that the complexes were 1:1 electrolytes in nitromethane suggested that they could be formulated as $[FeL_2Br_2][FeBr_4]$. A similar conclusion has been made as regards the iron(III) chloride complexes. The iron(III) chloride complex of vpp in this study displayed a strong band at 378 cm^{-1} which is identical to that previously found for the same complex and in the same region as the other iron(III) chloride complexes. This stretching frequency has been attributed to the tetrachloroferrate(III) anion.

Table 2.8

Acceptable ranges (found ranges) of molar conductivity for different electrolyte types in two different solvents [100]

10^{-3} M solutions	1:1	2:1	3:1
$MeNO_2$	75-95 (60-150)	150-180 (115-250)	220-260 (180-300)
1,2-Dichloroethane	10-24	~28	

It was noticed that the only cations which could be obtained were 1:2 (iron:ligand) regardless of the ratios adopted in their preparations. The cations, $[FeL_2Br_2]^+$, are postulated as being of trans geometry (D_{4h} symmetry), a single iron-bromine stretching frequency then being expected [191,285].

In a few of the iron(III) bromide complexes weak shoulders were observed on the $FeBr_4^-$ absorption which were probably attributable to the ν(Fe-Br) stretching frequency of the aforementioned cations. However in most of them it was likely that either ligand or $FeBr_4^-$ bands obscured this vibration.

The ratio ν(Fe-Br)/ν(Fe-Cl) was calculated and found to be ~0.77

which was in accordance with the 0.75-0.78 range previously reported for tetrahedral anions, MX_4^{n-} [191,286]. This gave further evidence for the presence of the FeX_4^- anion.

The metal isotope technique has been adopted by Konya and Nakamoto [533] in order to assign iron-arsenic and iron-halogen vibrations. These will both shift upon isotopic substitution. However the two vibrations are distinguished by assuming that the iron-halogen band is much more intense than the iron-arsenic band.

The electronic spectral data of the iron(III) bromide complexes are shown in Table 2.7. The solution and solid state spectra were similar. These spectra were of little use in the characterisation of the iron(III) bromide complexes due to very intense charge transfer bands obscuring the "d-d" transitions to a large extent. The spectra were typical of those observed for iron(III) compounds previously. It was possible however to place the ligands in reasonable 'ligand' spectrochemical series for the first intense band (14000-17000 cm^{-1}):

$$\text{dias} > \text{dapm} > \text{dpe} > \text{vpp} \sim \text{PA}\phi \sim \text{PP}\phi > \text{PCy}_3 > \text{P}\phi_3$$

As a result of the "d-d" bands being obscured it was not possible to calculate the various ligand parameters Dq, B and C. In previous studies Dq values for the PP_{me} and dias ligands have been calculated and have shown that the former is greater. This was thought to arise from the metal-phosphorus bonding being stronger than the metal-arsenic bonding. In general the ligands containing arsenic tended to be more labile than the analogous phosphorus ones.

In addition the green $[Fe(vpp)_2Cl_2][FeCl_4]$ complex, prepared here in order to check the method, gave electronic spectral bands at 16,800 and 24,000 cm^{-1} which agreed with the data of Levason [272].

The complexes of the methyl-substituted ligands dapm and dias were generally air-stable, and treatment of their absolute ethanol solutions with excess lithium perchlorate in absolute ethanol resulted in good yields of the green, $[FeL_2Br_2]ClO_4$ complexes. The new crimson $[Fe(PAs_{me})_2Cl]ClO_4$ complex was similarly prepared, (see Table 2.5). Only an impure green solid could be obtained however from the reaction of iron(III) bromide, PAs_{me} and lithium perchlorate in absolute ethanol.

The phenyl-substituted ligand iron(III) bromide complexes were less robust and attempts to replace the $[FeBr_4]^-$ anion with ClO_4^- were unsuccessful. The $[FeBr_4]^-$ anion clearly must exert a considerable stabilizing effect in these complexes.

The above formulation of $[FeL_2X_2]ClO_4$ (X = Cl, Br) was supported by the fact that these complexes were 1:1 electrolytes in 10^{-3} M nitromethane.

The presence of the perchlorate counter anion was shown by the presence of bands at 1080 and 620 cm^{-1} in the near infrared region.

A weaker band was observed in the far infrared spectrum of $[Fe(dapm)_2Br_2]ClO_4$ at 311 cm^{-1} which was probably due to the iron-bromine stretch in the trans-$[Fe(dapm)_2Br_2]^+$ cation.

The infrared spectra of these halide-perchlorate complexes also showed no evidence of phosphine or arsine oxide.

The data quoted in Table 2.6/7 for the $[Fe(PAs_{me})_2Cl_2]ClO_4$ complex closely parallelled the corresponding dias complex prepared by Levason [272]. The Mössbauer data in Table 2.6 indicated both for the dias [272] and PAs_{me} iron(III) chloride complex that they contained a tetragonally distorted, trans, d^5, low spin, iron(III) cation.

The green $[Fe(dias)_2Br_2]ClO_4$ complex exhibited its lowest intense absorption at 16230 cm^{-1} in its solid state electronic spectrum, the same region as that seen for the green $[FeL_2Cl_2][FeCl_4]$ (L = bidentate phosphine or arsine) compounds. The green $[Fe(dapm)_2Br_2]ClO_4$ similarly absorbed at 15875 cm^{-1}. The red iron(III) chloride complexes have been observed to absorb at ∿18000 cm^{-1} [272].

The Mössbauer spectrum of $[Fe(dapm)_2Br_2]ClO_4$ indicated that the cation was low spin and also that there was less distortion from octahedral (cubic) symmetry than both the $[Fe(vpp)_2Br_2]^+$ and $[Fe(PAs)_2Br_2]^+$ cations.

Reasonable ^{57}Fe Mössbauer spectra were obtained by Dr S M Nelson of Queen's University, Belfast, for the abovementioned complexes. There was considerable difficulty in obtaining the spectra especially those containing both arsenic and bromine, which have proved to be too absorbing.

Variable temperature magnetic studies were also carried out by Dr Nelson. It was found that for the $[Fe(dapm)_2Br_2][FeBr_4]$ compound that the effective magnetic moment decreased with temperature. The $[Fe(dapm)_2$

$Br_2]ClO_4$ complex was prepared in order to eliminate the error due to assuming a magnetic moment for the tetrabromoferrate anion and its magnetic moment was also observed to decrease with temperature. The same behaviour was found for the $[Fe(dias)_2Br_2]^+$ cation.

It was initially thought that these might be the first examples of a high spin $\rightleftharpoons$ low spin equilibrium involving iron(III) complexes of soft donor ligands. Previous examples had all contained 'hard' nitrogen or oxygen donors, e.g. Schiff's bases [190,287].

The room temperature effective magnetic moments procured by Levason for the $[FeL_2Cl_2]^+$ cations were in the range 2.14-2.4 BM. This is the range expected for a low spin d^5 cation. The $[Fe(vpp)_2Br_2]^+$ cation exhibits a room temperature magnetic moment of 2.57 BM which is slightly high but may still be considered acceptable for this same type of cation.

It was felt however that the magnetic moments obtained for the $[FeL_2Br_2]^+$ cations were in general too high. This led to the conclusion that hydrolysis was probably taking place in the samples resulting in the formation of compounds such as ferric oxide. Ferromagnetism was then proposed as the cause of the magnetic behaviour described.

Hydrolysis appears to occur more readily in the iron(III) bromide than the iron(III) chloride complexes of the phosphine and arsine ligands. The dark brown $[Fe(dias)_2Br_2][FeBr_4]$, for example, was noticed to be far less stable to water than the corresponding crimson iron(III) chloride complex.

It was also observed that the iron(III) bromide complexes gave brownish solutions in acetone which then became green on addition of water. This was thought to be a consequence of the $[FeL_2Br_2][FeBr_4]$ hydrolysing to $[FeL_2Br_2]Br$. The green, iron(III) bromide, vaa complex isolated may well be of the latter formulation.

The preparations of some iron(III) thiocyanate, nitrate and iodide complexes are now discussed.

The $[FeL_2Br_2][FeBr_4]$ (L = dpe, vpp) complexes were treated with excess potassium thiocyanate in an absolute ethanol solution and yielded brown and purple solids respectively. The infrared spectra, of those produced, showed both the presence of two types of thiocyanate with bands at

2040 and 2100 cm^{-1} possibly ionic and N-bonded respectively, and also phosphine oxide with a broad band at $\sim$1100 cm^{-1}.

Phosphine oxide bands in the infrared were similarly found for the brown solid which precipitated from the reaction of $[Fe(dpe)_2Cl_2][FeCl_4]$ with lithium iodide in absolute ethanol and also for the yellow solid obtained from the reaction of hydrated iron(III) nitrate, $Fe(NO_3)_3.9H_2O$, with the ligand dpe (1087 and 1150 cm^{-1}).

A band arising from the coordinated nitrate in this latter complex was found at 1276 cm^{-1}. In addition since no strong bands were found at 290 cm^{-1} the presence of the $[FeBr_4]^-$ was excluded.

The existence of phosphine oxide in these complexes was consistent with the reduction of the iron(III) accompanied by oxidation of anions and some oxidation of the ligands. This result was in agreement with previous work by Nyholm [288].

Table 2.9 lists the above mentioned complexes together with their elemental analyses and postulated empirical formulae.

Attempts were made to prepare the $[FeL_2X_2]^+$ (X = Cl, Br) cations by reacting the iron(III) halides with the ligands 1,2-bis(dimethylamino) benzene, 1,4-bis(dimethylamino)benzene and (o-dimethylaminophenyl)-dimethylarsine in sodium dried diethyl ether. Rigorously anhydrous conditions including dry nitrogen atmospheres were used for these preparations.

Brown and green solids were produced, three of which were consistent with the empirical formula "$(FeLX_3)_2O$" (X = Cl, Br) (see Table 2.9).

The iron(III) bromide complex of NAs_{me} and the iron(III) chloride complex of NN_{me}^{para} displayed medium to strong broad bands at 888 and 878 cm^{-1} respectively in their infrared spectra. A band in the 800-890 cm^{-1} region is characteristic of ν(Fe-O-Fe) in oxo-bridge complexes.

Oxo-bridged complexes of iron(III) have previously been found for other nitrogen containing ligands such as pyridines [287,289,290]. Some examples of which have been included in Table 2.10.

An X-ray crystal structure of the pyridine complex $[(HPy)_2(Cl_3Fe-O-FeCl_3)]$ in Table 2.10 has been obtained [291], and shows short iron-oxygen bonds and an approximately tetrahedral geometry about each iron. The local symmetry about each iron is C_{3v} which implies there are two infrared active iron-chlorine stretching vibrations. This has been observed for all four of the complexes in Table 2.10.

The iron(III) chloride complex of NN_{me}^{para} prepared in this study similarly gave two far infrared bands at 314 and 358 cm^{-1}.

The iron(III) bromide complex of NAs_{me} and the iron(III) chloride complex of NN_{me}^{para} displayed broad bands attributable to the N-H stretching frequency at 3310 and 3360 cm^{-1} respectively similar to the substituted ammonium cations of the complexes in Table 2.10. In addition the iron(III) chloride complex of NN_{me}^{para} was also a 2:1 electrolyte in 10^{-3} M nitromethane. These facts pointed to this latter complex being of the $(HNN_{me}^{para})_2(Cl_3Fe\text{-}O\text{-}FeCl_3)$ formulation.

It was not possible to measure the conductivity of the iron(III) bromide complex of NAs_{me} since it was only partially soluble in nitromethane. However it seems likely that this complex has the same formulation, $(HNAs_{me})_2(Br_3Fe\text{-}O\text{-}FeBr_3)$.

Previous work [289] has shown that different products could be isolated from the reaction between iron(III) chloride and various pyridines in ethanol depending upon the temperature. It has been thought that these different products represented stages in the base hydrolysis of iron(III). Examples of such compounds are $Fe_2(dipyam)_3Cl_4O.5H_2O$ and $Fe_2(dipyam)_3Br_3(OH)O$.

The uncharacterised NN_{me}^{para} and NAs_{me} complexes may be similar hydrolysed iron(III) compounds.

It was therefore concluded that it did not appear possible by this means to obtain the originally intended $[FeL_2X_2]^+$ (X = Br, Cl) cations regardless of how anhydrous a system was achieved. The oxo-bridge complexes are a result of the basic properties of the nitrogen in these ligands. The protons, which were present even if there was only a trace of moisture in the system, will be abstracted by the nitrogen.

Table 2.4 The iron(III) halide complexes of the monodentate phosphines and arsines

Iron(III) Salt	Ligand	Colour	Product/Elemental Analysis Found (Calculated)			Empirical Formula/ Comments
			C	H	X(Br,Cl)	
$FeBr_3$	PCy_3	red-brown	36.0(37.5)	5.5(5.73)	39.9(41.7)	$FeLBr_3$
$FeBr_3$	$PMe\phi_2$	red-brown	32.7(31.45)	2.7(2.62)		$FeLBr_3$
$FeBr_3$	$P\phi_3$	red-brown	52.0(52.6)	3.8(3.7)		FeL_2Br_3
$FeBr_3$	PPr^n_3	brown-black	33.0	6.8	35.6	Impure, possibly the 2:1, FeL_2Br_3 complex
$FeBr_3$	$As\phi_3$	red-brown	38.6	1.8	29.8	Impure, possibly the 1:1, $FeLBr_3$ complex
$FeCl_3$	PBu^n_3	yellow-brown	33.0	6.9	31.5	

Table 2.5 Some iron(III) halide complexes of the bidentate group VB ligands and other relevant complexes

Iron Salt	Reaction/ Ligand	Colour	Product Elemental Analysis Found (Calculated)			Empirical Formula	Postulated Formulation/ Comments
			C	H	X(Br,Cl)		
$FeBr_3$	dpe (2 samples)	red-brown	45.2(45.8) 46.6(45.8)	4.6(3.4) 4.4(3.4)		$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeBr_3$	vpp	green	46.6(45.2)	3.2(3.2)	33.0(34.7)	$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeCl_3$	vpp	green	55.3(55.86)	4.0(3.94)	18.8(19.06)	$FeLCl_3$	$[FeL_2Cl_2][FeCl_4]$
$FeBr_3$	dapm	dark-brown	15.35(15.35)	3.26(3.31)		$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeBr_3$	dapm + ClO_4	dark-green	20.76(20.51)	4.41(4.43)		$[FeL_2Br_2]ClO_4$	$[FeL_2Br_2]ClO_4$
$FeBr_3$	PP_{ϕ}	brown	47.8(48.5)	3.2(3.2)	32.1(32.3)	$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeBr_3$	AA_{ϕ}	brown	43.17(43.4)	3.01(2.9)		$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeBr_3$	dias	dark-brown	20.36(20.65)	2.9(2.8)		$FeLBr_3$	$[FeL_2Br_2][FeBr_4]$
$FeBr_3$	dias + ClO_4	dark-green	27.4(27.1)	3.6(3.6)		$[FeL_2Br_2]ClO_4$	$[FeL_2Br_2]ClO_4$
$FeCl_3$	PAs_{me} + ClO_4	green	34.2(33.8)	4.2(4.5)		$[FeL_2Cl_2]ClO_4$	$[FeL_2Cl_2]ClO_4$
$FeBr_3$	PAs_{me} + ClO_4	green	24.4	3.4		?	?
$FeBr_3$	PA_{ϕ}	brown	41.0	3.2	28.8	?	Impure, may be $[FeL_2Br_2][FeBr_4]$ complex
$FeCl_3$	dppm + LiBr	greenish-yellow	19.5	4.6	Br=26.4 Cl=14.6	?	Incomplete ligand exchange
$FeBr_3$	$\phi_3PMe^+Br^-$	red-brown	34.8(34.91)	2.7(2.75)	47.6(49.0)	$[\phi_3PMe][FeBr_4]$	$[\phi_3PMe][FeBr_4]$
$FeBr_3$	vaa	brown	47.5(49.3)	3.6(3.5)	17.9(18.9)	$[FeL_2Br]Br$	$[FeL_2Br]Br$

Table 2.6 Molar conductivity, infrared, Mossbauer and magnetic data of the iron III halide complexes of some group VB ligands

Complex	$\Lambda^a_m(\Omega^{-1}cm^{-1})$	$\nu(Fe\text{-}X)^{bg}(cm^{-1})$ other bands	$T(K)^e$	Mossbauer Data^h $[FeL_2Br_2]^+$ $\delta(mms^{-1})$	$\Delta E(mms^{-1})$	$[FeBr_4]^-$ $\delta(mms^{-1})$	$\Delta E(mms^{-1})$	μ_{eff}(BM)/Cation
$[Fe(dpe)_2Br_2][FeBr_4]$	81/$MeNO_2$							
$[Fe(vpp)_2Br_2][FeBr_4]$	11.2/DE 113/$MeNO_2$	295(s)m 284sh	293 77	0.31 0.36	1.95 1.98	0.36 0.34	0.41 0.20	2.57
$[Fe(PP\phi)_2Br_2][FeBr_4]$	10.4/DE	300(s), 291(s), 282(s) broad band						
$[Fe(dias)_2Br_2][FeBr_4]$	95.6/$MeNO_2$	296(s)		Mossbauer too absorbing				3.28
$[Fe(AA\phi)_2Br_2][FeBr_4]$	73.7/$MeNO_2$	302(vs), 282sh broad band						
$[Fe(dapm)_2Br_2][FeBr_4]$	72.8/$MeNO_2$	296(vs)						4.36
$[Fe(vaa)_2Br]Br$	47.25/DE	276m, 303s						
$[Fe(dias)_2Br_2]ClO_4$	94/$MeNO_2$	277s, 299w/m, 310m						3.26
$[Fe(dapm)_2Br_2\ \ ]ClO_4$	88.6/$MeNO_2$	311(m), 299(w), 278(w)	293 77	0.5 Spectrum too broad, impurity signal at 0.48 mms^{-1} could be $[FeBr_4]^-$	1.73			
$[Fe(vpp)_2Cl_2][FeCl_4]$	79.8/$MeNO_2$	378(s)						
$[Fe(PAs_{me})_2Cl_2]ClO_4$	73.9/$MeNO_2$	379(vs), 269sh	293 77	0.27 0.32	2.48 2.62			3.51

/continued.....

Table 2.6 continued.....

$(NN^{para}_{me}H)_2$ $(Cl_3Fe\text{-}O\text{-}FeCl_3)$	$161.8/MeNO_2$	314(s), 358(vs)	3360(N-H) 878 (Fe-O-Fe)
$(NAs_{me}H)_2$ $(Br_3Fe\text{-}O\text{-}FeBr_3)$	only partially soluble in $MeNO_2$		3310(N-H) 888 (Fe-O-Fe)
$[\phi_3PMe][FeBr_4]$	$95/MeNO_2$	290(vs)	
$Fe(P\phi_3)_2Br_3$	$37.56/MeNO_2$ 4.2/DE	294sh, 299(m), 306sh	
$Fe(PCy_3)Br_3$	$29.0/MeNO_2$	310(vs)-302(vs), 245(s)	
$Fe(PMe\phi_2)Br_3$	$48/MeNO_2$		

[a] DE = 1,2-dichloroethane; $MeNO_2$ = nitromethane

[b] ν(Fe-X) = Iron-halide stretching frequency

[c] 5 x 10^{-4} M solutions in dichloromethane

[d] E_{max} = position of band maxima; ε_{mol} = molar extinction coefficient

[e] T = temperature in degrees Kelvin

[f] Nujol Mull spectra

[g] Far infrared in the range 400-200 cm^{-1}; near infrared in the range 4000-600 cm^{-1}.

[h] δ = isomer shift and ΔE = quadrupole splitting

[j] 5 x 10^{-4} M solution in acetone

[k] 5 x 10^{-4} M solution in nitromethane

Table 2.7 The electronic spectral data of some iron(III) halide complexes of group VB ligands

Complex	E_{max} (ϵ_{mol}) x 10^{-3} cm^{-1} de	E_{max} x 10^{-3} cm^{-1} df
$[Fe(dpe)_2Br_2][FeBr_4]$	15.4(9900), 15.8sh, 16.3(2530) 23.1, 25.4 and 26.8 (very high)	16.0sh, 20.75, 22.5, 24.8, 29.0
$[Fe(vpp)_2Br_2][FeBr_4]$	15.35(67), 21.6(29.73), 24.75(3464)	15.15, 15.5sh, 20.35, 23.8
$[Fe(PP\phi)_2Br_2][FeBr_4]$	14.4(915), 21.0(6990), 23.0(6100), 23.4sh, 24.4sh, 24.75(10^5), 25.7(71000), 28.7(63000)	15.0, 20.45, 23.5, 24.5, 29.0
$[Fe(dias)_2Br_2][FeBr_4]$	21.4^j(26510), 23.6(27260), 25.4(24075), 30.1 (43500)	15.75sh, 16.2, 16.55sh, 16.8, 19.0sh 20.85, 24.0
$[Fe(AA\phi)_2Br_2][FeBr_4]$	21.2(32050), 23.0(26020), 25.1(32050), 26.9(21890), 30.3(23200), 31.3(25200)	15.150, 20.7, 23.4, 25.7
$[Fe(dapm)_2Br_2][FeBr_4]$	16.25(1012), 20.55(1204), 23.2(1204), 24.55(1243), 27.00(1243)	
$[Fe(vaa)_2Br]Br$	21.45(1288), 24.7(1958), 27.8(1958)	20.75, 24.0, 26.2sh, 28.0sh
$[Fe(dias)_2Br_2]ClO_4$	16.35(1656), 24.2(1656), 30.1(4823)(br)	16.23, 17.9sh, 21.0sh, 22,45sh, 23.7sh, 25.0
$[Fe(dapm)_2Br_2]ClO_4$	20.8(12040), 23.2(11370), 25.3(13980), 30.2(13560), 32.75(12760)	14.2sh, 15.75, 16.00, 17.85, 20.8, 22.0, 23.0, 24.0, 25.3
$[Fe(vpp)_2Cl_2][FeCl_4]$	16.7(1960), 19.4(3790), 25.3(2960), 26.1 (57145), 27.7(67700), 30.5(61100)	16.1, 16.8sh, 24.0sh
$[Fe(PAs_{me})_2Cl_2]ClO_4$	17.8(1335), 27.0(6110), 30.0(7280), 32.8(3340)	17.0, 24.3, 26.3, 29.0

/continued......

Table 2.7 continued.....

$(NN^{para}_{me}H)_2$ $(Cl_3Fe\text{-}O\text{-}FeCl_3)$	25.0sh[k]	18.5sh, 20.35sh, 24.8, 27.3
$(NAs_{me}H)_2$ $(Br_3Fe\text{-}O\text{-}FeBr_3)$	16.25, 21.5, 23.5sh, 25.4	21.5sh, 25.8sh, 26.75sh, 29.1sh, 30.8sh
$[\phi_3PMe][FeBr_4]$	21.2(2650), 23.1(2160), 25.2(2800) 30.5(2600), 32.7(2190)	20.1, 20.9, 22.9, 24.35
$Fe(P\phi_3)_2Br_3$	21.0sh, 23.6, 33.0(br sh)	14.25, 22.35sh, 29.0(br sh)
$Fe(PCy_3)Br_3$	21.7(939), 23.7(1602), 24.75(1523), 26.4(1523), 28.5(1523)	14.7, 29.75
$Fe(PMe\phi_2)Br_3$		15.7sh, 16.2

Table 2.9 The iron(III) nitrate, thiocyanate complexes of dpe and vpp and the iron(III) halide complexes of 1,2-bis(dimethylamino)benzene and (*o*-dimethylamino)dimethylarsine

Iron Salt	Ligand	Colour	Elemental Analysis Found (Calculated)			Empirical Formula
			C	H	N	
$Fe(NO_3)_3 9H_2O$	dpe	yellow	55.2(55.2)	3.9(4.6)	3.7(3.8)	$Fe(LO_2)(H_2O)_2(NO_3)_2$
'$Fe(NCS)_3$'	dpe	brown	53.2(54.0)	4.0(4.5)	2.4(3.8)	$Fe(LO_2)(H_2O)_2(NCS)_2$
'$Fe(NCS)_3$'	vpp	purple	55.3	4.2	0.6	?
$FeCl_3$	NN_{me}	brown	35.8(35.87)	4.5(4.78)		"$(FeLCl_3)_2O$"
$FeBr_3$	NN_{me}	brown	22.73	3.45	4.69	?
$FeCl_3$	NAs_{me}	green	27.88	4.35	4.07	?
$FeBr_3$	NAs_{me}	brown	21.64(22.68)	2.97(3.02)	2.65(3.49)	"$(FeLBr_3)_2O$"
$FeCl_3$	NN_{me}^{para}	brown	35.1(35.87)	5.0(4.78)	8.0(8.37)	"$(FeLCl_3)_2O$"

Table 2.10 Some oxo-bridged iron(III) chloride complexes of pyridines and their infrared spectral data

Complexes[a]	Colour	ν(Fe-Cl)[b] (cm^{-1})		Other bands (cm^{-1})	References
(1) $(Hdipyam)_2[(FeCl_3)_2O]^{2-}$	yellow	375	323	890 (Fe-O-Fe) 3320 (N-H)	[289]
(2) $(Htripyam)_2[(FeCl_3)_2O]^{2-}$	yellow	360	317	890 (Fe-O-Fe) 3320 (N-H)	[289]
(3) $(H5MPT)_2[(FeCl_3)_2O]^{2-}$	yellow	360	318	863 (Fe-O-Fe) 3320 (N-H)	[289]
(4) $(HPy)_2[(FeCl_3)_2O]^{2-}$	orange-yellow	360	311	860 (Fe-O-Fe) 3235 (N-H)	[291]

[a] dipyam = di-(2-pyridyl)amine; **tripyam** = tri-(2-pyridyl)amine;
5MPT = 5-methyl-2-pyridyldi(2-pyridyl)amine; py = pyridine.

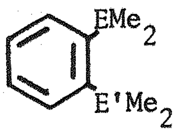
[b] ν(Fe-Cl) = iron-chlorine stretching frequency.

CHAPTER THREE

THE COBALT(II) COMPLEXES OF A SET OF LIGANDS OF THE TYPE *o*-$C_6H_4(EMe_2)(E'Me_2)$ (E=E'=N,P,As;E=N;E'=Sb AND E=P;E'=SMe)

3.1 INTRODUCTION

The main aim of this work was to investigate and compare the chemistry of the cobalt(II) complexes of the following mixed donor bidentate ligands:



E=N,E'=P	(*o*-dimethylaminophenyl)dimethylphosphine.
E=N,E'=As	(*o*-dimethylaminophenyl)dimethylarsine.
E=N,E'=Sb	(*o*-dimethylaminophenyl)dimethylstibine.
E=P,E'=As	(*o*-dimethylphosphinophenyl)dimethylarsine.
E=P,E'=S	(*o*-methylthiophenyl)dimethylphosphine.

Complexes of the corresponding diamine, diphosphine and diarsine ligands were also prepared and compared with both those above and the coresponding nickel(II) complexes [292].

i.e.

E = N, P, As

Some cobalt(III) complexes of dias were also prepared.

The chapter is divided into two parts. Firstly Section 3.1 which covers the general background to the chemistry of cobalt(II), cobalt(III) and nickel(II), the reported preparations of mixed donor ligands and a summary of their cobalt(II), (III) and nickel(II) complexes, and secondly the above-mentioned experimental work.

3.11 THE CHEMISTRY OF COBALT(II), COBALT(III) AND NICKEL(II) WITH SPECIAL REFERENCE TO THAT OF GROUP VB AND VIB LIGANDS

Cobalt and nickel are first row transition elements with electronic configurations $(Ar)4s^2 3d^7$ and $(Ar)4s^2 3d^8$ respectively [1].

Cobalt generally occurs in nature in association with nickel and the separation of these as the pure metals is not a simple process.

Cobalt exists in the oxidation states -1,0,+1,+2,+3,+4 and +5 and nickel in the same apart from the +5 oxidation state. The most commonly found of these are +2 and +3 for cobalt and +2 for nickel. Table 3.1 shows the more important coordination numbers and geometries for these states.

Table 3.1

The most common oxidation states and stereochemistries of cobalt and nickel

Oxidation state	Coordination number	Geometry	Examples
Co(II), d^7	4*	td	$[CoCl_4]^{2-}$, $[CoBr_2(PR_3)_2]$[a]
	5	TBP	$[Co(Me_6tren)Br]^{+}$[b]
	5	SP	$[Co(ClO_4)(Me\phi_2AsO)_4]^+$
	6*	oct	$CoCl_2$, $[Co(NH_3)_6]^{2+}$
Co(III), d^6	6*	oct	$[Coen_2Cl_2]^{+}$[c], $[Co(CN)_6]^{3-}$
Ni(II), d^8	4*	sq.pl	$[Ni(PEt_3)_2Br_2]$, $[Ni(CN)_4]^{2-}$
	4*	td	$[NiCl_4]^{2-}$, $[Ni(P\phi_3)_2Cl_2]$
	5	SP	$[Ni(CN)_5]^{3-}$
	5	TBP	$[Ni(QAS)X]^{+}$[d], $[Ni(CN)_5]^{3-}$
	6*	oct	$[Ni(NCS)_6]^{4-}$, $[Ni(bipy)_3]^{2+}$[e]

* Most commonly found coordination number and stereochemistry.

[a] R = alkyl or aryl group.

[b] Tris(2-dimethylaminoethyl)amine, $N[(CH_2)_2NMe_2]_3$.

[c] Ethylenediamine.

[d] QAS = tris-(o-diphenylarsinophenyl)arsine.

[e] Bipy = bipyridyl.

There is a trend toward increased stability of the +2 oxidation state relative to the +3 in traversing the first transition series from left to right. As a result of this, cobalt(III) is relatively unstable in simple compounds prepared in aqueous media but is stable in the presence of complexing agents such as nitrogen donor ligands. These nitrogen donor ligands make a strong contribution to the ligand field.

In the case of nickel the +3 oxidation state is even less stable and it is only the +2 state which is common.

Cobalt(II)

Cobalt(II) forms tetrahedral complexes more readily than any other transition metal ion [325,328,343]. This is due to the fact that the ligand field stabilisation energies disfavour this geometry relative to the octahedral one less than with any other d^n ($1 \leq n \leq 9$) ion. The difference in the stabilities of the octahedral and tetrahedral geometries is not great and as a result complexes containing the same ligands with both geometries exist, sometimes even in equilibrium with one another.

The tetrahedral or pseudotetrahedral complexes formed by cobalt(II) are often of the type $[CoL_2X_2]$ (L_2 = bidentate or two monodentate ligands) [343]. The tetrahedral $[CoX_4]^{2-}$ (X = Cl, Br, I, SCN, N_3, OH) anions are also common [356].

The high spin tetrahedral and octahedral cobalt(II) systems contain three unpaired electrons and therefore possess quartet ground states.

For both of these geometries there are three spin allowed electronic transitions.

The following energy level diagram, Figure 3.1, shows the quartet states of a d^7 ion in tetrahedral and octahedral ligand fields [1].

The electronic spectra due to these two geometries are both dominated by the highest energy transition.

i.e. $^4A_2 \longrightarrow {}^4T_1(P)$ (td)

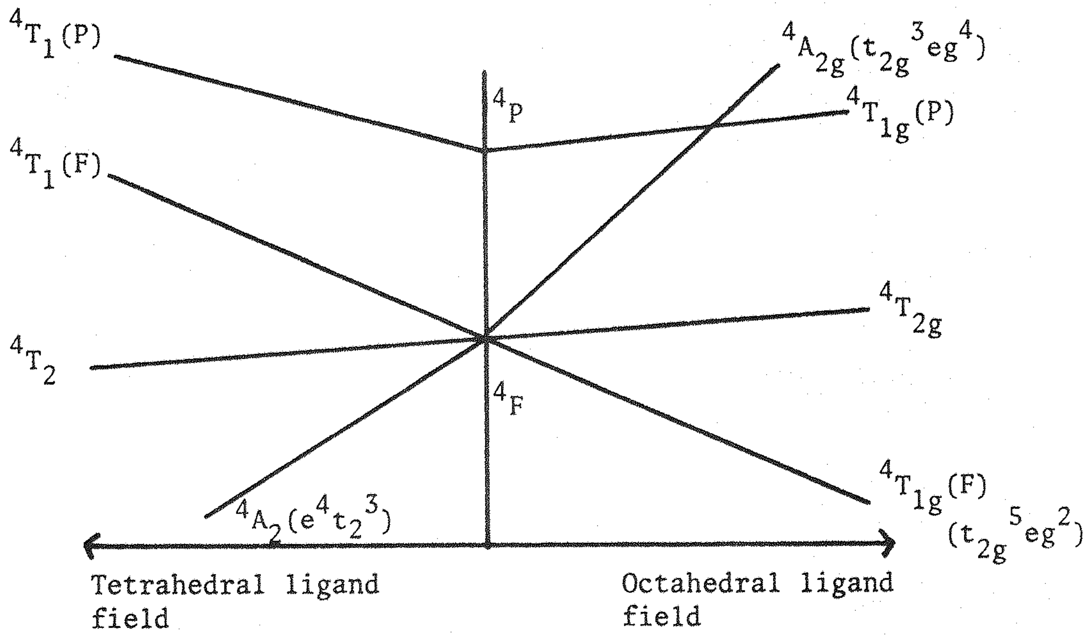
$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (oct)

It is observed that the tetrahedral complexes are typically an intense blue whereas the octahedral ones are pale red or purple.

This colour difference is attributed to the fact that the energy levels are split to a greater extent in an octahedral field ($^9/_4$ X) than in a tetrahedral one containing the same ligands. The transitions in the tetrahedral complexes are thus displaced to lower energies than the octahedral ones [1].

Figure 3.1

Schematic energy level diagram for quartet states of a d^7 ion in tetrahedral and octahedral ligand fields



The less intense colouration of the octahedral complexes is due to the fact that the transition from the $^4T_{1g}(F)$ ground state to the $^4A_{2g}$ level is close to that of the $^4T_{1g}(P)$ level. The former is essentially a two electron process and a mixing in of such a low probability transition results in a weakening of the intensity by a factor of 10^{-2} compared to the other transitions. The corresponding transition in a tetrahedral field is about an order of magnitude more intense.

The visible transitions in both cases, but particularly in the tetrahedral one, usually have complex envelopes. This results from the fact that there are also a number of transitions to doublet excited states occurring in this same region and these acquire intensity by means of spin orbit coupling.

The other spin-allowed transitions for tetrahedral and octahedral cobalt(II) are as follows:

${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}$	(oct, in near infrared region)
${}^4A_2 \longrightarrow {}^4T_1(F)$	(td, in near infrared region)
${}^4A_2 \longrightarrow {}^4T_2$	(td, $\sim$5000 cm^{-1}, orbitally forbidden and seldom observed)

The octahedral ground state possesses a considerable orbital angular momentum whereas the ground state of the tetrahedral cobalt(II) can only acquire such by an indirect mixing in of the ${}^4T_2$ state by spin orbit coupling. These facts lead to effective magnetic moments at room temperature for octahedral cobalt(II) being in the range 4.7-5.2 BM and for tetrahedral cobalt(II), 4.4-4.8 BM [309]. In addition the orbital contributions to these magnetic moments vary inversely with the strength of the ligand field.

e.g. $[CoCl_4]^{2-}$, μ_{eff} = 4.59 BM; $[CoBr_4]^{2-}$, μ_{eff} = 4.69 BM

and $[CoI_4]^{2-}$, μ_{eff} = 4.77 BM, [356a]

If a sufficiently strong ligand field is present then it is possible to obtain low spin octahedral cobalt(II) complexes. For the resulting electron configuration of $t_{2g}^{6}eg^{1}$ (a ${}^2E$ ground state) however Jahn Teller distortion is expected to occur rendering regular octahedral complexes unlikely.

In fact, strong field ligands tend to produce five rather than six-coordinate complexes [299].

Low spin square planar cobalt(II) complexes are also known to exist but these are rare, their magnetic moments at room temperature ranging from 2.2 to 2.7 BM [318].

Cobalt(II) can not only form low spin five-coordinate complexes as above but also high spin ones [308]. The former tend to be produced by the heavier donor (e.g. those containing P,As,S,Sb donor atoms) ligands and the latter by ligands containing for example nitrogen donors.

The geometries of these low and high spin five-coordinate complexes often lie somewhere between trigonal bipyramidal and square pyramidal, these two being the extremes.

Cobalt(III)

Virtually all the known cobalt(III) complexes are octahedral and most of these contain nitrogen donor ligands such as ammonia, amines and isothiocyanates. [360]

The general method for preparation is by oxidation of the cobalt(II) complex using either molecular oxygen or hydrogen peroxide in the presence of a surface active catalyst, such as activated charcoal.

Cobalt(III) is a d^6 ion possessing an $^1A_{1g}$ ground state and nearly all the known complexes are diamagnetic (an exception being $[CoF_6]^{3-}$ [1] which is paramagnetic with four unpaired electrons).

The electronic spectrum of octahedral cobalt(III) consists of two absorption bands which are transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ states.

For the cis and trans-pseudooctahedral complexes, there is a splitting of the $^1T_{1g}$ state. This will be marked in the latter case when there is a substantial difference in the ligand field strengths of the ligands in the axial and equatorial positions.

The cis-complexes are expected to produce more intense spectra than the trans as a result of lacking a centre of symmetry.

Nickel(II)

Nickel(II), a d^8 ion, forms a large number of octahedral complexes.

High spin octahedral nickel(II) contains two unpaired electrons which leads to a $^3A_{2g}$ ground state and room temperature magnetic moments lying between 2.9 and 3.4 BM, depending upon the orbital contribution [292].

In the electronic spectra three spin allowed transitions are expected:

$$^3A_{2g} \rightarrow {}^3T_{2g}$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(F)$$

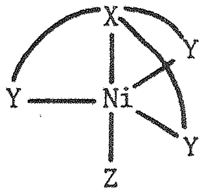
$$^3A_{2g} \rightarrow {}^3T_{1g}(P)$$

The extinction coefficients of these transitions generally lie in the 1-10 range.

A considerable number of five-coordinate nickel(II) complexes both high (S = 1) [294] and low spin (S = 0) exist [292]. Trigonal bipyramidal and square pyramidal geometries and distortions of these are known for both these spin states.

Many of the trigonal bipyramidal complexes have resulted from tetradentate 'tripod' type ligands.

e.g.



X = N, P, As.
Y = N, P, As, S, Se.
Z = Cl, Br, I.

These complexes are cationic, $[NiL\ Z]^+$ [293], having C_{3v} symmetry.

There are fewer high spin five-coordinate nickel(II) complexes known as compared with low spin. Two examples of high spin nickel(II) cations are $[Ni(Me_6tren)Br]^+$ (TBP) and $[Ni(\phi_2MeAsO)_4(ClO_4)]^+$ (SP) [294].

The low spin cations, as with cobalt(II), occur when the ligand's donor set consists mainly of heavier atoms such as P, As, S, Se, Br and I.

The tetrahedral nickel(II) complexes usually possess the following stoichiometries $[NiX_4]^{2-}$, $[NiX_3L]^-$ and $[NiL_2X_2]$ (X = halogen; L = neutral monodentate ligand). Obviously true tetrahedral complexes can only result from stoichiometries such as $[NiX_4]^{2-}$ all the others lying somewhere between a tetrahedral and a square planar geometry.

The complexes which are tetrahedral or near so are all paramagnetic with magnetic moments of 3.0-3.5 BM. A truly tetrahedral nickel(II) cation should have a magnetic moment of $\sim$4.2 BM at room temperature and any distortion from this geometry produces splitting of the orbital degeneracy and thus a reduction of the magnetic moment.

Regular or nearly regular tetrahedral complexes also show characteristic spectral properties. Tetrahedral nickel(II) gives rise to a ${}^3T_1(F)$ ground state and the transition in the visible region (∿15000 cm^{-1}) to the ${}^3T_1(P)$ state is relatively strong ($\varepsilon \approxeq 10^2$) as compared to the corresponding transition for an octahedral complex.

These tetrahedral complexes are similar to the cobalt(II) in their intensity of colour. They are often blue or green the exceptions being when charge transfer transitions tail into the visible region.

The majority of four-coordinate nickel(II) complexes possess a square planar geometry [292]. The square planar ligand set causes one of the d orbitals ($dx^2 - y^2$) to be uniquely high in energy and the eight d electrons thus occupy the other four d orbitals leaving this other strongly antibonding one vacant.

These square planar nickel(II) complexes are always diamagnetic. They are usually red, yellow or brown as a result of an absorption band of medium intensity ($\varepsilon \approxeq 60$) in the range, 16600-22000 cm^{-1}. Equilibria can exist between the square planar and tetrahedral forms of a complex, e.g. NiL_2X_2 (L = alkyldiarylphosphine ligand; X = halogen) and it is sometimes possible to isolate both forms [356b].

The square planar complexes can also combine with more ligand to form the high spin five and six-coordinate complexes.

3.12 THE SYNTHESIS OF THE MIXED DONOR BIDENTATE LIGANDS OF GROUP VB AND VIB

This study is mainly concerned with mixed donor bidentate ligands with o-phenylene backbones. As a result, the variety of precursors and ligands mentioned is restricted to only those which are directly relevant to Chapters Two, Three or Four.

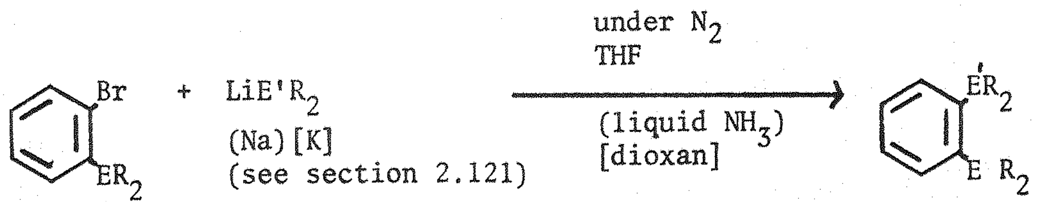
Mixed donor ligands, $R_2E\frown E'R_n$ ($E \neq E'$, E = group VB element (P, As, Sb) and $E'R_n = NR_2, PR_2, AsR_2, SbR_2$, OR, SR etc, and $\frown$ = alkyl, alkenyl, aryl backbone) are usually prepared by firstly synthesising the intermediates of the types $Cl\frown ER_2$ or $Cl\frown E'R_n{}'$ [28]. It may be that only one of these intermediates is easily obtainable rendering the order in which the donors are added to the backbone important.

Some intermediates are commercially available for example *o*-chlorobenzoic acid, chloroacetic acid, *o*-bromoaniline, *o*-bromoanisole and *o*-aminobenzenethiol.

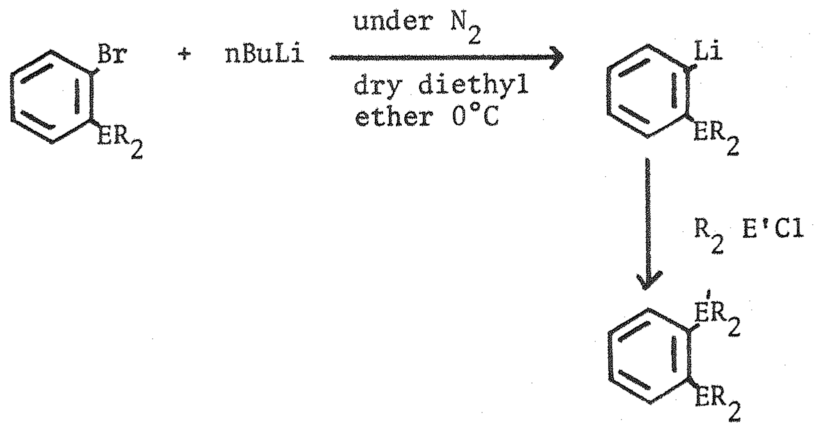
The intermediates generally required for the *o*-phenylene backboned ligands are of the type *o*-$C_6H_4X(ER_2)$ (X = Cl, Br) (see section 2.212 for (*o*-chlorophenyl)dimethylphosphine, (*o*-bromophenyl)dimethylarsine and (*o*-bromo(chloro)phenyl)diphenylphosphine).

The *o*-phenylene backboned ligands can be prepared by three routes from these intermediates:

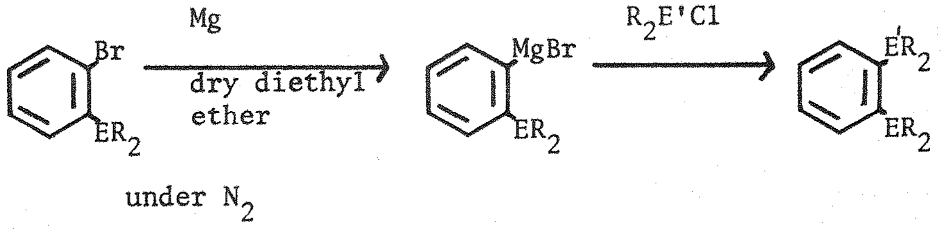
(i)



(ii)

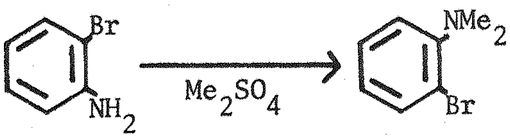


(iii)



Some basic outlines of the preparations of the intermediates which are used in the syntheses of the ligands are:

(iv) o-Bromo-N,N-dimethylaniline [220,295]



(v) o-Bromothioanisole [150]

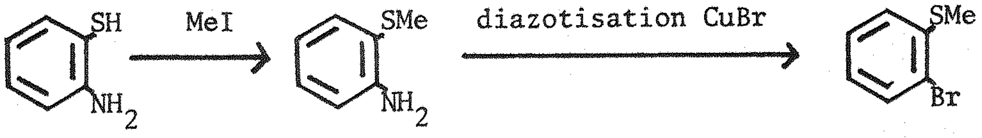


Table 3.2 now summarises the syntheses of some of the mixed donor bidentates.

The syntheses of the ligands diphenylphosphinoalkylcarboxylic acids, o-diphenylphosphinobenzoic acid, 1,2-bis(dimethylamino)benzene and tris(2-diphenylphosphinoethyl)amine are now outlined.

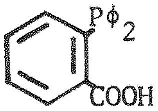
8. Diphenylphosphinoalkanoic acids. $\phi_2P(CH_2)_nCOOH$ (n = 1-3)

These ligands are prepared by route (i) [302,303].

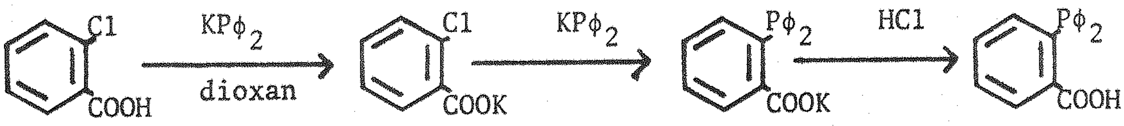
$$\begin{tikzcd}
\begin{array}{l} X(CH_2)_nCOOEt \\ (X{=}Cl,Br) \end{array} \arrow[r, "KP\phi_2", "\begin{array}{l}\text{dioxan or}\\ \text{THF}\end{array}"'] & \phi_2P(CH_2)_nCOOEt \arrow[d, "\begin{array}{l}\text{hydrolysed (i) NaOH}\\ \text{(ii) HCl}\end{array}"] \\
 & \underline{\phi_2P(CH_2)_nCOOH} \quad \text{(Yield = 29\%)}
\end{tikzcd}$$

white crystalline solids

9. o-Diphenylphosphinobenzoic acid.

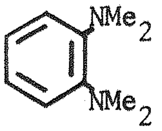


This ligand is prepared by route (i) [304].



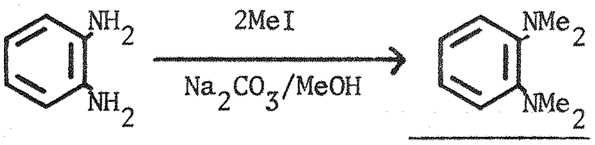
Pale-yellow solid

10. 1,2-Bis(dimethylamino)benzene.



NN_{me}

This ligand can be obtained commercially but is often prepared in the laboratory by the methylation of the corresponding 1,2-bis(amino) benzene [305].



orange oil

11. Tris(2-diphenylphosphinoethyl)amine. $N(CH_2CH_2P\phi_2)_3$ NP_3

The preferred route for ligands such as this is via the chloroalkylamine and MER_2 (M = Li, Na, K; R = ϕ; E = P, As) [306].

$$N(CH_2CH_2Cl)_3 \xrightarrow[THF, N_2]{3KP\phi_2} \underline{N(CH_2CH_2P\phi_2)_3}$$

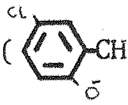
colourless needles

3.13 SOME COBALT(II), COBALT(III) AND NICKEL(II) COMPLEXES OF PRIMARILY BIDENTATE MIXED DONOR LIGANDS

The mixed donor ligands containing for example nitrogen and phosphorus or nitrogen and arsenic form interesting complexes with cobalt(II) and nickel(II). These complexes reflect the different stereochemistries preferred by the 'hard' and 'soft' donor atoms. The 'hard' N donors favour a tetrahedral or octahedral geometry whereas the heavier group VB or VIB donors such as P, As or S favour five-coordination and, for nickel(II), square planar also. In addition the 'harder' donors tend to form high spin complexes and the 'softer' donors low spin complexes. The donor capacity of the ligands is also dependent on the substituent groups for example alkyl or phenyl. An alkyl substituted donor atom results in a stronger ligand field.

Some of the complexes will of course lie close to a high spin-low spin crossover point.

Sacconi et al [307] have carried out the most detailed work regarding the factors governing spin multiplicity in the five-coordinate complexes of cobalt(II) and nickel(II). Sacconi has ranked the various donor sets according to their electronegativities or nucleophilic constants in order to predict the crossover point between high and low spin complexes. The result of this is that the capacity for spin pairing has been observed to increase with the nucleophilic activity and decrease with the electronegativity of the donor atoms, (spin pairing increases in the order Cl < Br < I). In fact until recently all the known five-coordinate complexes of cobalt(II) and nickel(II) have been low spin and it was only in 1965 that the first high spin five-coordinate complexes were described.

e.g. (
$CH{=}N(CH_2)_2NEt_2)_2Co$ [308]

The important factor here as to whether low or high spin, trigonal bipyramidal (D_{3h}) or square pyramidal (C_{4v}), d^7 or d^8 complexes form is whether the energy separation between the two highest energy levels is higher or lower than the spin pairing energy. Low spin complexes have been observed to occur more readily for the d^8 configuration [307].

A comparison of the known cobalt(II) and nickel(II) complexes of the bidentate mixed donor ligands is now made. Complexes of the ligands 1,2-bis(dimethylarsino)benzene, 1,2-bis(dimethylphosphino)benzene, 1,2-bis(dimethylamino)benzene and tris(2-diphenylphosphinoethyl)amine are also included. Some of the phenyl-substituted ligands mentioned are relevant also to Chapter Four.

3.131 The cobalt(II) complexes

(i) Some P-N and As-N ligands containing a pyridine ring

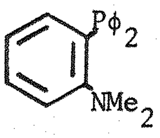
2-Diphenylphosphinomethyl-6-methylpyridine, and 2-diphenylphosphinoethyl-6-methylpyridine form tetrahedral complexes, $CoLX_2$, with cobalt(II) halides [309]. The 2-(diphenylphosphinoethyl)pyridine ligand also forms high spin complexes but these are octahedral (X = Cl, Br, NCS) [310]. The iodo-complex of this latter ligand occurs at the point of high-low spin crossover. The perchlorate complex is the low spin, five-coordinate complex formulated as $[CoL_2\ ClO_4\ ]ClO_4$.

The phenyl-substituted ligands 8-diphenylphosphinoquinoline [311] and 2-diphenylarsinomethylpyridine [312] give high spin complexes. The former has given a tetrahedral $[CoLI_2]$ complex with a N_2I_2 donor set and the latter both a tetrahedral and an octahedral thiocyanate complex of stoichiometry $[CoL_2(NCS)_2]$.

The alkyl-substituted ligand, 2-diethylphosphinomethylpyridine [313], however, forms the complexes $[CoL_2][CoX_4]$ (X = Cl, Br) which contain a square planar cation and a tetrahedral anion, the low spin five-coordinate $[CoL_2X]X$ (X = I, ClO_4) and the high spin, pseudooctahedral $[CoL_2(NCS)_2]$.

(ii) (o-Dimethylaminophenyl)diphenylphosphine.

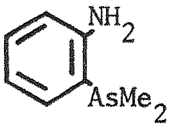
This ligand forms pseudotetrahedral complexes $[CoLX_2]$ (X = Cl, Br, I) when reacted with cobalt(II) halide in ethanol (X = Cl, Br) or n-butanol (X = I).



PN$_\phi$

(iii) o-Dimethylarsinoaniline. [314]

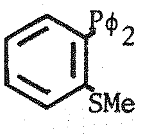
This ligand reacts with cobalt(II) salts (X = Cl, Br) in ethanol under nitrogen to form complexes formulated as $[CoL_2][CoX_4]$. It is thought that the cation here is in an essentially octahedral environment, the $[CoX_4]^{2-}$ ion functioning as a bridging group.



The nitrate complex is high spin, octahedral and formulated as $[CoL_2(NO_3)_2]$ whereas the iodide and perchlorate are low spin, octahedral and formulated as $[CoL_2I_2]$ and $[CoL_3](ClO_4)$ respectively. This latter complex extremely readily oxidises to cobalt(III) and in fact all the above complexes of this ligand give the diamagnetic, six-coordinate cobalt(III) cations, trans-$[CoL_2X_2]^+$ (X = Cl, Br, I, NCS) when these reactions are performed in air.

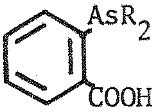
(iv) (o-Methylthiophenyl)diphenylphosphine. [299]

This ligand forms the red, crystalline, low spin, five-coordinate complexes $[CoL_2X]^+$ when reacted with '$CoXClO_4$' (X = Cl, Br, I). These complexes are stable to air and moisture and their solution and solid state electronic spectra compare well with that of other cobalt(II) complexes possessing a square pyramidal geometry.



PS$_\phi$

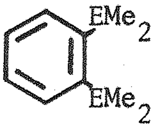
(v) o-Dimethylarsinobenzoic acid and o-diphenylarsinobenzoic acid



(R = Me, ϕ)

These carboxylic acids react with cobalt(II) acetate to give complexes of stoichiometry, $[CoL_2]$ [315]. The complexes possess magnetic moments typical of an octahedral geometry, they are insoluble in all common organic solvents and also they exhibit coordination of either the $-As\phi_2$ or $-AsMe_2$ and the carboxylate ion. These facts have implied a polymeric structure with the carboxylate ion acting in a bidentate fashion [316].

(vi) 1,2-Bis(dimethylarsino)benzene and 1,2-bis(dimethylphosphino)-benzene.



(E = P, As)

These ligands react with cobalt(II) halides to form complexes of stoichiometry, CoL_2X_2 (X = Cl; L = PP_{me} and X = Cl, Br, I, NCS; L = dias). The complexes are only sparingly soluble and possess magnetic moments indicative of only one unpaired electron (μ_{eff} = 1.97-2.4 BM). It was initially thought [317] for the dias complexes that they contained a square planar cation $[CoL_2]^{2+}$. However Rodley et al [191] have since suggested a tetragonally distorted octahedral geometry on the basis of the X-ray powder patterns of the complexes being identical to the corresponding nickel(II) complexes and also the X-ray crystal structure of $[NiL_2I_2]$, which has this geometry. The lack of a ν(Co-X) in the far infrared spectra of both the PP_{me} and dias complexes supports this geometry. However theoretically a five-coordinate structure cannot be discounted.

The cobalt(II) complexes $[CoL_2]Y_2$ [318,319] (Y = ClO_4, NO_3) and $[CoL_3](ClO_4)_2$ [320] have also been isolated. The former from their infrared and X-ray data possess some association of the oxyanions in the trans positions [318,319].

The stable, octahedral, diamagnetic, cobalt(III) complexes,

$[CoL_2X_2]Y$ (X = Cl, Br, I, CNS; Y = X, ClO_4, ½$CoCl_4$, ½$Co(SCN)_4$; L = dias and X = Cl, Br; Y = ClO_4; L = PP_{me} [253,275]) and $[CoL_3](ClO_4)_3$ [320] (L = dias) have been prepared.

The $[Co(dias)_2X_2]ClO_4$ (X = Cl, Br) complexes exist in both a purple and a green form and have been shown by their electronic spectra to be the cis and trans complexes respectively [321,322]. X-ray structural data has shown the green $[Co(dias)_2Cl_2]Cl$ [323] and $[Co(dias)_2Cl_2]ClO_4$ [285] and the purple $[Co(PP_{me})_2Cl_2]ClO_4$ [324] complexes to be trans.

The electronic spectra in the visible region of the corresponding complexes of these two ligands are virtually identical except for the fact that the bands are shifted to higher energies for the phosphine derivatives as expected from the greater ligand field strength.

(vii) <u>1,2-Bis(dimethylamino)ethane, 1,2-bis(dimethylamino)propane and 1,3-bis(dimethylamino)propane</u>. (Me_4en, Me_4pn and Me_4 tn resp)

These ligands react with cobalt(II) salts, CoX_2 (X = Cl, Br, I, NCS, NO_3) to form blue complexes of stoichiometry, $CoLX_2$ [325]. The chloro and bromo complexes are pseudotetrahedral and fairly insensitive to moisture. They do however decompose in aqueous solution.

The $Co(Me_4tn)(NCS)_2$ complex is of similar geometry in both the solid and solution states. However the corresponding complexes of Me_4pn and Me_4en exhibit reflectance spectra and magnetic moments indicative of an octahedral structure.

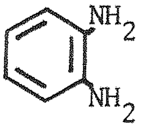
The $Co(Me_4en)(NCS)_2$ complex is insoluble in organic solvents but the $Co(Me_4pn)(NCS)_2$ complex gives an electronic spectrum in dichloromethane similar to that of the pseudotetrahedral complexes above. As a result a polymeric octahedral structure has been proposed for the $CoL(NCS)_2$ (L = Me_4en, Me_4pn) complexes in the solid state, the $Co(Me_4pn)(NCS)_2$ becoming pseudotetrahedral in solution.

The above claims have been confirmed by the infrared spectra which imply terminal N-bonded thiocyanate groups for the $Co(Me_4tn)(NCS)_2$ complex and bridging thiocyanate groups for the $CoL(NCS)_2$ (L = Me_4pn, Me_4en) complexes [64,326].

The purple nitrate complexes of these ligands have been postulated as pseudooctahedral even though their magnetic moments are rather low

(μ_{eff} = 4.65-4.80 BM) with respect to those found for octahedral cobalt(II) complexes [327].

(viii) 1,2-Bis(diamino)benzene [328]



This ligand forms green pseudotetrahedral [$CoLX_2$] complexes.

Pink to red high spin, octahedral [CoL_2SO_4], [CoL_3](ClO_4)$_2$ and [CoL_3](NO_3)$_2$ complexes have also been prepared. The latter two complexes are 1:2 electrolytes in N,N-dimethylformamide and their infrared spectra indicate ionic nitrate and perchlorate.

(ix) Tris(2-diphenylphosphinoethyl)amine [294] $N(CH_2CH_2P\phi_2)_3$, NP_3

Cobalt(II) halides (X = Cl, Br, I, NCS) react with this ligand to form air-stable, five-coordinate complexes, soluble in organic solvents, and formulated as [CoLX]Y (Y = X, $B\phi_4$).

The [CoLX]$B\phi_4$ (X = Cl, Br, I) complexes and the [CoLBr]Br complex are 1:1 electrolytes and contain high spin five-coordinate cations. Their solid and solution electronic spectra are virtually identical and similar to those found for high spin five-coordinate complexes such as [Co(Me_6tren)Br]Br [294].

The complexes [CoL(NCS)]$B\phi_4$ and [CoLI]I are low spin five-coordinate and are 1:1 electrolytes in 1,2-dichloroethane or nitromethane.

As a result of the fact that [CoLI]$B\phi_4$ is high spin and [CoLI]I low spin, the donor set NP_3I has been concluded as the crossover point between high and low spin in these five-coordinate cobalt(II) complexes.

X-ray work on examples of both the low and the high spin complexes has been undertaken [329,330]. The [CoLI]I complex has been found to possess a square pyramidal geometry [329] whereas [CoLCl]PF_6 appears to be a very distorted trigonal bipyramid [330]. It has been suggested that the square pyramidal arrangement of the NP_3 ligand favours the low spin state.

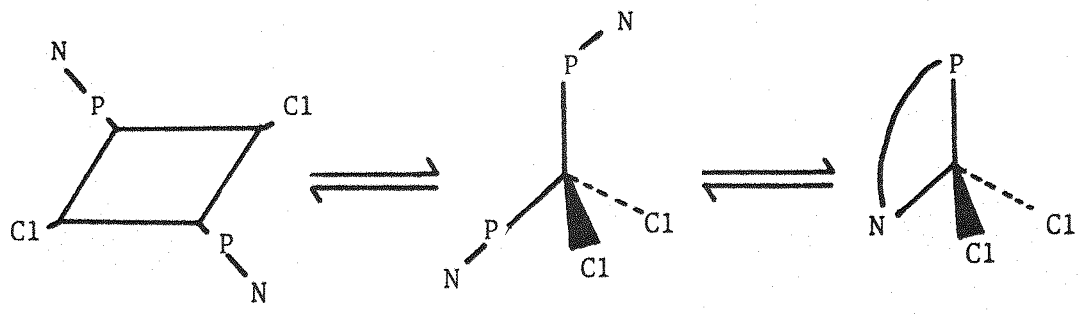
3.132 The nickel(II) complexes

(i) The P-N and As-N ligands containing a pyridine ring

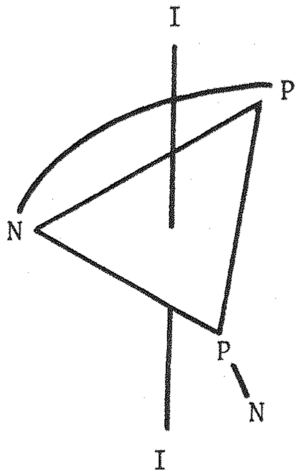
Fewer high spin complexes are formed by nickel(II) with these ligands than with cobalt(II).

High spin octahedral $[NiL_2X_2]$ complexes are formed by nickel(II) chloride and thiocyanate and 2-diphenylphosphinomethylpyridine (DPMMP) [310] but the bromide and iodide are five-coordinate, diamagnetic $[NiL_2X]X$ (X = Br, I) complexes. An X-ray crystal structure of the $[NiL_2I]I$ complex shows it to be a distorted square pyramid [331].

High spin, dimeric, trigonal bipyramidal, air-stable complexes of stoichiometry $NiLX_2$ (X = Cl, Br, NCS) and containing bridging X, are produced by 2-diphenylphosphinomethyl-6-methylpyridine [309]. In solution the chloro and bromo-complexes dissociate into tetrahedral and the thiocyanate into planar monomers. This same ligand and also 2-diphenylphosphinoethyl-6-methylpyridine (DPEMP) [309] give square planar $[NiL_2X_2]$ (X = Cl, NCS) complexes which contain uncoordinated pyridyl groups. The chloro-complex in solution varies in structure depending upon the concentration, the solvent polarity and the temperature. See below.



Nickel(II) iodide forms both a violet square planar and also a yellow, diamagnetic, tetragonal, six-coordinate $[NiL_2I_2]$ with 2-diphenylphosphinomethyl-6-methylpyridine (DPMMP) [309]. Both forms yield the same five-coordinate species in solution, viz:

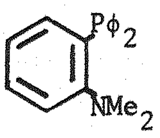


The DPMMP and DPEMP ligands [309] also form the diamagnetic, square planar perchlorate complexes $[NiL_2](ClO_4)_2$.

2-Diethylphosphinomethylpyridine (DEPM) [311,313,332], a stronger donor ligand, forms complexes of several coordination numbers. Nickel(II) chloride and bromide give two types of complexes, a $[NiL_2][NiX_4]$ containing a square planar cation and a tetrahedral anion as well as 1:2 (metal:ligand) complexes. The latter have been postulated as five-coordinate with the donor sets N_2P_2Cl and N_2P_2Br . These donor sets lie close to the high spin-low spin crossover point.

Nickel(II) iodide forms five-coordinate $[NiL_2I]I$ and nickel(II) perchlorate, square planar $[NiL_2](ClO_4)$.

(ii) (o-Dimethylaminophenyl)diphenylphosphine [333]

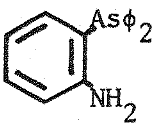


PN_ϕ

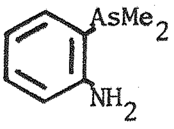
Complexes of stoichiometry, $NiLX_2$ (X = Cl, Br, I) are formed by the reaction of nickel(II) halides and the ligand in hot n-butanol.

The brown chloro- and bromo-complexes are pseudotetrahedral in dichloromethane solution and five-coordinate and dimeric with bridging halogens in the solid state. The black iodo-complex is pseudotetrahedral in both these states.

(iii) o-Diphenylarsinoaniline [334], o-dimethylarsinoaniline [334] and 1-amino-2-(diphenylarsino)ethane [334]



NAs_ϕ,

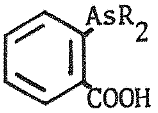


NAs and $H_2NCH_2CH_2As\phi_2$ (AsMN) resp.

These ligands react with nickel(II) salts, NiX_2 (L = NAs; X = halides, NCS, NO_3 and L = NAs_ϕ, AsMN; X = Br, I) in ethanol to give a series of high spin, octahedral complexes, $[NiL_2X_2]$. Nickel(II) perchlorate gives diamagnetic, square planar $[NiL_2](ClO_4)_2$ (L = NAs, AsMN, NAs_ϕ) complexes.

The solubility of the NAs complexes is low but in hot methanol the $[Ni(NAs)_2X_2]$ (X = NO_3, Cl) and $[Ni(NAs)_2](ClO_4)_2$ complexes are all bi-univalent electrolytes implying that some decomposition occurs. The $[Ni(NAs)_2Cl_2]$ complex is however a non-electrolyte in nitrobenzene.

(iv) o-Dialkyl or o-diarylarsinobenzoic acid [315]



(R = Me, ϕ, p-tolyl)

These ligands give insoluble complexes of stoichiometry, NiL_2, when reacted with hydrated nickel(II) acetate in alcoholic solution. The complexes of the diphenyl and di-p-tolyl arsines possess magnetic moments and reflectance spectra which favour an octahedral stereochemistry whereas that of the dimethylarsine favour a tetrahedral geometry. The infrared spectra also indicate there is coordination of both the $-AsR_2$ and the carboxylate groups.

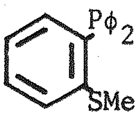
It has been thought that the $[NiL_2]$ (R = ϕ, p-tolyl) complexes acquire an octahedral geometry through polymerisation, the carboxylate ion acting in a bidentate fashion.

(v) Diphenylphosphinoacetic acid [303] ϕ_2PCH_2COOH (HAc)

A blue-green, air-stable, distorted tetrahedral $Ni(Ac)_2 4H_2O$ complex has been prepared by firstly neutralising the ligand in ethanol using aqueous sodium bicarbonate and then adding nickel(II) perchlorate in the same solvent.

The ligand itself when dissolved in glacial acetic acid reacts with nickel(II) salts, NiX_2 (X = Cl, Br, I, SCN) to form the air-stable, square planar $[NiL_2X_2]$ complexes. The infrared data shows that the ligand bonds through the phosphorus only in these complexes.

(vi) (o-Methylthiophenyl)diphenylphosphine [299] and 1-diethylphosphino-2-ethylthioethane [335]

 (PS_ϕ) and $EtS(CH_2)_2P\phi_2$ (PS_{Et}) resp.

These ligands react with nickel(II) halide to give the square planar complexes $[NiLX_2]$ ($L = PS_\phi$; $X = Cl, Br, I$ and $L = PS_{Et}$; $X = Br$) and $[NiL_2](ClO_4)_2$ ($L = PS_{Et}$), the five-coordinate cations, $[NiL_2X]^+$ ($L = PS_\phi$; $X = Cl, Br$ and $L = PS_{Et}$; $X = Br, I$), the six-coordinate complexes $[NiL_2X_2]$ ($L = PS_\phi$; $X = Cl$ and $L = PS_{Et}$; $X = I, NCS$) and the mixed salt $[Ni(PS_{Et})_2](ClO_4)_2 2Ni(PS_{Et})_2Cl(ClO_4)$.

The $[Ni(PS_\phi)_2Cl_2]$ complex dissolves in dichloromethane and in polar organic solvents to form deep red solutions whose electronic spectra are typical of planar nickel(II) complexes. When a suspension of this complex in benzene is heated, diamagnetic, deep red crystals of $[NiLCl_2]$ result. The latter has the same solution electronic spectrum to the NiL_2Cl_2 complex and the following equilibrium has been thought to take place:

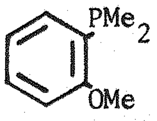
$$NiL_2Cl_2 \rightleftharpoons NiLCl_2 + L$$

The six-coordinate $[Ni(PS_{Et})_2I_2]$ complex becomes five-coordinate in solution.

Thiocyanate complexes of stoichiometry $[NiL_2(NCS)_2]$ have been obtained for both these ligands. The brown PS_ϕ complex has an anomalous but reproducible magnetic moment ($\mu_{eff} = 1.22$ BM) and when dissolved in halocarbon solvents precipitates a green complex of stoichiometry, $NiL(NCS)_2$. This former complex is thought possibly to consist of equal numbers of diamagnetic and paramagnetic nickel(II) species.

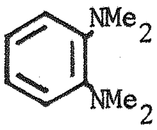
The PS_{Et} thiocyanate complex exists as both a yellow diamagnetic and an olive paramagnetic isomer. In solution they are both diamagnetic. It is thought that the olive form possesses an octahedral configuration in the solid state, but in solution, the nickel-sulphur bonds break forming a four-coordinate, square planar complex identical to the yellow form.

(vii) (o-Methoxyphenyl)dimethylphosphine [301]



This ligand gives trans, square planar $[NiL_2X_2]$ (X = Cl, Br, NCS) complexes where the phosphorus is coordinated and the oxygen uncoordinated. The thiocyanate complex contains N-bonded thiocyanate.

(viii) 1,2-Bis(dimethylamino)benzene [292]

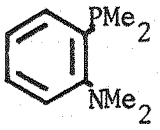


Pink solutions result from the reaction of nickel(II) halide (X = Cl, Br) and the ligand in n-butanol under nitrogen. On concentration of these, red crystals are deposited. These solutions and solids exhibit electronic spectra typical of pseudotetrahedral structures. However on exposure to air the red crystals rapidly turn pale green forming the octahedral $[NiL(H_2O)_2X_2]$ (X = Cl, Br) complexes.

This ligand also gives a green insoluble polymeric nickel(II) thiocyanate complex of stoichiometry, $NiL(NCS)_2$ where the nickel centres are octahedrally coordinated and the thiocyanates bridging [336].

The turquoise nickel(II) nitrate complex $[NiL(NO_3)_2]$ is also octahedrally coordinated and has an N_2O_4 donor set consisting of two bidentate nitrate groups [325] and the diamine ligand.

(ix) (o-Dimethylaminophenyl)dimethylphosphine [292]



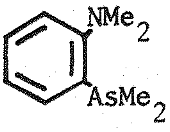
PN_{me}

This ligand gives red, square planar complexes, $[NiLX_2]$ [337] when reacted with nickel(II) halide, NiX_2 (X = Cl, Br).

A paramagnetic $[NiL(NCS)_2]$ complex analogous to the NN_{me} complex is also formed which gives a yellow solution in dichloromethane whose electronic spectrum is consistent with a planar species.

The diamagnetic, square planar $[NiL_2]^{2+}$ and square pyramidal [338] $[NiL_2X]^+$ (X = Cl, Br, I) cations are readily formed by the ligand in ethanol, the former in the presence of weakly coordinating anions such as perchlorate or tetrafluoroborate and the latter from '$NiXClO_4$' [339].

(x) (o-Dimethylaminophenyl)dimethylarsine [292]



NAs_{me}

This ligand reacts with nickel(II) halides (X = Cl, Br, I) to form complexes of stoichiometry,

NiL_2X_2.

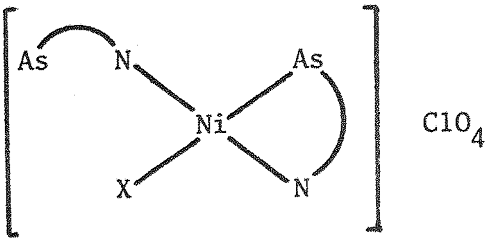
The green chloro- and bromo-complexes are paramagnetic and tetragonal octahedral [337]. In dichloromethane they give pink non-conducting solutions with electronic spectra similar to the $[Ni(NN_{me})X_2]$ (X = Cl, Br) complexes. The octahedral form is recovered on evaporation.

The brown $[NiL_2I_2]$ complex is diamagnetic and has a planar structure (an N_2As_2 donor set) in the solid state. In solution it rearranges to a pseudotetrahedral form (N_2I_2 donor set) [253].

A blue thiocyanate complex similar to that of the NN_{me} ligand has also been obtained.

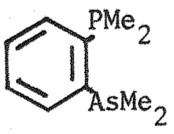
Evaporation of n-butanol solutions containing a 1:1:4 ratio of $NiX_2:Ni(ClO_4)_2:NAs_{me}$ gives red (X=Cl, Br) or purple (X = I), diamagnetic $[NiL_2X]ClO_4$ complexes. Similar complexes have been obtained using tetrafluoroborate or hexafluorophosphate as counter anions.

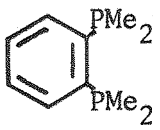
The following structure has been proposed for the $[NiL_2X]ClO_4$ complexes:

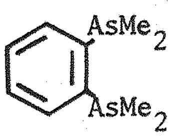


All the attempts to isolate the planar $[NiL_2]Y_2$ (Y = ClO_4, BF_4) have produced only green oils.

(xi) (o-Dimethylphosphinophenyl)dimethylarsine [292], 1,2-bis(dimethylphosphino)benzene [253,275,292] and 1,2-bis(dimethylarsino) benzene [89,338,340]



(PAs_{me}),


(PP_{me}) and


(dias) resp.

These strong field ligands produce the following low spin complexes, five-coordinate $[NiL_2X]X$ (L = PAs_{me}; X = NCS, NO_3), six-coordinate $[NiL_2X_2]$ (L = PP_{me}; X = Cl and L = dias; X = Cl, Br, I, NCS, NO_3), square planar $[NiL_2](ClO_4)_2$ (L = PAs_{me}, PP_{me} and dias) and five-coordinate $[NiL_2X]ClO_4$

(L = PAs_{me}; X = Cl, Br, I, L = PP_{me}; X = Cl and L = dias; X = Cl, Br, I, NCS).

The dias and PAs_{me} complexes of stoichiometry, NiL_2X_2, are both 1:1 electrolytes in nitromethane but in the solid state the dias complexes have previously been considered as tetragonally distorted octahedral [341]. A five-coordinate structure has also been proposed for the PAs_{me} and dias complexes [292].

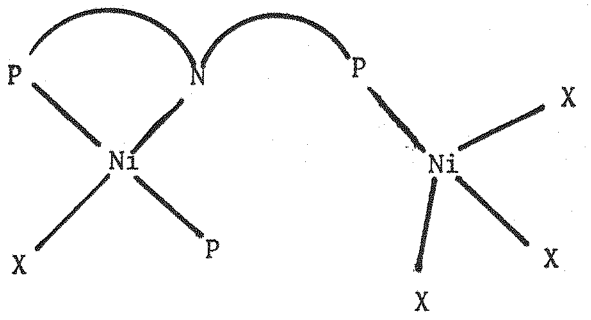
A few 1:1 complexes are also known, e.g. orange, square planar $[Ni(PAs_{me})Cl_2]$ [292] and $[N(dias)X_2]$ (X = Cl, Br, I) [342].

(xx) Tris(2-diphenylphosphinoethyl)amine [294] $N(CH_2CH_2P\phi_2)_3$ NP_3

This ligand forms two types of complex depending upon the metal: ligand ratio adopted.

A 1:1 ratio produces the diamagnetic, five-coordinate (assigned trigonal bipyramidal) complexes formulated as [NiLX]Y (X = Cl, Br, I, NCS; Y = X, $B\phi_4$). These are 1:1 electrolytes in nitroethane or 1,2-dichloroethane and their solid and solution electronic spectra are similar and typical of low spin five-coordinate nickel(II) [355].

A 2:1 ratio produces the binuclear, non-ionic complexes formulated as Ni_2LX_4. These are postulated to contain a sq pl 'core' with a $NiNP_2X$ chromophore, and a pseudotetrahedral 'core' with a $NiPX_3$ chromophore.



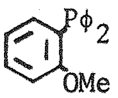
3.2 EXPERIMENTAL WORK AND DISCUSSION

3.21 THE SYNTHESES OF SOME MIXED DONOR BIDENTATE LIGANDS

This section contains mixed donor bidentates primarily but also includes one mixed donor multidentate ligand and one diamine ligand.

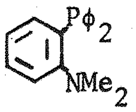
The following ligands were synthesised:

1. o-(Diphenylphosphino)anisole,



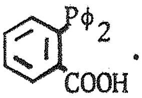
PO_ϕ.

2. (o-Dimethylaminophenyl)diphenylphosphine,



PN_ϕ.

3. o-Diphenylphosphinobenzoic acid,

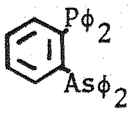


.

4. Diphenylphosphinoacetic acid, ϕ_2PCH_2COOH.

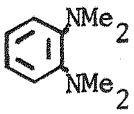
5. Tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2P\phi_2)_3$, NP_3.

6. (o-Diphenylphosphinophenyl)diphenylarsine,



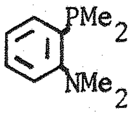
AP_ϕ.

7. 1,2-Bis(dimethylamino)benzene,



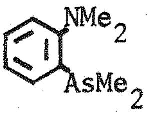
NN_{me}.

8. (o-Dimethylaminophenyl)dimethylphosphine,



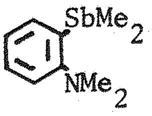
PN_{me}.

9. (o-Dimethylaminophenyl)dimethylarsine,



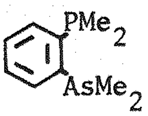
NAs_{me}.

10. (o-Dimethylaminophenyl)dimethylstibine,



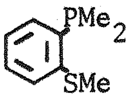
SbN_{me}.

11. (o-Dimethylphosphinophenyl)dimethylarsine,



PAs_{me}.

12. (o-Methylthiophenyl)dimethylphosphine,



PS_{me}.

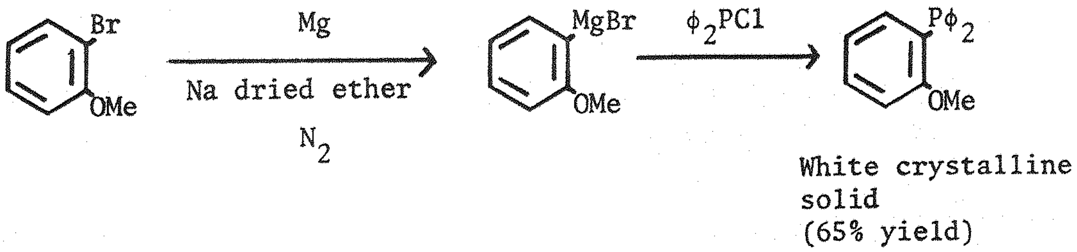
The apparatus used is the same as that quoted in Section 2.21. The preparations were all similarly performed in a dry dinitrogen atmosphere.

The proton nuclear magnetic resonance spectra were all recorded in deuterochloroform with a tetramethylsilane internal standard.

1. o-(Diphenylphosphino)anisole

This ligand was prepared by a literature method [300] from o-bromoanisole via a grignard reagent in sodium dried diethyl ether.

Reaction sequence



^{1}H nmr

3.75δ(s)[3H], OMe.

7.38δ(m), aromatic protons.

Attempted preparation of o-diphenylphosphinophenol from o-diphenylphosphinoanisole

To o-diphenylphosphinoanisole (14.4 g, 0.049 mol) in ethanol (150 cm^3) was added dropwise hydriodic acid (6.5 cm^3, 0.097 mol) with stirring. Upon complete addition the solution was neutralised using sodium hydroxide solution. The organic layer was separated off and the solvent removed on a rotary evaporator. A white solid remained whose ^{1}H nmr closely resembled the starting material. No phenolic protons were present.

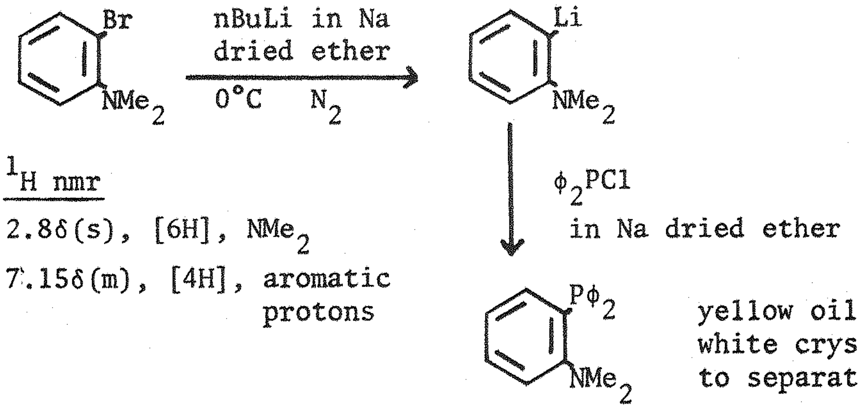
^{1}H nmr: 3.78δ(s), [3H], OMe.

7.38δ(m), aromatic protons.

2. (o-Dimethylaminophenyl)diphenylphosphine

This ligand was prepared by the method of Venanzi et al [298] from o-bromodimethylaniline. (See Section 3.12).

Reaction sequence



^{1}H nmr

2.8δ(s), [6H], NMe_2

7.15δ(m), [4H], aromatic protons

yellow oil from which white crystals began to separate

^{1}H nmr

2.73δ(s), [6H], NMe_2

7.5δ(m), [14H], aromatic protons

3. o-Diphenylphosphinobenzoic acid

Stage (1) Preparation of the sodium salt of o-bromobenzoic acid

o-Bromobenzoic acid (25 g, 0.124 mol) was treated with sodium bicarbonate (10.46 g, 0.125 mol) in aqueous solution (50 cm^3). The sodium salt was filtered off and dried in vacuo for several hours. The yield was quantitative.

Stage (2) Preparation of lithium diphenylphosphide (in situ)

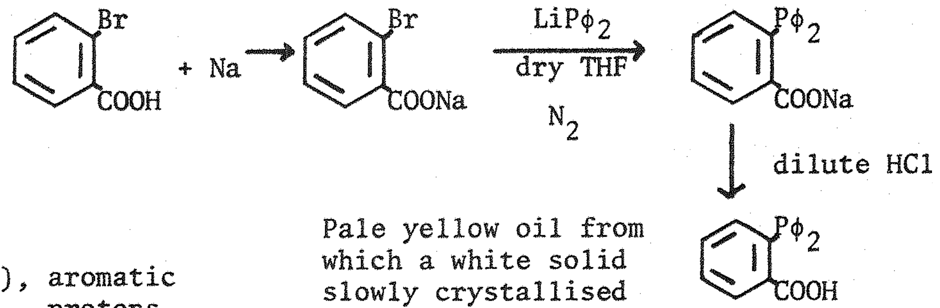
(See Section 2.21).

Stage (3) Preparation of the ligand

A suspension of the sodium o-bromobenzoate (40.6 g, 0.124 mol) was added dropwise to the lithium diphenylphosphide (∿0.124 mol) in sodium dried THF (150 cm^3) over an hour.

A white solid was deposited and the mixture hydrolysed using dilute hydrochloric acid in order to obtain the free acid.

Reaction sequence



^{1}H nmr

7.32δ(m), aromatic protons

Pale yellow oil from which a white solid slowly crystallised out

4. Diphenylphosphinoacetic acid

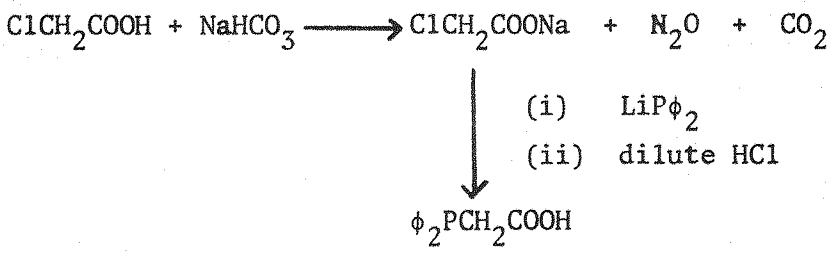
Stage (1) Preparation of the sodium salt of chloroacetic acid

To a stirred aqueous solution (100 cm^3) of chloroacetic acid (40 g, 0.423 mol) was added an aqueous solution (100 cm^3) of sodium bicarbonate (35.7 g, 0.425 mol). The white precipitate was filtered off and dried *in vacuo* for several days. The yield was quantitative.

Stage (2) Preparation of the ligand

A solution of lithium diphenylphosphide (0.423 mol) (prepared as in 3) was added dropwise to a cooled, stirred suspension of sodium chloroacetate (49 g, 0.423 mol) in sodium dried THF (150 cm^3). The $LiP\phi_2$ solution decolourised as it entered the solution and a white solid precipitated. Upon complete addition the mixture was refluxed for one hour, allowed to cool and then hydrolysed using dilute hydrochloric acid. Two layers separated. The upper THF layer was separated off and diethyl ether extracts of the aqueous layer (pH ∿6) added to it. The total organic layer was dried over anhydrous sodium sulphate and the solvent then removed on a rotary evaporator. A yellow oil resulted which solidified slowly on standing. Yield = 80%.

Reaction sequence



$$\begin{tikzcd}[column sep=small] ClCH_2COOH + NaHCO_3 \arrow[r] & ClCH_2COONa + N_2O + CO_2 \arrow[d, "\text{(i) } LiP\phi_2 \text{ (ii) dilute HCl}"] \\ & \phi_2PCH_2COOH \end{tikzcd}$$

^1H nmr

3.15δ(s), CH_2

7.34δ(s), aromatic protons

5. Tris(2-diphenylphosphinoethyl)amine

This ligand was prepared by a literature route [307] except that lithium diphenylphosphide (see 3) rather than potassium diphenylphosphide was used.

Reaction sequence

$$\begin{tikzcd}
N(CH_2CH_2OH)_3 \arrow[dr, "SOCl_2"'] & \\
& N(CH_2CH_2Cl)_3 \arrow[dl, "LiP\phi_2"'] \\
N(CH_2CH_2P\phi_2)_3 &
\end{tikzcd}$$

$N(CH_2CH_2Cl)_3$

B.pt 101°C/3 mm Hg

^1H nmr

3.59δ(t), [6H], CH_2

2.98δ(t), [6H], CH_2

$N(CH_2CH_2P\phi_2)_3$

White crystalline solid

Elemental analysis, Found (calculated) C = 77.1(77.1), H = 6.2(6.4),
N = 2.3(2.14)

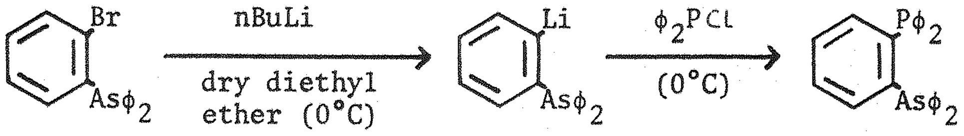
^1H nmr

2.2δ(s), [12H], CH_2

7.35δ(m), [30H], aromatic protons

6. (o-Diphenylphosphinophenyl)diphenylarsine

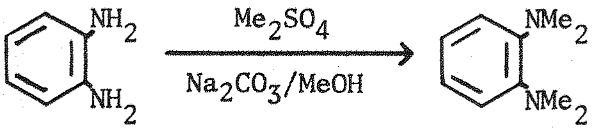
This was prepared by a literature method [296]:



white air-stable crystalline solid

7. 1,2-Bis(dimethylamino)benzene

This ligand was prepared by a literature method [305] from 1,2-bis(diamino)benzene and using dimethyl sulphate rather than methyl iodide as the methylating agent.



yellow oil

^1H nmr

2.77δ(s), [12H], NMe_2

7.0δ(m), [4H], aromatic protons

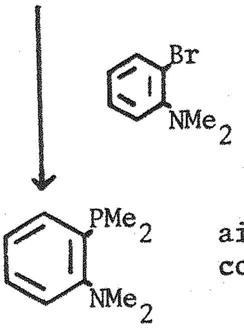
8. (*o*-Dimethylaminophenyl)dimethylphosphine

(See Section 2.21 for the preparation of LiPMe$_2$).

o-Bromodimethylaniline (37 g, 0.185 mol) was added dropwise to a LiPMe$_2$ (∿0.185 mol) in THF (250 cm^3) with stirring, the mixture refluxed for one hour and then allowed to cool. The mixture was hydrolysed using deoxygenated water (200 cm^3) and the THF layer separated. The aqueous layer was extracted twice using diethyl ether and the extract added to the THF layer. The total organic layer was then dried over anhydrous sodium sulphate. The organic solvents were removed by distillation under dry dinitrogen at atmospheric pressure and the residual oil distilled *in vacuo*. B.Pt = 57°C/0.3 mm Hg.

Reaction sequence

$Me_2\phi P + Li \longrightarrow Li\phi + LiPMe_2$ (Liφ removed)



air-sensitive
colourless oil

^{1}H nmr

2.74δ(s), [6H], NMe$_2$

1.31δ(d), [6H], PMe$_2$ J_{P-H} = 5Hz

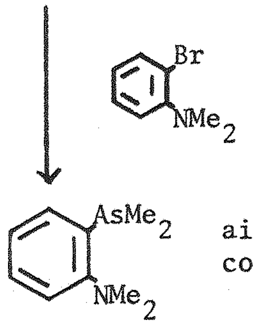
7.55δ(m), aromatic protons

9. (*o*-Dimethylaminophenyl)dimethylarsine

Iododimethylarsine (75 g, 0.32 mol) was added to sodium dried THF (200 cm^3) containing pellets of sodium (15.6 g, 0.68 mol), dropwise over a two hour period. Efficient agitation and cooling of the solution was required. *o*-Bromodimethylaniline (30 g, 0.15 mol) in sodium dried THF (200 cm^3) was added dropwise. The mixture was then refluxed for one hour, allowed to cool and subsequently hydrolysed with deoxygenated water (250 cm^3). This ligand was then worked up as with ligand 8 and distilled at 38°C/0.5 mm Hg. Yield = 65%.

Reaction sequence

$IMe_2As + 2Na \longrightarrow NaAsMe_2 + NaI$



air-sensitive,
colourless oil

^{1}H nmr

2.85δ(s), [6H], NMe_2
1.15δ(s), [6H], $AsMe_2$
6.95δ(m), aromatic protons

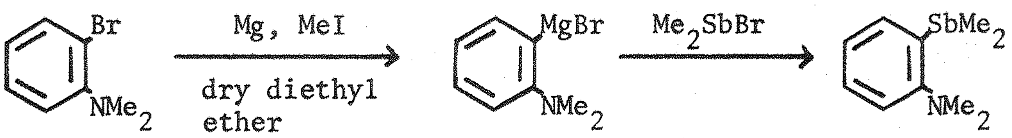
^{1}H nmr of methiodide

2.69δ(s), [6H], NMe_2
2.49δ(s), [9H], $AsMe_3$

10. (o-Dimethylaminophenyl)dimethylstibine

This ligand was prepared by the method of Levason et al [220].

Reaction sequence



yellow, air-
sensitive liquid

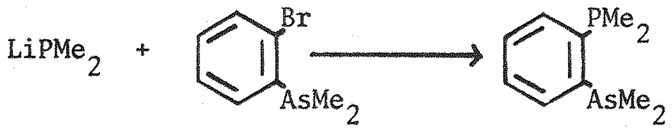
B.pt 72°C/1 mm Hg

(lit [220] B.pt
82°C/1 mm Hg)

11. (o-Dimethylphosphinophenyl)dimethylarsine

A solution of lithium dimethylphosphide (prepared as in Section 2.21) (0.07 mol) in sodium dried THF (100 cm^3) was added dropwise to o-bromophenyldimethylarsine (14.1 cm^3, 18 g, 0.07 mol) in THF (150 cm^3) with stirring and cooling. After the complete addition, the mixture was refluxed for one hour, allowed to cool and then hydrolysed using deoxygenated water (200 cm^3). This ligand was then worked up as with ligand 8 and distilled at 74°C/0.2 mm Hg.

Reaction sequence



air-sensitive
colourless oil

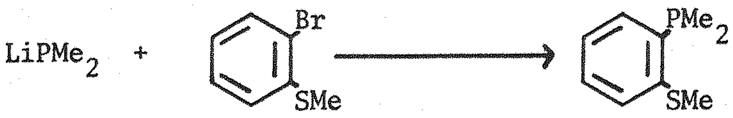
^{1}H nmr
1.275δ(s), [6H], AsMe$_2$
1.25δ(d), [6H], PMe$_2$
7.3δ(m), aromatic protons

12. (o-Methylthiophenyl)dimethylphosphine

o-Bromothioanisole was prepared by the method shown in Section 3.12.

Lithium dimethylphosphide (0.17 mol) (prepared as in Section 2.21) in sodium dried THF (200 cm^3) was added dropwise to a stirred, ice-cooled o-bromothioanisole (35 g, 0.17 mol) in the same solvent (100 cm^3). A vigorous reaction ensued and upon complete addition of the nucleophile the mixture was refluxed for one hour to ensure complete reaction. The mixture was cooled and hydrolysed using deoxygenated water (200 cm^3). This ligand was then worked up as with ligand 9 and distilled at 74°C/3 mm Hg. Yield = 55%.

Reaction sequence



air-sensitive
pale yellow oil

^{1}H nmr
2.36δ(s), [3H], SMe
1.59 (d), 1.28 (d) (4) [3H] [3H], PMe$_2$
7.2δ(m), aromatic protons

A methiodide derivative was prepared by addition of a methyl iodide ethanol solution to a few drops of the ligand, subsequent heating and then cooling. White crystals result. M.pt = 139°C.

^{1}H nmr

2.35δ(s), [3H], SMe

2.7δ(d), [9H], PMe_3

7.77δ(m), aromatic protons

3.22 THE PREPARATION OF COMPLEXES OF SOME METHYL SUBSTITUTED BIDENTATE LIGANDS, WITH O-PHENYLENE BACKBONES

The elemental analyses and colours of the individual complexes are found in Tables 3.3-3.6.

The preparations are all carried out under nitrogen (except those of cobalt(III)) and the solutions magnetically stirred.

1. 1,2-Bis(dimethylamino)benzene

$CoLX_2$ (X = Cl, Br, I, NCS, NO_3)

To the ligand (0.164 g, 1 mmol) in ethanol (10 cm^3) was added the cobalt(II) salt (1 mmol) in the same solvent (10 cm^3). The mixture was refluxed and allowed to cool. Blue (Cl, Br), green (I), deep pink (NO_3) and pale violet (NCS) solids were precipitated. The products were filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane and dried in vacuo. Yields ∿75%.

The '$Co(NCS)_2$' was prepared from cobalt(II) bromide (1 mmol) and potassium thiocyanate (5 mmol) in ethanol. The potassium bromide was filtered off leaving an ethanolic cobalt(II) thiocyanate solution.

$CoLBr_2 2H_2O$

[$CoLBr_2$] (0.383 g, 1 mmol) was left exposed to the atmosphere for two weeks. A mauve solid resulted.

$NiLCl_2(H_2O)_2$ [292]

Hydrated nickel(II) chloride (0.238 g, 1 mmol) was dissolved in ethanol (15 cm^3) and treated with the ligand (0.164 g, 1 mmol) in the same solvent (10 cm^3). Red solutions resulted from which a pale green solid was isolated. This product was filtered off, washed with ethanol and diethyl ether and dried in vacuo. Yield = 70%.

$\underline{CuLX_2}$ (X = Br, Cl)

To the ligand (0.164 g, 1 mmol) in ethanol (15 cm^3) was added copper(II) halide (1 mmol) in the same solvent (15 cm^3). Violet-brown solids precipitated upon refluxing and cooling. These were filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane and dried *in vacuo*. Yields ∿70%.

$\underline{PdLCl_2}$

To sodium tetrachloropalladate(II) (0.394 g, 1 mmol) in ethanol (15 cm^3) was added the ligand (0.164 g, 1 mmol) in the same solvent (15 cm^3). The solution was refluxed for 30 minutes, allowed to cool and the resulting brownish-yellow precipitate filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane and dried *in vacuo*. Yield = 75%.

2. (*o*-Dimethylaminophenyl)dimethylphosphine

$\underline{CoLX_2}$ (X = Cl, Br, I)

To cobalt(II) halide (1 mmol) in propan-2-ol (10 cm^3) was added the ligand (0.12 cm^3, 0.181 g, 1 mmol). Blue and green solutions resulted. Upon addition of diethyl ether blue (Cl, Br) and green (I) solids precipitated out. These were filtered off, washed with diethyl ether and dried *in vacuo*. Yields ∿55%.

$\underline{CoL(NO_3)_2}$

To cobalt(II) nitrate (0.291 g, 1mmol) in ethanol (10 cm^3) was added the ligand (0.12 cm^3, 0.181 g, 1 mmol). A dark brown solution resulted from which a dark brown solid was obtained. This was filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 55%.

$\underline{[CoL_2X]ClO_4}$ (X = Cl, Br, I)

To the filtrate, from a mixture of cobalt(II) halide (1 mmol) and cobalt(II) perchlorate (0.366 g, 1 mmol) in ethanol, was added the ligand (0.5 cm^3, 0.725 g, 4 mmol). Dark violet-brown solids precipitated upon refluxing and cooling. These were filtered off quickly, washed with dry diethyl ether and dried *in vacuo*. Yields ∿75%.

$\underline{[CoL_2Br]B\phi_4}$

To the filtrate, from a mixture of cobalt(II) bromide (0.327 g, 1 mmol) and sodium tetraphenylborate (0.342 g, 1 mmol) in ethanol, was added the ligand (0.5 cm^3, 0.725 g, 4 mmol). A dark violet solid precipitated upon refluxing and cooling, which was rapidly filtered off, washed with dry diethyl ether and dried in vacuo. Yield = 65%.

$[CoL_2](ClO_4)_2$

To cobalt(II) perchlorate (0.366 g, 1 mmol) in ethanol (10 cm^3) was added the ligand (0.25 cm^3, 0.36 g, 2 mmol). Upon refluxing and cooling a dark brown solid precipitated. This was filtered off, washed with dry diethyl ether and dried in vacuo. Yield = 75%.

3. (o-Dimethylaminophenyl)dimethylarsine

$CoLI_2$

To cobalt(II) iodide (0.349 g, 1 mmol) in n-butanol (10 cm^3) was added the ligand (0.15 cm^3, 1 mmol). A brown solid precipitated out after refluxing for a few minutes and then cooling. The solid was filtered off, washed with dry diethyl ether and dried in vacuo. Yield = 45%.

$MLCl_2$ (M = Pd(II), Pt(II))

To a solution of either sodium tetrachloropalladate(II) or potassium tetrachloroplatinate(II) (1 mmol) in ethanol/water (15 cm^3) was added the ligand (0.15 cm^3, 1 mmol). The mixture was refluxed for a few minutes and then allowed to cool whereupon yellow-orange (Pd) and yellow (Pt) solids precipitated. These were filtered off, washed with diethyl ether and dried in vacuo. Yields ∿75%.

4. (o-Dimethylphosphinophenyl)dimethylarsine

CoL_2X_2 (X = Cl, Br, I, NO_3)

To the cobalt(II) salt (1 mmol) in ethanol (15 cm^3) was added the ligand (0.3 cm^3, 2 mmol). The mixture was refluxed, allowed to cool whereupon green (Cl, Br) and brown (I, NO_3) solids precipitated. These were sticky and were triturated with dry diethyl ether, to obtain powders and then dried in vacuo. Yields ∿45%.

$CoL(NCS)_2$

To '$Co(NCS)_2$' (1 mmol) (prepared as in 1) in ethanol (15 cm^3) was added the ligand (0.3 cm^3, 2 mmol). The solution was refluxed for 10 minutes, allowed to cool and dry diethyl ether added. A green solid precipitated out which was filtered off, washed with dry diethyl ether and then dried in vacuo. Yield = 50%.

$[CoL_2X]ClO_4$ (X = Cl, Br, I)

To '$CoXClO_4$' (prepared as in 2) (2 mmol) in ethanol (15 cm^3) was added the ligand (0.6 cm^3, 4 mmol). The mixture was refluxed for several minutes, allowed to cool, and dry diethyl ether added (10 cm^3) whereupon green (Cl, Br) and brown (I) solids precipitated out. On filtering, these solids became sticky but repeated washing with dry diethyl ether and trituration led to fine powders. Yields ∿45%.

$[CoL_2X]B\phi_4$ (X = Cl, Br)

These complexes were prepared similarly to the $[Co(PN_{me})_2Br]B\phi_4$ complex from the appropriate cobalt(II) halide. They were green solids. Yields ∿ 50%.

5. (o-Methylthiophenyl)dimethylphosphine

$CoLI_2$

To cobalt(II) iodide (0.349 g, 1 mmol) in propan-2-ol (10 cm^3) was added the ligand (0.48 cm^3, 4 mmol). The mixture was refluxed for a few minutes, allowed to cool, the solvents removed and dichloromethane (10 cm^3) added. This green solution was left for two weeks until some green crystals appeared. Solutions of this complex were stable for at least two months exposed to air. Yield = 30%.

6. 1,2-Bis(dimethylarsino)benzene

$[CoL_2Cl]ClO_4$

This was prepared similarly to the $[Co(PAs_{me})_2Cl]ClO_4$ complex. The product was a yellowish-green solid. Yield = 80%.

$[CoL_2][CoCl_4]$

To cobalt(II) chloride (0.474 g, 2 mmol) in ethanol (15 cm^3) was added the ligand (0.34 cm^3, 2 mmol). The mixture was refluxed for a few minutes and then allowed to cool. A green solid precipitated out and was filtered off, washed with dry diethyl ether and dried *in vacuo*. Yield = 80%.

$[CoL_2Cl]Cl$

This complex was prepared similarly to $[CoL_2][CoCl_4]$ except that the cobalt(II) chloride:L ratio used is 1:2. The yield of this yellow-green solid was 80%.

7. 1,2-Bis(dimethylphosphino)benzene

$[CoL_2][CoCl_4]$

This was prepared similarly to the corresponding dias complex above. A turquoise-green solid resulted in 30% yield.

$[CoL_2Cl]ClO_4$

This was prepared similarly to the $[Co(PAs_{me})_2Cl]ClO_4$ complex. The khaki green product was obtained in a 45% yield.

8. Preparations of some cobalt(III) complexes of 1,2-bis(dimethylarsino)benzene

$[CoL_2Cl_2]Cl$

$[CoL_2Cl]Cl$ (0.738 g, 1 mmol) was suspended in carbon tetrachloride (15 cm^3) and chlorine in carbon tetrachloride (5 cm^3) added dropwise. The mixture was refluxed for 30 minutes and then allowed to cool. A green precipitate was filtered off, washed with dry diethyl ether and dried *in vacuo*. Yield = 80%.

$[CoL_2Cl_2]ClO_4$

This was prepared from $[CoL_2Cl]ClO_4$ by the same method as for $[CoL_2Cl_2]Cl$. A green product resulted in 80% yield.

3.23 THE COBALT(II) COMPLEXES OF A SET OF LIGANDS OF THE TYPE *o*-$C_6H_4(EMe_2)(E'Me_2)$ E,E' = N,P,As and E = P, E' = S)

This section discusses primarily the cobalt(II) complexes of a set of *o*-phenylene ligands containing methyl-substituted group V and VIB donor atoms. Some palladium(II), platinum(II), copper(I), copper(II), nickel(II) and cobalt(III) complexes are also included.

The set of ligands used in this study form interesting cobalt(II) complexes of various geometries. The different structures and spins preferred by the 'hard' and 'soft' donor atoms are apparent in these complexes and are discussed.

The ligands concerned here are:

1. 1,2-Bis(dimethylamino)benzene.
2. (o-Dimethylaminophenyl)dimethylphosphine.
3. (o-Dimethylaminophenyl)dimethylarsine.
4. (o-Dimethylaminophenyl)dimethylstibine.
5. (o-Dimethylphosphinophenyl)dimethylarsine.
6. (o-Methylthiophenyl)dimethylphosphine.
7. 1,2-Bis(dimethylphosphino)benzene.
8. 1,2-Bis(dimethylarsino)benzene.

The complexes of each of these ligands are now discussed in a ligand by ligand manner followed by an overall comparison.

1. <u>1,2-Bis(dimethylamino)benzene</u> (see Tables 3.3 and 3.7)

The reaction of the cobalt(II) halides, CoX_2 (X = Cl, Br, I) with NN_{me} in ethanol under nitrogen produced blue or green solutions from which the blue (Cl, Br) and green (I) complexes, stoichiometry, $CoLX_2$, were deposited. The chloro- and bromo-complexes change from blue to mauve on exposure to air over a matter of days. This mauve solid had a stoichiometry $CoLBr_2(H_2O)_2$ and on the basis of this formula its magnetic moment (μ_{eff} = 5.2 BM) indicated a pseudooctahedral geometry (μ_{eff} = 5.2 BM). In dichloromethane it dissolved to form a blue solution whose electronic spectrum is typical of a tetrahedral species. Its infrared spectrum displayed evidence of coordinated water by bands at 1650 and 3400 cm^{-1}. As a result the following equilibrium has been thought to occur:

$$\underset{\text{blue (td)}}{[CoLBr_2]} \xrightleftharpoons[CH_2Cl_2]{\text{air } 2H_2O} \underset{\text{mauve (oct)}}{[CoLBr_2(H_2O)_2]}$$

The deep pink and pale violet nitrate and thiocyanate complexes respectively, also of a $CoLX_2$ stoichiometry, were similarly prepared.

All attempts to prepare the 2:1 or 3:1 (ligand:metal) complexes failed.

The room temperature magnetic moments of the above $CoLX_2$ (X = Cl, Br, I, NCS, NO_3) complexes all lie in the range expected for tetrahedral cobalt(II) (μ_{eff} = 4.4-4.8 BM) [269,313,343] and their infrared spectra all show the absence of uncoordinated $-NMe_2$ groups (no bands in the 2750-2800 cm^{-1} region) [333].

The halide and nitrate complexes readily dissolved in 10^{-3} M 1,2-dichloroethane and were non electrolytes in this solvent. However, in 10^{-3} M nitromethane, the iodo-complex showed some evidence of dissociation occurring. This has been observed in other iodo-complexes, for example $[CoL_2I_2]$ (L = 2-(diphenylphosphinoethyl)pyridine) [310].

The electronic spectra were recorded in the 6-30,000 cm^{-1} region. However any bands below 12,000 cm^{-1} were frequently quite weak and it was sometimes difficult to distinguish them from noise and solvent overtones.

The cobalt(II) halide (X = Cl, Br, I) complexes possessed electronic spectra which were similar in the solid and in dichloromethane solution. The spectra displayed the multicomponent envelope in the 14-18,000 cm^{-1} region expected for pseudotetrahedral cobalt(II) complexes [325,328,344].

The centre of gravity of these bands was assigned to the $^4A_2 \rightarrow {}^4T_1(P)$, "d-d", transition of rigid tetrahedral symmetry and this increased in energy in accordance with the spectrochemical series I < Br < Cl < NCS.

The far infrared spectra of these halide complexes each exhibited two strong bands and these were assigned to the two cobalt-halogen stretching frequencies expected for a pseudotetrahedral geometry (C_{2v} symmetry). These frequencies were comparable with the values obtained for other pseudotetrahedral cobalt(II) halide complexes [333,345].

The nitrate complex did not show electronic spectral bands typical of a pseudotetrahedral structure. Only weak bands were observed in the 14-18,000 cm^{-1} region in the solid state spectrum. It seems possible that this complex has an octahedral stereochemistry, the single band in the near infrared region at 18,900 cm^{-1} then being attributed to the $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition.

The infrared nujol spectrum displayed bands at 1440, 1316, 1280 and 813 cm^{-1} which indicated coordinated nitrate groups [346-8].

The room temperature magnetic moment of 4.44 BM for the nitrate complex was rather low for octahedral cobalt(II) but this was not without precedent. Values for example of 4.65-4.80 BM have previously been obtained for the complexes of stoichiometry, $CoL(NO_3)_2$ (L = Me_4en, Me_4pn, Me_4tn) [325]. These latter complexes also exhibited similar electronic spectra to the nitrate complex of the NN_{me} ligand. For example $[Co(Me_4en)(NO_3)_2]$ [325] exhibits bands at 9.3, 15.9sh and 19.4 x 10^3 cm^{-1}.

The electronic spectra of the thiocyanate complex in the solid and solution states differed but both appear to exhibit the presence of a tetrahedral species.

The infrared nujol mull spectrum showed a strong sharp band at 2100 cm^{-1} indicative of terminal N-bonded thiocyanate and this together with the previously mentioned magnetic moment implied a formulation of $[CoL(NCS)_2]$ in the solid state.

In 10^{-3} M nitromethane this violet complex gave a turquoise solution the complex acting as a 1:1 electrolyte. Some dissociation obviously occurring in solution.

Copper(II) chloride and bromide reacted in ethanol with the NN_{me} ligand to give the violet-brown complexes of stoichiometry $CuLX_2$.

These complexes were readily soluble in both 1,2-dichloroethane and nitromethane. In the former they were non-electrolytes whilst in the latter the bromide was a 1:1 electrolyte and the chloride also partly dissociated.

The room temperature magnetic moment of 1.66 BM, although slightly low, indicated one unpaired electron and the presence of copper(II).

Previous copper(II) complexes of diamine ligands have been either of the stoichiometry $CuLX_2$ (X = Cl, Br, NCS; L = ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, the symmetric and antisymmetric N,N-dimethyl and diethylethylenediamines and 1,2-diaminobenzene) [349] or CuL_2X_2 (X = Cl, Br, I, NCS, BF_4, NO_3, ClO_4; L as for $CuLX_2$ apart from the 1,2-diaminobenzene) [350]. These $[CuL_2X_2]$ complexes were postulated as having an in-plane CuN_2X_2 microsymmetry from the broad bands at ∿15,000 cm^{-1} observed in the electronic spectra [292,351]. The latter could be resolved at liquid nitrogen temperatures to show a variation with X [349]. No ν(Cu-X) bands were observed for these complexes [351].

The copper(II) complexes prepared in this study appeared to have similar electronic spectra and far infrared spectra. No ν(Cu-X) were observed and this was probably due to strong ligand absorptions obscuring these bands.

A single pale green nickel(II) chloride complex of stoichiometry, $NiLCl_22H_2O$ was prepared for comparative purposes. It was identical in its chemical properties to that previously obtained by Levason et al [292].

The brownish-yellow palladium(II) chloride complex of stoichiometry $PdLCl_2$ was also obtained. This was diamagnetic and a non-electrolyte in 10^{-3} M 1,2-dichloroethane and nitromethane. Its electronic spectra were identical in both the solid and solution states, the band at ∿25,800 cm^{-1} being attributed to $^1A_{1g} \rightarrow {}^1A_{2g}$ in D_{4h} symmetry.

The far infrared bands, ν(Pd-Cl) are in the region expected for cis-$PdCl_2$ [66] (see Section 1.13 and Table 1.6).

2. <u>(o-Dimethylaminophenyl)dimethylphosphine</u> (see Tables 3.4 and 3.8)

Cobalt(II) halides (X = Cl, Br, I) reacted with the ligand, in either a 1:1 or 1:2 ratio, in propan-2-ol under nitrogen to give blue (Cl, Br) or green (I) solutions from which blue (Cl, Br) or green (I) solids of stoichiometry $CoLX_2$ were obtained.

In 1,2-dichloroethane, the chloride was insoluble but the bromide and iodide complexes were non electrolytes. In nitromethane however all three halides dissociated to varying degrees (I > Br > Cl).

The room temperature magnetic moments (μ_{eff} = 4.44-4.62 BM) and electronic spectra, which were similar in both the solid and solution states, were typical of pseudotetrahedral cobalt(II) [269,325,328,333,343]. The band maxima of the bands in the 13-17,000 cm^{-1} region ($^4A_2 \rightarrow {}^4T_1(P)$) shifted to higher energy as expected from the spectrochemical series, i.e. Cl > Br > I.

The far infrared spectra were also consistent with a pseudotetrahedral geometry, each exhibiting the two bands expected for a C_{2v} symmetry.

A dark brown, cobalt(II) nitrate complex of stoichiometry $CoL(NO_3)_2$ was obtained by reaction with the ligand in a 1:1 ratio in ethanol in a nitrogen atmosphere.

This complex was only partially soluble in nitromethane forming a pink solution so preventing both conductivity and magnetic measurements

[352] in solution.

The infrared spectrum in hexachlorobutadiene showed a broad band at 1367 cm^{-1} which was attributed to the presence of ionic nitrate. It was thought that this complex contained one ionic nitrate and one bidentately coordinated nitrate, the bands of the latter being weak and obscured by the former [346-348].

Violet-brown complexes of stoichiometry $[CoL_2X]Y$ (X = Cl, Br, I; Y = ClO_4 and X = Br; Y = $B\phi_4$) were obtained by the reaction of either '$CoXClO_4$' or '$CoXB\phi_4$' with the ligand in a 1:2 ratio in ethanol in a nitrogen atmosphere. These complexes turned to green solids on exposure to air over a period of several days and as a result of this the violet-brown solids were stored in vacuo.

The violet-brown and green solids all gave infrared spectra indicating $-NMe_2$ coordination [333] (no band in the 2750-2800 cm^{-1} range).

The perchlorate complexes all displayed a strong unsplit broad band in the 1080-1100 cm^{-1} region showing that the perchlorate was uncoordinated.

The green solids showed a broad band at 3330 and a sharp band at 1615 cm^{-1} indicative of the presence of water.

The bromo- and chloro-perchlorate complexes gave violet solutions which were 1:1 electrolytes in both 10^{-3} M 1,2-dichloroethane and nitromethane. These solutions turned blue or green after about an hour. The iodo-perchlorate and bromo-tetraphenylborate complexes however very rapidly gave blue or green solutions which were also 1:1 electrolytes in the above mentioned solvents.

The molar conductivity of the tetraphenylborate complex was lower than the corresponding perchlorate complex as would be expected from the lower specific conductance of such a large anion.

The room temperature magnetic moments of the halide-perchlorates and the bromide-tetraphenylborate complexes (μ_{eff} = 2.07-2.65) was approximately in the range expected for low spin five-coordinate cobalt(II) (μ_{eff} = 1.9-2.5 BM) [299,313,353]. The value obtained for the iodide-perchlorate was slightly high but this has been observed for other iodide complexes for example $[Co(2\text{-diethylphosphinomethylpyridine})_2I]I$ where μ_{eff} = 2.58 BM [313].

The electronic spectral data of these complexes was similar in both the solid and solution states and was also consistent with a low spin five-coordinate structure [299,313].

Previously Meek et al [354] have determined crystal structures of both the red and green isomers of the complex $[CoL_2Cl]SnCl_3$ (L = 1,2-bis(diphenylphosphino)ethane) and have found that the green complex has a trigonal bipyramidal cation and the red complex a square pyramidal cation. It has also been observed [307] that many of the known low spin five-coordinate cobalt(II) complexes can be split into either those which are green with room temperature magnetic moments in the range 1.89-1.97 BM or those which are red, with magnetic moments in the 2.03-2.4 BM range. The dark violet-brown solids prepared in this study resembled the latter type and were thus by analogy tentatively postulated as square pyramidal. Without X-ray data no definite conclusion could really be made.

A complex of stoichiometry $CoL_2(ClO_4)_2$ was obtained from cobalt(II) perchlorate and the ligand in ethanol under nitrogen. It was stored <u>in vacuo</u> as on exposure to air it rapidly turned green.

In 1,2-dichloroethane the complex was a 1:2 electrolyte. In nitromethane it was however only partially soluble.

Its room temperature magnetic moment was 2.84 BM and this lies within the range expected for square planar cobalt(II) (μ_{eff} = 2.1-2.9 BM). An example of a complex previously postulated as square planar is the $Co(vpp)_2(ClO_4)_2$ (L = 1,2-cis-bis(diphenylphosphino)ethylene) complex with a magnetic moment of 2.65 BM. This latter complex also exhibited a band in its electronic spectrum at ∿21,000 cm^{-1} which compared well with the bands at 21,700 and 20,600 cm^{-1} in the solution and solid spectra of the PN_{me} complex.

In the infrared spectrum of this complex no bands was observed in the 2750-2800 cm^{-1} region thus showing that the $-NMe_2$ group [333] was coordinated. A strong broad unsplit band at 1095 cm^{-1} also indicated the presence of ionic perchlorate.

The complex was therefore formulated as the square planar $[CoL_2](ClO_4)_2$.

An attempt was made to obtain a cobalt(II) thiocyanate complex but only an impure yellow-brown solid resulted.

3. (*o*-Dimethylaminophenyl)dimethylarsine (see Tables 3.6 and 3.10)

The reaction of cobalt(II) iodide with NAs_{me}, in a 1:1 ratio, in n-butanol, under nitrogen, produced a deep brown solution from which a dark brown solid of stoichiometry $CoLI_2$ was obtained.

Repeated attempts to obtain similar chloro, bromo, nitrato and thiocyanato complexes resulted in brightly coloured solids whose elemental analysis displayed a carbon content approximately half of what would be expected for a 1:1 complex. Several mauve-coloured samples were precipitated which were insoluble in dichloromethane or nitromethane and also exhibited a definite paramagnetism. These solids may well be polymeric.

The iodo-complex did not appear to be particularly air-sensitive unlike the corresponding complex of *o*-dimethylarsinoaniline, $[CoL_2I_2]$ which oxidises readily forming the cobalt(III) compound. [314] The complex was also a non electrolyte in 10^{-3} M 1,2-dichloroethane. However, in nitromethane, there was some evidence of dissociation.

The complex exhibited an anomalously high solid state, room temperature magnetic moment of 6.58 BM and as a result of this a structure for the complex has not been postulated.

Two complexes of stoichiometry $MLCl_2$ (M = Pd(II), Pt(II)) were prepared from sodium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) respectively in an ethanol/water mixture. These were diamagnetic orange-yellow (Pd) and yellow (Pt) solids and were non electrolytes in 1,2-dichloroethane. The same palladium(II) complex has previously been reported by Mann and Stewart [225].

Their solution and nujol mull spectra in dichloromethane are similar and typical of other cis-$MLCl_2$ complexes (see Section 1.13).

The far infrared spectra displayed strong ligand bands making the assignment of the ν(M-Cl) difficult.

Their nujol mull infrared spectra exhibited no band in the 2750-2800 cm^{-1} region indicating that the $-NMe_2$ group was coordinated [333] and also showed bands in the 860-920 cm^{-1} region attributable to the rocking modes of the coordinated $-AsMe_2$ group.

These complexes were thus formulated as square planar $[MLCl_2]$.

4. (o-Dimethylaminophenyl)dimethylstibine

No cobalt(II) halide complexes of this ligand could be isolated.

5. (o-Dimethylphosphinophenyl)dimethylarsine (see Tables 3.5 and 3.9)

Cobalt(II) halides, CoX_2 (X = Cl, Br, I) in either a 1:1 or 1:2 ratio in ethanol under nitrogen reacted with the PAs_{me} ligand to give green (Cl, Br) and brown (I) complexes of stoichiometry, CoL_2X_2. These were generally sparingly soluble in solvents such as 1,2-dichloroethane or nitromethane but their conductivities indicated they were 1:1 electrolytes in these solvents.

The magnetic moment of the iodo-complex was measured by an nmr method [352] using approximately a 1% solution of the complex in nitromethane. The chloro- and bromo-complexes did not prove to be soluble enough for such a measurement however. The magnetic moment of the iodide implied only one unpaired electron and was in the range expected for low spin five-coordinate cobalt(II).

The electronic solution spectra in nitromethane and 1,2-dichloroethane closely resembled the solid state spectra. The intense peak in the 20-26,000 cm^{-1} region contrasted with the weak peaks seen in the 15-17,000 cm^{-1} region and such spectra were typical of those observed previously for low spin five-coordinate cobalt(II) [299,313].

The infrared nujol mull spectra displayed bands at ∿870 and 915 cm^{-1} attributable to the rocking modes of coordinated $-AsMe_2$.

These halide complexes were therefore formulated as $[CoL_2X]X$ (X = Cl, Br, I).

A green cobalt(II) thiocyanate complex of stoichiometry $CoL(NCS)_2$ was obtained by the reaction between '$Co(NCS)_2$' and the ligand in either a 1:1 or a 1:2 ratio in ethanol under nitrogen. This complex was only partially soluble in nitromethane giving a green solution whose conductivity although still in the range expected for a non electrolyte did imply some degree of dissociation was occurring.

The electronic solution (nitromethane) and solid state spectra are similar and are indicative of pseudotetrahedral cobalt(II).

The infrared spectrum displayed a sharp strong band at 2075 cm^{-1} which was indicative of N-bonded thiocyanate.

A light-brown cobalt(II) nitrate complex of stoichiometry $CoL_2(NO_3)_2$ was prepared similarly to the halide complexes above. The complex was dissociated to some extent in 10^{-3} M nitromethane.

Its infrared spectrum indicated the presence of ionic nitrate groups by a band at 1378 cm^{-1} [346-348].

The magnetic moment of this complex implied a square planar structure (μ_{eff} = 3.1 BM).

The complex was thus formulated as square planar $[CoL_2](NO_3)_2$.

Complexes of stoichiometry, $[CoL_2X]Y$ (X = Cl, Br, I; Y = ClO_4 and X = Cl, Br; Y = $B\phi_4$) were produced by the reaction of 'CoXY' and the ligand in a 1:2 ratio in ethanol under nitrogen. These were all green solids except for the bromo- and iodo-perchlorate which were yellowish-green and dark brown respectively.

The perchlorates were all 1:1 electrolytes in 1,2-dichloroethane or nitromethane. The tetraphenylborates were however only partially soluble in these solvents.

A room temperature magnetic moment was obtained for the bromide-tetraphenylborate salt and implied only one unpaired electron and a low spin five-coordinate structure. The other complexes however either were not obtained in high enough yield or were not soluble enough for solution nmr [352] measurements.

The electronic spectra of these five complexes were similar in both the solid and solution states and were consistent with a low spin five-coordinate species [299,313].

6. (o-Methylthiophenyl)dimethylphosphine (see Tables 3.6 and 3.10)

Cobalt(II) iodide reacted with this ligand in propan-2-ol under nitrogen in a 1:1 or 1:2 ratio to form a green complex of stoichiometry, $CoLI_2$. The complex was first obtained as a green oil and then as a solid after standing for some weeks. The oil appeared to be stable both to hydrolysis and oxidation.

In 10^{-3} M 1,2-dichloroethane solution the complex was a non electrolyte whilst in nitromethane some dissociation occurred.

The solid complex was obtained in only a low yield rendering solid state magnetic measurements impossible.

The solid state electronic spectrum was however typical of pseudotetrahedral cobalt(II) [325,328,344].

7. 1,2-Bis(dimethylphosphino)benzene (see Tables 3.6 and 3.10)

Cobalt(II) chloride reacted with PP_{me} in ethanol under nitrogen, in a 1:1 ratio, to produce a turquoise solid of stoichiometry, $CoLCl_2$.

In 10^{-3} M 1,2-dichloroethane and nitromethane the complex (dimeric formulation) behaved as a 1:1 electrolyte.

A pale green complex of a 1:2 stoichiometry has previously been prepared by Warren and Bennett [253,275] and postulated to be a low spin six-coordinate species in the solid state.

The solid and solution electronic spectra of the 1:1 complex prepared here were similar and consistent with the presence of a tetrahedral $[CoCl_4]^{2-}$ anion.

The complex was therefore formulated as $[Co(PP_{me})_2][CoCl_4]$.

The ligand reacted with '$CoClClO_4$' in ethanol under nitrogen in a 2:1 ratio to form a green complex of stoichiometry, CoL_2ClClO_4.

This complex was a 1:1 electrolyte in 10^{-3} M nitromethane and possessed a magnetic moment indicative of one unpaired electron and low spin, five-coordinate cobalt(II). The electronic spectra were not inconsistent with such a geometry and the complex was thus formulated as $[CoL_2Cl]ClO_4$.

8. 1,2-Bis(dimethylarsino)benzene (see Tables 3.6 and 3.10)

Cobalt(II) chloride reacted with the ligand in ethanol under nitrogen, in a 1:1 ratio, to form a green complex of stoichiometry $CoLCl_2$.

This complex was a 1:1 electrolyte (dimeric formulation) in 10^{-3} M nitromethane but its solubility in this solvent was not great enough to permit a determination of the magnetic moment by the nmr method [352].

The infrared spectrum exhibited bands attributed to the rocking modes of coordinated $-AsMe_2$ at 883 and 929 cm^{-1}.

The above data and also the electronic spectra in the solid and solution states were consistent with a $[CoL_2][CoCl_4]$ formulation.

The above reaction was also carried out using a 1:2 ratio and produced a yellow complex of stoichiometry, CoL_2Cl_2. This complex was only partially soluble in nitromethane but did appear, to some extent, to dissociate in this solvent. Its room temperature magnetic moment (μ_{eff} = 2.11 BM) indicated only one unpaired electron and low spin cobalt(II). In addition the infrared nujol mull spectrum displayed bands at 869 and 920 cm^{-1} attributable to the rocking modes of only coordinated $-AsMe_2$.

A similar yellow compound with an identical magnetic moment has been prepared previously by Nyholm [317]. He regarded it as a tetragonally distorted octahedral complex in the solid state. This conclusion was based on the fact that no ν(Co-Cl) were observed and also the X-ray powder patterns of the corresponding nickel(II) complexes were identical and the X-ray structure of the $[NiL_2I_2]$ [341] complex was of this geometry.

The complex prepared here was thought to be the same compound.

The electronic solution spectrum of the complex was however consistent with the presence of a five-coordinate species and as a result in solution it was formulated as $[CoL_2Cl]Cl$.

The ligand reacted with '$CoClClO_4$' in ethanol in a 2:1 ratio under nitrogen to give a yellow-green complex of stoichiometry CoL_2ClClO_4.

The complex had a limited solubility preventing the solution state measurements such as conductivity and magnetic susceptibility. However in the solid state a room temperature magnetic moment of 2.23 BM was obtained. This suggested low spin five-coordinate cobalt(II). The latter was also supported by the electronic solid and solution state spectra as well as by the infrared nujol mull spectrum which exhibited a band at 1088 cm^{-1} attributable to uncoordinated perchlorate and bands at 861 and 912 cm^{-1} attributable to the rocking modes of coordinated $-AsMe_2$ groups.

The complex was therefore formulated as $[CoL_2Cl]ClO_4$.

Two cobalt(III) complexes of the above dias ligand of stoichiometries CoL_2Cl_3 and $CoL_2Cl_2ClO_4$ were prepared by bubbling chlorine in carbon tetrachloride through each of the cobalt(II) complexes, $[CoL_2Cl_2]$ and $[CoL_2Cl]ClO_4$, suspended in carbon tetrachloride. Green diamagnetic complexes resulted and these were 1:1 electrolytes in 10^{-3} M nitromethane. They also all exhibited bands in their nujol mull infrared spectra attributable to the rocking modes of coordinated $-AsMe_2$ and also the complex prepared from $[CoL_2Cl]ClO_4$ showed uncoordinated perchlorate by a broad unsplit band at 1095 cm^{-1}.

The electronic spectra in both the solid and solution states of these complexes were very similar and typical of octahedral cobalt(III). It was postulated therefore that these complexes contained the same six-coordinate cation $[CoL_2Cl_2]^+$ and were formulated as $[CoL_2Cl_2]Cl$ and $[CoL_2Cl_2]ClO_4$ respectively.

These complexes were identical to those previously prepared by Nyholm [317].

3.24 THE COBALT(II) COMPLEXES OF THE METHYL-SUBSTITUTED O PHENYLENE BACKBONED LIGANDS

The ligands prepared for this study contained a range of donor atoms N, P, As, Sb and S.

Nitrogen donors are generally 'hard' whereas the others are 'soft' and as a result of this these mixed donor bidentate ligands result in a variety of stereochemistries.

The 1,2-bis(dimethylamino)benzene ligand contains two nitrogen donors and the expected and found result was the formation of high spin tetrahedral complexes. This high spin has similarly been found in the case of the nickel(II) complexes [292], the complexes here being octahedral.

The 1,2-bis(dimethylphosphino)benzene and 1,2-bis(dimethylarsino) benzene ligands produce strong ligand fields and both here and in previous cobalt(II) work [253,275,317] were found to produce low spin complexes. The nickel(II) complexes are similarly low spin [292].

The (o-dimethylphosphinophenyl)dimethylarsine ligand having a combination of the above phosphorus and arsenic donors was expected to and in fact did form only low spin, 2:1 complexes. Here again the nickel(II) complexes are low spin [292].

The (o-methylthiophenyl)dimethylphosphine ligand contains two 'soft' donor atoms and from this a low spin, 2:1 complex was anticipated. However a 1:1 complex was obtained. Room temperature magnetic moments were not obtained but the solid and solution state electronic spectra of the complex were typical of that of a tetrahedral species [269].

The other ligands (o-dimethylaminophenyl)dimethylphosphine, (o-dimethylaminophenyl)dimethylarsine and (o-dimethylaminophenyl)dimethylstibine contain both 'hard' and 'soft' donor atoms. The spin of the complexes formed from these depended on a balance between these two donor types.

The PN_{me} ligand formed both high spin, 1:1 complexes and low spin, 2:1 complexes. The proportion of high spin complexes to low spin complexes was greater than in the nickel(II) case [292]. This was presumably the result of cobalt(II) being harder than nickel(II).

The AsN_{me} ligand gave only a paramagnetic cobalt(II) iodide complex. Generalisations regarding the cobalt(II) complexes of this ligand could not therefore be made. Nickel(II) however has given an equal number of high and low spin complexes and it appeared that with this ligand that the $-NMe_2$ had a more pronounced effect on the spin of these products. Further work to obtain the cobalt(II) complexes may give a similar result.

The SbN_{me} ligand gave no cobalt(II) halide complexes. No nickel(II) halide complexes have been produced either [292].

It might be expected that the amine donor would increase the tendency of the stibine ligand to bond to cobalt(II). This argument however led to the implication that the NAs_{me} complexes formed more readily than the dias ones and this was clearly untrue. It was therefore thought that the SbN_{me} ligand must have a weaker ligand field than AsN_{me}, the $-SbMe_2$ donors having little tendency to bond to high spin cobalt(II) in the conditions adopted.

It was generally noticed that complexes where the metal:ligand ratio in the neutral complex or cation was 1:1, were high spin and those where it was 1:2, were low spin.

The different ligands reflected, in their ability to form complexes their different ligand field strengths.

The $-NMe_2$ donors in NN_{me} exhibited a weak ligand field as is shown by the formation of only high spin complexes whereas the $-AsMe_2$ and $-PMe_2$ donors in dias, PP_{me} and PAs_{me} a strong ligand field by their corresponding production of only low spin complexes.

The $-PMe_2$ donor in the PN_{me} ligand increased the latter's ligand field strength more than the $-AsMe_2$ or $SbMe_2$ in the AsN_{me} and SbN_{me} ligands which led to the isolation of a number of low spin, 2:1 (ligand: cobalt) complexes. In the presence of only one PN_{me} ligand however, only high spin complexes were obtained, the ligand field not being sufficiently strong to produce low spin complexes.

Table 3.2 Syntheses of some mixed donor bidentate ligands

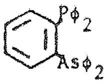
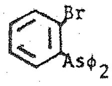
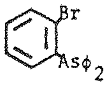
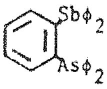
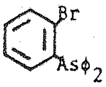
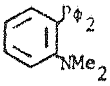
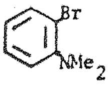
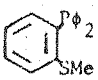
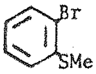
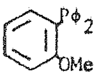
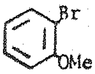
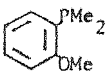
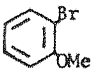
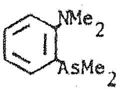
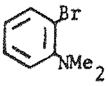
Ligand	State	Yield (%)	Route	Reagents	Reference
1.  (AP$_\phi$)	white solid	50	(ii)	 and ϕ_2PCl	[296]
			(i)	 and LiPϕ_2	[181]
2.  (SbA$_\phi$)	white solid	35	(ii)	 and ϕ_2SbCl	[297]
3.  (PN$_\phi$)	air-stable white solid (soluble in organic solvents)	55	(ii)	 and ϕ_2PCl	[298]
4.  (PS$_\phi$)	white solid	74	(ii)	 and ϕ_2PCl	[97,299]
5.  (PO$_\phi$)	white crystalline solid	44	(iii)	 and ϕ_2PCl	[300]
6.  (PO$_{me}$)	air-sensitive oil	53	(i)	 and LiPMe$_2$	[301]
7.  (NAs$_{me}$)	air-sensitive colourless liquid	68	(iii)	 and Me$_2$AsI	[225]

Table 3.3 Analytical data and physical measurements of the complexes of NN_{me}

Complex	Colour	Elemental Analysis[a] C	 H	 X	$\Lambda^{b}_{M}(\Omega^{-1}cm^{-1})$	$\chi_{corr}{}^{f}$/ $\mu_{corr}{}^{g}$(BM)	Infrared Data (cm^{-1})
$NiLCl_2(H_2O)_2$	pale green	36.4(36.4)	6.1(6.1)	N=8.4(8.49) Cl=21.3(21.5)	-	-	-
$CoLCl_2$	blue	40.7(40.8)	5.2(5.4)	X=Cl 9.7(9.5)	0.31 (d)[c] 23.2 (N)[d]	$1.128x10^{-7}$/ 4.62	314 356 ν(Co-Cl)
$CoLBr_2$	blue	31.33(31.0)	4.17(4.0)	X=Br 41.77(41.7)	0.5 (d)	$1.059x10^{-7}$/ 4.48	261 287 ν(Co-Br)
$CoLI_2$	green	24.8(25.1)	3.2(3.3)	X=N 5.41(5.8)	4.18 (d) 46.1 (N)	$1.666x10^{-7}$/ 5.62	231 244 ν(Co-I)
$CoL(NO_3)_2$	deep pink	34.8(34.5)	3.4(4.6)	X=N 15.9(16.1)	0.20 (d) 22.71 (N)	$1.041x10^{-7}$/ 4.44	818 1280 1316 1440 $\nu(NO_3)$
$CoL(NCS)_2$	pale violet	42.05(42.4)	4.8(4.72)		94.4 (N)	$1.079x10^{-7}$/ 4.52	2110 ν(C-N)
$CuLCl_2$	violet-brown	40.5(40.2)	5.1(5.3)	X=Cl 8.9(9.3)	1.77 (d) 44.77 (N)	-	-
$CuLBr_2$	dark violet-brown	30.2(30.9)	3.9(4.1)	X=N 7.5(7.2)	2.88 (d) 76.42 (N)	1.66	-
$PdLCl_2$	brownish-yellow	34.9(35.1)	4.0(4.6)	X=N 8.1(8.2)	0.35 8.32 (N)	D^{m}	285(?) 321-340 br ν(Pd-Cl)
$CoLBr_2(H_2O)_2$	mauve	28.8(28.4)	4.9(4.8)	X=N 7.0(6.1)		$1.451x10^{-7}$/ 5.2	

** For footnotes see Page 174.

Table 3.4 Analytical data and the physical measurements of the cobalt(II) complexes of PN_{me}

Complex	Colour	Elemental Analysis[a]			$\Lambda^{b}_{M}(\Omega^{-1}cm^{-1})$	$\chi_{corr}{}^{f}$/ $\mu_{corr}{}^{g}$(BM)	Infrared Data (cm^{-1})
		C	H	X			
$CoLCl_2$	blue	37.9(38.5)	4.9(5.1)	X=N 4.6(4.5)	52.9 (N)[d]	$1.079x10^{-7}$/ 4.52	317 370 ν(Co-Cl)
$CoLBr_2$	blue	30.7(30.0)	3.9(4.0)	X=N 3.5(3.5)	2.47 (d)[c] 36.83 (N)	$1.127x10^{-7}$/ 4.62	245 291 ν(Co-Br)
$CoLI_2$	green	24.0(24.2)	3.2(3.2)	X=N 2.6(2.8)	2.15 (d) 66.0 (N)	$1.041x10^{-7}$/ 4.44	202-223 br
$CoL(NO_3)_2$	dark brown	33.0(33.0)	3.8(4.39)	X=N 11.5(11.5)	e (N)	-	1367 (NO_3)
$[CoL_2Cl]ClO_4$	dark violet-brown	42.6(43.1)	5.6(5.7)	X=N 4.8(5.0)	27.8 (d) 101.9 (N)	$2.265x10^{-8}$/ 2.07	1088 sbr (ClO_4)
$[CoL_2Br]ClO_4$	dark violet	39.9(39.9)	5.2(5.3)	X=N 4.6(4.6)	104.8 (N)	2.48 2.17	1100 sbr (ClO_4)
$[CoL_2I]ClO_4$	deep violet	36.8(37.1)	4.8(4.94)	X=N 4.1(4.3)	26.2 (d) 121.55 (N)	$3.715x10^{-8}$/ 2.65	1090 sbr (ClO_4)
$[CoL_2](ClO_4)_2$	dark brown	38.0(38.7)	5.2(5.16)	X=N 4.5(4.5)	34.1 (d) e (N)	$4.311x10^{-8}$/ 2.84	1090 sbr (ClO_4)
$[CoL_2Br]B\phi_4$	dark violet	64.6(64.39)	6.2(6.34)	X=N 3.4(3.4)	66.6 (N)	$2.692x10^{-8}$/ 2.25	-

** For footnotes see Page 174.

Table 3.5 Analytical data and the physical measurements of the cobalt(II) complexes of PAs_{me}

Complex	Colour	Elemental Analysis^a			$\Lambda^b_M(\Omega^{-1}cm^{-1})$	$\chi_{corr}{}^f/$ $\mu_{corr}{}^g$(BM)	Infrared Data (cm^{-1})
		C	H	X			
$[CoL_2Cl]Cl$	emerald green	38.6(39.0)	4.8(5.2)		13.82 (d) 43.86 (N)	4.717×10^{-8}/ 2.965	870 925 ($AsMe_2$ rock)
$[CoL_2Br]Br$	green	34.4(34.14)	4.5(4.55)		e (d) 60.48 (N)	h	870 880 925 ($AsMe_2$ rock)
$[CoL_2I]I$	brown	29.89(30.11)	4.0(4.015)		56.2 (N)	2.831×10^{-8}/ 2.35^h	870 915 ($AsMe_2$ rock)
$CoL(NCS)_2$	green	34.6(34.53)	4.1(3.836)		e (N)	-	2075 (NCS)
$CoL_2(NO_3)_2$	light brown	35.9(35.9)	4.6(4.79)	X=N 3.9(4.19)	49.23 (N)	3.1	1378 (NO_3)
$[CoL_2Cl]ClO_4$	green	35.9(35.4)	4.8(4.72)		23.85 (d) 63.44 (N)	-	1086 (ClO_4) 860 875 918 ($AsMe_2$ rock)
$[CoL_2Br]ClO_4$	yellowish-green	33.0(33.2)	4.2(4.4)		15.62 (d)	-	1060 (ClO_4) 870 925 ($AsMe_2$ rock)
$[CoL_2I]ClO_4$	dark brown	30.8(31.18)	4.0(4.15)		84.4 (N)	-	1095 (ClO_4) 862 905 ($AsMe_2$ rock)
$[CoL_2Cl]B\phi_4$	green	59.2(58.8)	5.9(5.8)		e (N)	h	-
$[CoL_2Br]B\phi_4$	green	56.6(56.05)	5.5(5.5)		e (d)	2.201/ 2.05	-

** For footnotes see Page 174.

Table 3.6 Analytical data and the physical measurements of the complexes of the ligands PS_{me}, PP_{me}, dias and AsN_{me}

Complex	Colour	Elemental Analysis[a] C	H	X	$\Lambda^{b}_{M}(\Omega^{-1}cm^{-1})$	$\chi_{corr}{}^{f}$/ $\mu_{corr}{}^{g}$(BM)	Infrared Data (cm^{-1})
$Co(PS_{me})I_2$	green	20.9(21.7)	2.6(2.6)		3.7 (d)[c] 51.0 (N)[d]	h	-
$[Co(PP_{me})_2][CoCl_4]$	turquoise	37.0(37.5)	4.45(5.0)		29.2 (d) 50.2 (N)	h	-
$[Co(PP_{me})_2Cl]ClO_4$	green	40.6(40.67)	5.4(5.42)		75.0 (N)	1.953×10^{-8}/ 1.95[h]	1090 (ClO_4)
$[Co(dias)_2][CoCl_4]$	green	28.3(28.8)	3.6(3.8)		81.74 (N)	h	870 883 920w 929 ($AsMe_2$ rock)
$Co(dias)_2Cl_2$	yellow	33.7(34.1)	4.3(4.5)		e (N)	1.967×10^{-8}/ 2.12	869 920 ($AsMe_2$ rock)
$[Co(dias)_2Cl_2]ClO_4$	yellow-green	30.9(31.3)	4.1(4.17)		e (N)	4.529×10^{-8}/ 2.23	1088 (ClO_4) 861 912 ($AsMe_2$ rock)
$[Co(dias)_2Cl_2]Cl$	green	31.4(32.5)	4.2(4.3)		78.3 (N)	D[m]	869 883 920w 929 ($AsMe_2$ rock)
$[Co(dias)_2Cl_2]ClO_4$	green	29.7(29.9)	4.2(4.0)		84.0 (N)	D	1095 (ClO_4) 869 883 910w 929 ($AsMe_2$ rock)
$Co(AsN_{me})I_2$	brown	22.0(22.3)	1.8(2.9)	X=N 2.8(2.6)	5.4 (d) 39.4 (N)	2.309×10^{-7}/ 6.58	-
$Pd(AsN_{me})Cl_2$	orange-yellow	29.6(29.8)	4.1(4.0)	X=N 3.3(3.48)	4.4 (N)	D	866 916 ($AsMe_2$ rock)
$Pt(AsN_{me})Cl_2$	yellow	24.0(24.4)	3.3(3.26)	2.8(2.85)	4.5 (N)	D	856-886 916 ($AsMe_2$ rock)

** For footnotes see Page 174.

Table 3.7 Electronic spectral data for some complexes of NN_{me}

Complex	$E_{max}^{\ n}$ (ε^{P}) x 10^{-3} cm^{-1}	E_{max} x 10^{-3} cm^{-1}
$CoLCl_2$	(d)^c 13.4(222) 15.8(81) 25.25sh 27.3sh	8.25 14.25sh 16.4 17.0sh 18.5sh 32.85sh
$CoLBr_2$	(d) 7.9(32) 15.35(248) 17.1(110) 17.7sh 18.4sh 20.9wsh 23.3wsh 25.35(13)	6.7 14.4sh 15.25 15.8sh 16.75sh 17.4sh 21.1sh
$CoLBr_2 2H_2O$	-	6.5sh 14.8
$CoLI_2$	(d) 9.5 14.3sh 15.25(888) 16.1(628) 16.9sh 19.7sh 26.2(1240)	6.5 9.0 14.6sh 15.2 16.1sh 16.8sh 20.3wsh
$CoL(NO_3)_2$	(d) 18.9 19.8sh 20.8sh 23.75sh 24.4 24.8sh	6.75 8.9sh 15.25 16.25sh 19.35sh 19.35sh 20.2 21.25sh
$CoL(NCS)_2$	(N)^d 15.9(674) 17.35sh 20.2sh 23.5sh	14.0sh 16.15 18.2 19.1 20.5sh 26.6brsh
$CuLCl_2$	(d) 18.7(69) 25.0(291)	6.5 15.3w 18.3sh
$CuLBr_2$	(d) 15.1w(48) 19.4(194) 24.3sh 30.3(1988)	6.5sh 8.3 15.1 19.9
$PdLCl_2$	(d) 25.8(137) 33.4(498)	25.0

** For footnotes see Page 174.

Table 3.8 Electronic spectral data of the cobalt(II) complexes of PN_{me}

Complex	E_{max}^{n} (ϵ^{p}) x 10^{-3} cm^{-1}	E_{max} x 10^{-3} cm^{-1}
$CoLCl_2$	$(N)^d$ 12.2wbr(18) 15.25(160) 17.0(142) $(d)^c$ 8.35(24) 15.2(54) 16.0sh(32) 30.7sh(32)	5.7 8.8sh 14.4sh 15.3 16.0sh 17.3sh 18.7sh
$CoLBr_2$	(N) 14.65(120) 15.1(151) 16.25(120) 17.0(54) (d) 15.1sh 15.8 16.8sh 30.0sh	6.4 8.8sh 14.3sh 15.8 17.1sh 18.1sh
$CoLI_2$	(d) 12.8sh 13.4 14.3sh 15.0sh 21.3wsh 25.45 31.5	5.1 12.8sh 14.5 14.9 16.4sh 18.2sh 20.2sh 22.7sh 25.45
$CoL(NO_3)_2$	(N) 18.6br	7.7wsh 18.8 21.2
$[CoL_2Cl](ClO_4)$	(N) 15.65(72) 17.0(72) 21.8(226) (d) 15.7(35) 21.75br(75)	7.7sh 15.25sh 20.6br
$[CoL_2Br](ClO_4)$	(N) 14.7sh(32) 15.1(52) 16.0sh(43) 23.5sh (63) (d) 15.25(35) 17.1sh(18) 20.8(16) 24.8sh(16)	7.4 14.7sh 15.6 17.6 21.6br
$[CoL_2I](ClO_4)$	(N) 15.7(63) 17.2sh(60) 21.75sh(97) (d) 14.7sh(63) 15.25(94) 16.0(21) 23.75sh(144)	6.7sh 7.7sh 17.8 20.8 27.5sh
$[CoL_2](ClO_4)_2$	(N) 21.7(201)	7.4brsh 17.2sh 20.6br
$[CoL_2Br]B\phi_4$	(d) 15.1w 18.9w 21.3br	18.0sh 20.9br

** For footnotes see Page 174.

Table 3.9 Electronic spectral data of the cobalt(II) complexes of PAs_{me}

Complex	E_{max}^{n} (ϵ^{P}) x 10^{-3} cm^{-1}	E_{max} x 10^{-3} cm^{-1}
$[CoL_2Cl]Cl$	(N)^d 14.75sh 15.0(87) 15.4sh 15.85sh 17.0(87) (d)^c 14.7 15.15 16.4 17.6 25.8 31.9	6.2w 8.2w 14.7 15.2 15.75sh 15.9sh 16.5 18.6sh 24.9 27.0sh
$[CoL_2Br]Br$	(N) 15.0sh 15.75(60) 23.75(1758) 25.85(877) (d) 15.75w 23.75br 29.15sh	15.5w 22.9br 28.85 31.5
$[CoL_2I]I$	(N) 15.0sh(121) 17.75sh(272) 20.75(2770) 25.6(1767) (d) 15.150w 18.0sh 20.75 28.6sh	15.4wsh 20.35 25.1sh 28.1
$CoL(NCS)_2$	(N) 16.0 17.0 17.9sh 21.0wsh	6.8sh 7.7 8.7sh 15.75 17.1sh 21.0wsh 25.6wsh 28.7wsh
$CoL_2(NO_3)_2$	(d) 17.8w 19.2w 20.8w 26.0 33.0	17.25w 33.2sh
$[CoL_2Cl]ClO_4$	(d) 13.5w 16.3w(18) 17.15sh(18) 25.75(699) 31.9sh	6.4 8.4 14.9sh 16.25 17.9sh 20.7wsh 24.8sh 31.75sh
$[CoL_2Br]ClO_4$	(d) 15.4(26) 17.1(13) 23.75(628) 30.5(1276)	15.1 16.0w 22.7sh 24.25sh 30.0sh
$[CoL_2I]ClO_4$	(N) 17.7sh(364) 20.8(3682)	6.4 8.75 11.00 wsh 14.4sh 15.1sh 17.35sh 20.1 24.8sh 33.5
$[CoL_2Cl]B\phi_4$	(N) 17.0w 25.4	8.1w 14.6-16.5brw 24.75 25.8
$[CoL_2Br]B\phi_4$	(N) 15.0w(69) 23.75(945) 26.2sh(424) (d) 14.2br 23.8 31.0sh	6.9w 8.25wsh 11.0wsh 15.85wbr 23.45 28.9sh 33.2sh

** For footnotes see Page 174.

Table 3.10 Electronic spectral data for some cobalt(II) complexes of PS_{me}, PP_{me}, dias and NAs_{me} and cobalt(III) complexes of dias

Complex	E_{max}^{n} (ϵ^{P}) x 10^{-3} cm^{-1}	E_{max} x 10^{-3} cm^{-1}
$CoPS_{me}I_2$	$(N)^d$ 16.0br	6.5 14.8 16.2 17.75 27.25brsh
$Co(AsN_{me})I_2$	(d) 15.0(78) 17.7sh(120) 20.7(404) 24.9(597)	10.9wsh 15.25 17.1 20.4sh 26.0sh
$Pd(AsN_{me})Cl_2$	(d) 16.3w 23.75	16.0sh 23.4
$Pt(AsN_{me})Cl_2$	(d) 15.5wbr 24.8sh 26.6sh	16.6brsh 26.75sh
$[Co(PP_{me})_2][CoCl_4]$	$(d)^c$ 17.25sh(134) 18.2(51) 26.6(1607) (N) 14.9(242) 17.0(263)	8.25 15.0 16.6 25.25 26.25sh 28.75wsh 33.2wsh
$[Co(PP_{me})_2Cl]ClO_4$	17.2wsh(10) 18.0(16) 26.6(490) (N) 17.25w(52) 18.1wsh(43)	6.5sh 15.25sh 17.25 24.25sh 25.4
$[Co(dias)_2][CoCl_4]$	(N) 17.0w(120)	10.8w 14.6 15.8sh 17.0sh 25.0sh 31.5
$Co(dias)_2Cl_2$	(d) 17.75brw(22) 20.3sh(44) 25.6(2168)	15.35 14.0w 24.65brsh
$[Co(dias)_2Cl]ClO_4$	(N) 15.4vw(48) 18.5sh(64)	16.0 25.3
$[Co(dias)_2Cl_2]Cl$	(N) 16.55(75) 20.0wsh(27) 23.5(1628)	16.2 23.0sh
$[Co(dias)_2Cl_2]ClO_4$	(n) 16.6(51) 17.2(46) 19.5w(37) 24.0(145)	6.9w 16.4 23.8br 25.6sh

** For footnotes see Page 174.

Footnotes for Tables

[a] Found (calculated) percentage.

[b] Molar conductivity in 10^{-3} M solutions at room temperature 295K.

[c] 1,2-Dichloroethane.

[d] Nitromethane.

[e] Partially soluble.

[f] Molar susceptibility

[g] Room temperature magnetic moment.

[h] Not soluble enough for a solution nmr measurement.

[j] *o*-Diphenylphosphinobenzoic acid.

[k] Diphenylphosphinoacetic acid.

[m] Diamagnetic.

[n] Energy maximum.

[p] Molar extinction coefficient

CHAPTER FOUR

THE COBALT(II) AND NICKEL(II) COMPLEXES OF SOME AIR-STABLE MIXED DONOR LIGANDS AND THE POTENTIAL USE OF THESE LIGANDS AS EXTRACTANTS FOR NICKEL IN A SOLVENT EXTRACTION PROCESS

4.1 INTRODUCTION

The aim of this work was to find an extractant for nickel which is suitable for use in a solvent extraction plant. Research into this area has arisen due to the depletion of the high grade nickel sulphide ores.

There are in fact vast quantities of nickel oxide ores in the earth's crust which as yet have not been tapped and these together with various waste liquors containing nickel in low concentration can be stripped of their nickel content by means of a solvent extraction type process.

This method requires the nickel to be selectively removed from an impure nickel solution rather than the opposite process of removing the impurities. The process has an advantage in that the nickel(II) concentration in solution is increased so allowing the leached solutions of low grade ores to be feasible sources of nickel in the future. In addition the solvent extraction technique is a very clean and economical process, the extractant, the solvent and the aqueous stripping solution being reused continuously. It is therefore an attractive economic prospect. The process itself will now be explained.

Solvent extraction [357] (or liquid-liquid extraction) is an equilibrium process generally described by either of the following two equations:

$$M + L \rightleftharpoons ML \qquad (A)$$

or

$$M + LH \rightleftharpoons ML + H^+ \qquad (B)$$

(where M = metal ion, and L = ligand)

Figure 4.1 is a flowchart showing the practical processes involved in a solvent extraction plant.

The first stage, the extraction stage, is the transferrence of the metal from an aqueous phase to an organic phase as some complex ML. The equilibrium has been shifted to the right in equations (A) or (B).

The second stage is the reverse of the first and the metal is transferred back to an aqueous phase from the organic. In other words the metal ion has been stripped of the ligand and the equilibrium lies on the left hand side. See equations (A) or (B).

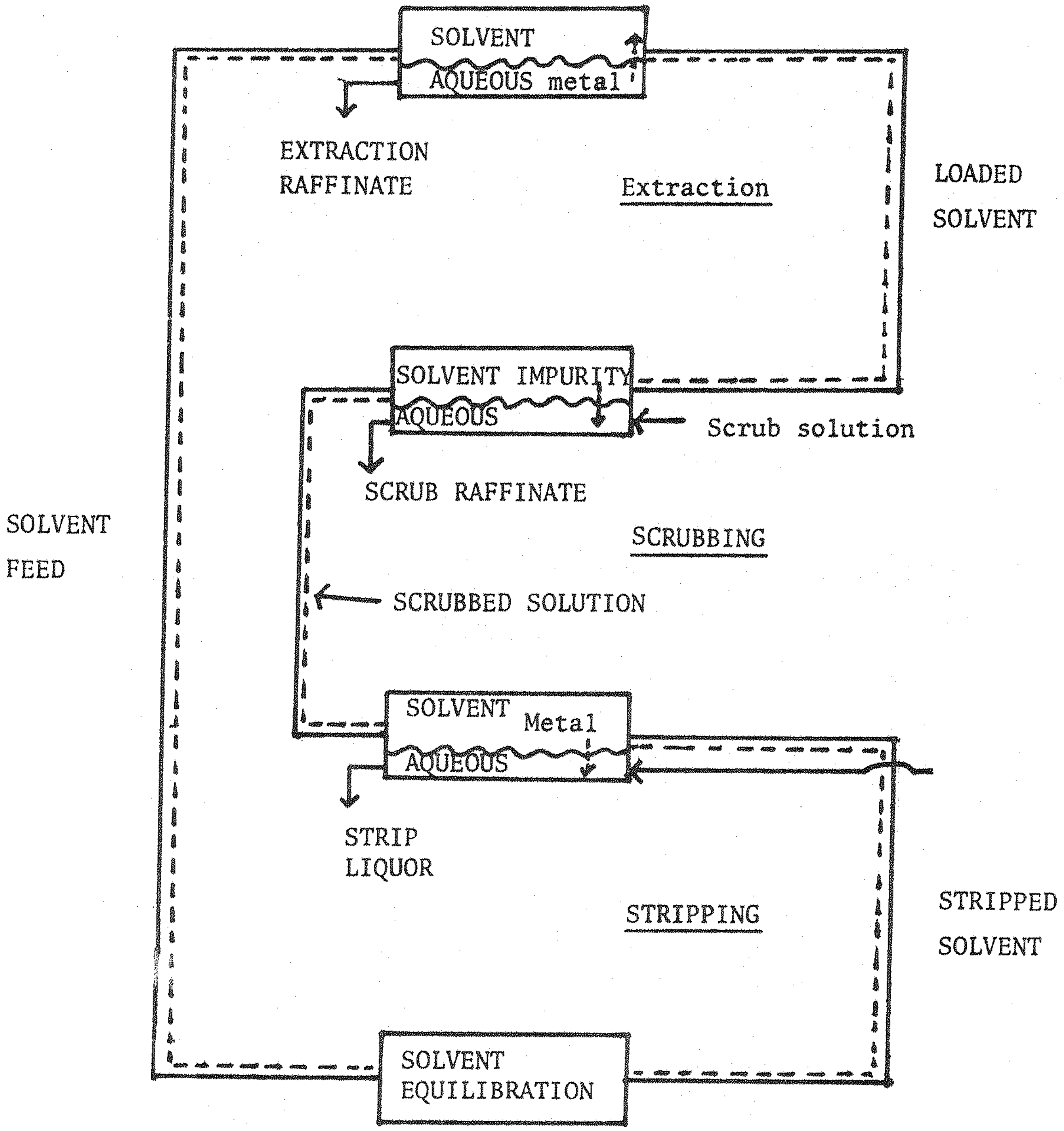


Figure 4.1 Solvent Extraction Process

In practice the metal-bearing aqueous feed solution and the ligand in the organic solvent are fed in a counter-current manner into a contactor in which the two phases are mixed. The metal is transferred from the aqueous to the organic phase here.

After settling, the aqueous phase or raffinate is separated and treated for the recovery of other metals and then either recycled into the solvent extraction circuit or goes to waste.

The loaded solvent may then go into another contactor where it is scrubbed with a suitable aqueous solution to remove small amounts of metals or impurities which were also extracted in the extraction stage. The aqueous scrub raffinate from this may then either by recycled elsewhere to the leaching stage or to the solvent extraction feed tank.

The scrubbed loaded solvent now passes to a third stage where it is stripped by a suitable aqueous solution, frequently concentrated acid, to produce a fairly concentrated aqueous solution of the metal salt. The stripped solvent containing the ligand is recycled back to the extraction stage.

Each of the three stages, extraction, scrubbing and stripping may involve several contactors in each stage.

The concentration of the required metal ion can be increased in this way. The metal is most often finally removed by depositing it electrolytically.

In the commercial process several criteria have to be met for the process to be viable.

(i) The extractant is readily available and is of low cost.
(ii) The extractant must have a high solubility in the organic solvent and a low aqueous solubility.
(iii) There must be easy complex formation with the metal of interest (in this case nickel) and a high solubility of the ML species in the organic phase.
(iv) There must be a selectivity of formation of the ML species, with respect to the solution impurities.
(v) There must be an ease of recovery of metal from the organic phase and a regeneration of ligand for recycling.

Until now specific chelating agents have been found for metals such as uranium, copper and cobalt and now one is required for nickel [357].

It is not easy to find a selective chelating agent for nickel.

Nickel is usually found in nature in association with cobalt and the separation of these two metals is difficult due to their similarity chemically. The areas where there are differences therefore need to be investigated.

The cobalt(II) and nickel(II) cations often form complexes of different stereochemistries and the stabilities of these may vary according to the conditions. In addition the ionic radius [358] of nickel (II) (0.69 Å) is smaller than cobalt(II) (0.72 Å) and ligands with particular steric demands may well prefer one to the other.

Cobalt(II) is a 'harder' acid than nickel(II) and so will tend to form more complexes with 'harder' bases such as nitrogen or oxygen [359]. Cobalt(II) frequently however combines with nitrogen donors to produce cobalt(III) complexes which are generally inert and remove the ligand out of the process [360]. This latter process would thus be uneconomical and hinder the continuous flow.

Consideration of the above facts has led to the proposal of mixed donor ligands containing at least one 'soft' and one 'hard' donor atom as possibly providing a specific chelating agent for nickel.

In Chapter Three the cobalt(II) complexes of some strong field, methyl-substituted, mixed donor ligands were discussed and compared with their nickel(II) counterparts. These ligands however were unsuitable for a solvent extraction process due to their air sensitivity. As a result some air-stable phenyl-substituted mixed donor ligands were synthesised and tested for their suitability as extractants of nickel(II). Cobalt(II), nickel(II) and a few copper and iron complexes of these ligands were prepared in non-aqueous solvents and their chemistry discussed (see Section 4.2).

The ligands prepared were of both the L type and the LH type (i.e. neutral and containing an acidic proton). The two LH type ligands were investigated by means of a titration method and the L-type ligands by means of 'shake-up' tests. A number of other readily available mixed donor ligands were similarly tested for their potential as extractants of nickel.

Reviews on the solvent extraction of nickel are found in references [361-363].

4.2 EXPERIMENTAL SECTION

4.21 THE PREPARATION OF SOME MIXED DONOR LIGAND COMPLEXES OF PRIMARILY COBALT(II) AND NICKEL(II) IN NON AQUEOUS SOLVENTS

The elemental analyses and colours of the individual complexes are found in Tables 4.1 and 4.2.

In these preparations there was an efficient stirring of the solutions.

1. o-Diphenylphosphinoanisole (see Table 4.1)

NiL_2X_2 (X = Br, I, NCS)

To the ligand (0.584 g, 2 mmol) in 1,2-dichloroethane (10 cm^3) was added hydrated nickel(II) halide (X = Br, I) (1 mmol) or nickel(II) thiocyanate, '$Ni(NCS)_2$' (1 mmol) in propan-2-ol (15 cm^3). Dark green (Br) and brown solids (I, NCS) precipitated immediately. They were filtered off, washed with propan-2-ol and diethyl ether, recrystallised from dichloromethane (10 cm^3) and then dried *in vacuo*. Yields ∿70% (except for the iodide (10%)).

CoL_2X_2 (X = Cl, Br, I, NCS)

To the ligand (0.584 g, 2 mmol) in 1,2-dichloroethane (10 cm^3) was added the hydrated cobalt(II) halide (X = Cl, Br, I) or pseudohalide (NCS) (1 mmol) in ethanol (15 cm^3). The solution volume was then reduced to 10 cm^3 by heating on a hotplate. On cooling blue to green complexes precipitated out. These were filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane (10 cm^3) and then dried *in vacuo*. Yields ∿70%.

'$Co(NCS)_2$' was prepared *in situ* from cobalt(II) bromide (1 mmol) and potassium thiocyanate (5 mmol) in ethanol.

CuL_3Cl and CuL_2Br

To the ligand (0.584 g, 2 mmol) in 1,2-dichloroethane (10 cm^3) was added copper(II) halide (X = Cl, Br) (1 mmol) in ethanol (15 cm^3). After a few minutes the solution colour changed from brown to colourless and a white solid was precipitated. The product was filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane (10 cm^3) and then dried *in vacuo*. Yields ∿70%.

$Pd_2L_2Cl_4$

To the ligand (0.292 g, 1 mmol) in ethanol (10 cm^3) was added sodium tetrachloropalladate(II) (0.294 g, 1 mmol) in the same solvent (15 cm^3). After refluxing for five minutes and then cooling a red solid precipitated out. This was filtered off, washed with diethyl ether, recrystallised from dichloromethane (10 cm^3) and then dried *in vacuo*. Yield ∿70%.

2. (*o*-Dimethylaminophenyl)diphenylphosphine [333]

$CoLX_2$ (X = Cl, Br, I)

To the ligand (0.610 g, 2 mmol) in dichloromethane (10 cm^3) was added the hydrated cobalt(II) halide (1 mmol) in propan-2-ol (10 cm^3).

The green iodide complex precipitated out after concentration of the solution to 10 cm^3 and addition of diethyl ether. This solid was filtered off, washed with propan-2-ol and diethyl ether recrystallised from dichloromethane and then dried *in vacuo*. Yield = 60%.

The chloro- and bromo-complexes however gave intense blue solutions. These were reduced to blue oils by removing the solvents on a rotary evaporator, washed with diethyl ether, and left in a stoppered vessel for two weeks to crystallise out. Trituration with diethyl ether produced royal blue powders which were then dried *in vacuo*. These products were very soluble in common organic solvents such as dichloromethane or acetone and very readily became oils upon exposure to air. Yields ∿60%.

$[CoL_2X]B\phi_4$ (X = Cl, Br)

To the ligand (0.610 g, 2 mmol) in dichloromethane (10 cm^3) was added '$CoXB\phi_4$' in ethanol (20 cm^3). On standing blue solids precipitated out. These were washed with ethanol and diethyl ether and then dried *in vacuo*. Yields ∿60%. On exposure to air these solids became oils.

'$CoXB\phi_4$' was obtained from the filtrate from the reaction between hydrated cobalt(II) halide (1 mmol) and sodium tetraphenylborate (0.35 g, 1.03 mmol) in ethanol (15 cm^3).

$\underline{NiLBr_2}$

This complex was prepared in the attempted preparation of the tetraphenylborate complex.

To the ligand (0.610 g, 2 mmol) in ethanol (15 cm^3) was added '$NiBrB\phi_4$' (or so it was thought) (1 mmol) in the same solvent (0.35 g, 1.03 mmol).

A green solid resulted, which was filtered off, washed with ethanol and diethyl ether and then dried in vacuo. Yield = 45% ($NiLBr_2$).

3. o-Diphenylphosphinobenzoic acid

$\underline{CoL_2Br_2}$

To cobalt(II) bromide (0.327 g, 1 mmol) in ethanol (10 cm^3) was added the ligand (0.306 g, 1 mmol) in dichloromethane (10 cm^3).

A turquoise blue powder was obtained in 60% yield.

4. Diphenylphosphinoacetic acid

$\underline{CoL_2I_2}$

To cobalt(II) iodide (0.349 g, 1 mmol) in propan-2-ol (10 cm^3) was added the ligand (0.488 g, 2 mmol) in dichloromethane (15 cm^3). The mixture was refluxed, allowed to cool and diethyl ether added (10 cm^3). A green solid precipitated out. This was filtered off, washed with propan-2-ol and diethyl ether, recrystallised from dichloromethane and dried in vacuo. Yield = 60%.

5. Tris(2-diphenylphosphinoethyl)amine

$\underline{[CoLX]_2[CoX_4]}$ (X = Cl, Br)

To cobalt(II) halide (1.5 mmol) in acetone (15 cm^3) was added the ligand (0.653 g, 1 mmol) in the same solvent (15 cm^3). Dark green solutions resulted. These were reduced in volume to 10 cm^3 whereupon green solids rapidly precipitated out. These were filtered off, washed with diethyl ether, recrystallised from dichloromethane and acetone and then dried in vacuo. Yield = 80%.

$\underline{Ni_2LX_4}$ (X = Cl, Br)

To nickel(II) halide (2 mmol) in ethanol (15 cm^3) was added the ligand (0.653 g, 1 mmol) in dichloromethane (20 cm^3). Reddish-brown solids precipitated out immediately. These were filtered off, washed with ethanol and diethyl ether, recrystallised from dichloromethane and then dried *in vacuo*. Yields = 80%.

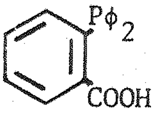
4.22 THE COBALT(II), NICKEL(II) AND COPPER(I) COMPLEXES OF SOME MIXED DONOR LIGANDS IN NON-AQUEOUS SOLVENTS

The mixed donor ligands involved here are:

1. ϕ_2PCH_2COOH

Diphenylphosphinoacetic acid

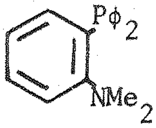
2.



o-Diphenylphosphinobenzoic acid

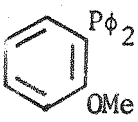
3. $N(CH_2CH_2P\phi_2)_3$ Tris(2-diphenylphosphinoethyl)amine

4.



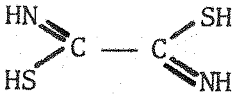
(*o*-Dimethylaminophenyl)diphenylphosphine

5.



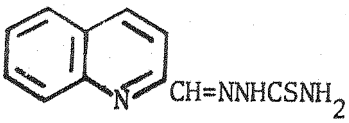
(*o*-Diphenylphosphino)anisole

6.



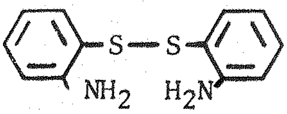
Dithiooxamide

7.

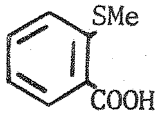


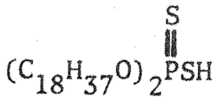
Quinoline-2-aldehydethiosemicarbazone

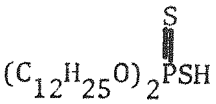
8.



2,2'-Diaminodiphenyldisulphide

9. 
o-Methylthiobenzoic acid

10. 
$(C_{18}H_{37}O)_2P(=S)SH$ Dioctadecyldithiophosphoric acid

11. 
$(C_{12}H_{25}O)_2P(=S)SH$ Didodecylodithiophosphoric acid

12. $NH_2CH_2CH_2SH$ 2-Aminoethanethiol

13. $S(CH_2CH_2NH_2)_2$ Bis(2-aminoethyl)sulphide

The syntheses of ligands 1-5 are found in Section 3.21.

The complexes of the ligands 1-13 are now discussed in a ligand by ligand manner. Several of these have in fact been previously prepared.

1. Diphenylphosphinoacetic acid. HAc (see Tables 4.2 and 4.4)

Cobalt(II) iodide reacted with the ligand in a 1:2 ratio in a propan-2-ol/dichloromethane mixture to form a green complex of stoichiometry CoL_2I_2.

In 10^{-3} M 1,2-dichlorethane or nitromethane the complex was virtually a 1:1 electrolyte.

Its electronic spectra in the solid and solution states were similar and contained the multicomponent band in the 14-17000 cm^{-1} usually attributed to a tetrahedral species [269]. The presence of shoulders at higher energies did not exclude however the presence of an octahedral or five-coordinate species.

The broad band at 220 cm^{-1} in the far infrared spectrum was attributed to ν(Co-I).

2. o-Diphenylphosphinobenzoic acid. HB (see Tables 4.2 and 4.4)

Cobalt(II) bromide reacted with this ligand in an ethanol/dichloromethane mixture in a 1:2 ratio to form a turquoise solid of stoichiometry CoL_2Br_2. This complex was soluble in and a non-electrolyte in 1,2-dichloroethane and nitromethane. Its electronic solid and solution state spectra were similar and displayed an intense band in the 15-16,000 cm^{-1} region typical of tetrahedral cobalt(II).

An impure turquoise cobalt(II) chloride complex was also prepared.

3. Tris(2-diphenylphosphinoethyl)amine. NP_3 (see Tables 4.2 and 4.4)

Cobalt(II) halide (X = Cl, Br) reacted with the ligand in a 1:2 ratio in acetone to form green complexes of stoichiometry $Co_3L_2X_6$.

The conductivity of the bromo-complex in 10^{-3} M dichloromethane was indicative of a 2:1 electrolyte.

The electronic solid and solution spectra were similar and not inconsistent with the postulated formulation of $[CoLX]_2[CoX_4]$. The multicomponent band in the 14-17,000 cm^{-1} region was attributable to the $[CoX_4]^{2-}$ and the band in the 20-25,000 cm^{-1} region to the five-coordinate $[CoLX]^+$ cation. The far infrared spectra exhibited bands at 290 and 215 cm^{-1} due to the ν(Co-X) of the $[CoX_4]^{2-}$ (X = Cl, Br resp) anion.

Previously magenta or brown complexes [CoLX]Y (X = Br, I; Y = X, $B\phi_4$ and X = Cl, NCS; Y = $B\phi_4$), have been prepared [307]. The complexes prepared here were thought to be of the same type also containing the $[CoLX]^+$ cation only the counter anion being different, i.e. $[CoX_4]^{2-}$. The change in counter anion also accounted for the difference in colour.

The reaction of the nickel(II) halides (X = Cl, Br) with the ligand in a 2:1 ratio in an ethanol/dichloromethane mixture produced reddish-brown solids of stoichiometry, Ni_2LX_4 (X = Cl, Br).

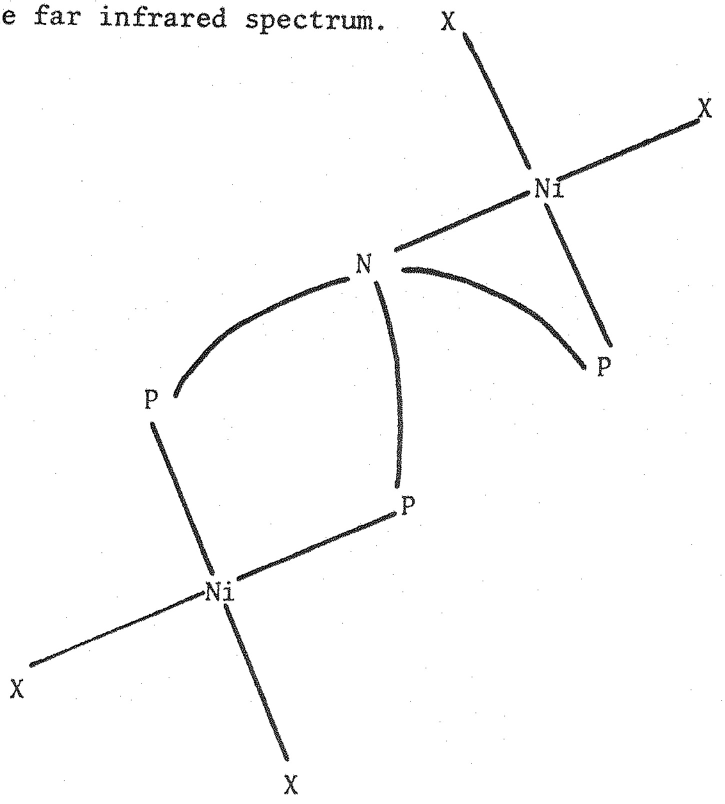
Previously from a 1:1 ratio in an acetone/n-butanol or ethanol mixture the [NiLX]X (X = Cl, Br, I, NCS) were obtained [307].

However the complexes prepared here were both diamagnetic and non-electrolytes in 10^{-3}M 1,2-dichloroethane and nitromethane. The electronic spectra in the solid and solution states both showed a broad band in the 20-22,000 cm^{-1} region and nothing at lower energies. These facts pointed to a square planar species.

This of course contrasted with previous results where either the five-coordinate [NiLX]X (X = Cl, Br) [307] or the binuclear $NiNi(L)X_4$ (X = Cl, Br) complexes were formed depending on the metal:ligand ratio adopted. The latter has been postulated as containing both a tetrahedrally coordinated and a square planar coordinated nickel atom.

In the complexes prepared here there must be a different orientation of the ligand and the two nickel centres for the latter to both be square planar. See below.

The possibility of $[NiX_4]^{2-}$ anions being present was eliminated due to the absence of bands at 280 cm^{-1} (X = Cl) or at 228 cm^{-1} (X = Br) in the far infrared spectrum.



4. (o-Dimethylaminophenyl)diphenylphosphine. PN_ϕ (see Tables 4.2 and 4.4)

Cobalt(II) halides (X = Cl, Br, I) reacted with this ligand in a propan-2-ol/dichloromethane mixture in either a 1:1 or 1:2 ratio to form complexes of stoichiometry $CoLX_2$

These complexes were identical to those previously reported by Vananzi et al [333]. Their conductivities, electronic spectra and far infrared spectra were in agreement with those quoted by Venanzi [333].

The ligand reacted with '$CoXB\phi_4$' (X = Cl, Br) in an ethanol/dichloromethane mixture in a 2:1 ratio to form blue complexes of stoichiometry $CoL_2XB\phi_4$.

These complexes were not very soluble in nitromethane or 1,2-

dichloroethane but the chloro-complex gave a conductivity in a 10^{-3} M solution of the former attributable to that of a 1:1 electrolyte. This latter value was low as would be expected for tetraphenylborate salts due to the low specific conductivity of the tetraphenylborate anion.

The electronic spectra in the solid and solution states were consistent with a five-coordinate structure and the formulation $[CoL_2X]B\phi_4$ (X = Cl, Br).

In the attempted preparation of the complex $[NiL_2Br]B\phi_4$ in ethanol solution a green complex of stoichiometry, $NiLBr_2$ was obtained. This was of the same stoichiometry as that prepared by Venanzi et al [333].

5. o-Diphenylphosphinoanisole. PO_ϕ (see Tables 4.1 and 4.3)

The reaction of nickel(II) halides (X = Br, I) in propan-2-ol with the ligand in either a 1:1 or 1:2 ratio produced dark green (Br) and brown (I) complexes of stoichiometry, NiL_2X_2. The same reaction with nickel(II) chloride produced a maroon solid which was insoluble in common solvents and whose elemental analysis indicated a high carbon content.

The nickel(II) halide (X = Br, I) complexes were essentially non conductors in 10^{-3} M 1,2-dichloroethane and nitromethane. However in the latter there was some evidence of dissociation.

The room temperature magnetic moment of the bromo-complex (μ_{eff} = 3.3 BM) implied high spin nickel(II) with two unpaired electrons.

This same complex also exhibited bands at 1019 (Me-O) and 1250 cm^{-1} (aryl-O) which indicated uncoordinated methoxy groups [300].

The electronic spectra of the bromide in the solid and solution states were similar and typical of tetrahedral nickel(II) [364,365] (see Section 3.11). The iodo complex exhibited similar type spectra, the band in the 14-18,000 cm^{-1} region being shifted to lower energy as expected for coordinated halide groups.

The far infrared spectrum of the bromo-complex displayed two medium/strong bands, (see Table 4.1) the positions of which closely resembled those observed for the tetrahedral $[Ni(P\phi_3)_2Br_2]$ complex [345], i.e. 267 and 218 cm^{-1}. The iodide complex of PO_ϕ also gave two strong bands at 204 and 238 cm^{-1}. Two bands would be expected for a C_{2v} symmetry and a pseudotetrahedral geometry.

The complexes were therefore formulated as the pseudotetrahedral $[NiL_2X_2]$ (X = Br, I), the ligands being bonded only through the phosphorus donor.

The reddish-brown nickel(II) thiocyanate complex of stoichiometry $NiL_2(NCS)_2$ was prepared similarly to the halide complexes but from '$Ni(NCS)_2$'.

The complex was insoluble in 1,2-dichloroethane and partially soluble in nitromethane in which it appeared to conduct.

The nujol mull spectrum was characteristic of square planar nickel(II). (See Section 3.11) [301,309,335].

The PO_ϕ ligand resembled the triphenylphosphine ligand in its formation of tetrahedral chloro- and bromo-complexes and square planar thiocyanate [364].

The $[NiL_2X_2]$ (X = Br, I) complexes of the PO_ϕ ligand were high spin whereas the $[NiLX_2]$ (X = Cl, Br, I) complexes of the PO_{me} have been found to be square planar [301]. This demonstrated their weaker and stronger ligand fields respectively.

Turquoise (Cl, Br) or green (I) complexes of stoichiometry CoL_2X_2 were obtained by the reaction of cobalt(II) halide and the ligand in an ethanol/dichloromethane mixture in either a 1:1 or 1:2 ratio.

In 10^{-3} M 1,2-dichloroethane and nitromethane they produced blue-green non conducting solutions. However in the latter there was some evidence of dissociation.

The room temperature magnetic moments of these cobalt(II) samples lay in the range expected for high spin pseudotetrahedral structures. Their electronic solid and solution state spectra similarly indicated this geometry [269] (see Section 3.11).

Their infrared spectra each exhibited two ν(Co-X) in the range normally observed for a pseudotetrahedral, C_{2v} symmetry around the cobalt [345] and also bands attributable to uncoordinated methoxy groups [300], 1019 (OMe) and 1253 (aryl-O).

These complexes were thus formulated as pseudotetrahedral CoL_2X_2 (X = Cl, Br, I).

The blue cobalt(II) thiocyanate complex of stoichiometry, $CoL_2(NCS)_2$ was prepared similarly to the halides but using '$Co(NCS)_2$'. In 10^{-3} M nitromethane it was a non-conductor but there was some evidence of dissociation.

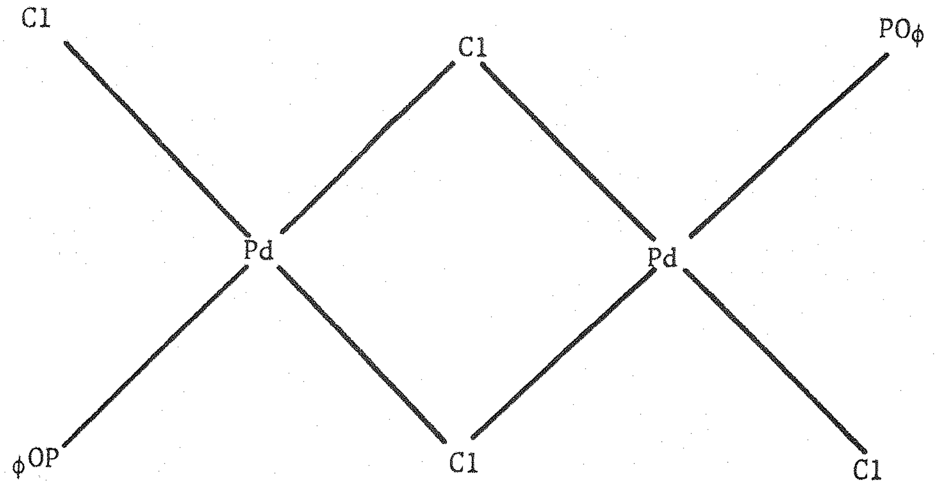
Its infrared spectrum displayed a strong band at 2090 cm^{-1} attributed to N-bonded thiocyanate [326] and bands a 1020 (MeO) and 1250 cm^{-1} attributed to uncoordinated methoxy groups [300].

The electronic solution and solid state spectra were typical of tetrahedral cobalt(II) and also the room temperature magnetic moment, (μ_{eff} = 4.01) although low implied this geometry [309,343]. The complex was therefore formulated as $[CoL_2(NCS)_2]$.

Previously a palladium(II) chloride complex of stoichiometry PdL_2Cl_2 has been prepared with the ligand acting in monodentate fashion [300]. Although the colour was not mentioned mononuclear square planar palladium(II) complexes are usually yellow-orange (see Section 1.2)

The red complex reported in this study had electronic solution and solid state spectra also typical of square planar palladium(II).

The $[PdL_2Cl_2]$ [300] complex exhibited a single ν(Pd-Cl) at 350 cm^{-1} indicating a trans square planar arrangement whereas the complex obtained here possessed three strong bands at 270, 303 and 350-365 cm^{-1} which could indicate the presence of a dimeric type structure as shown below.



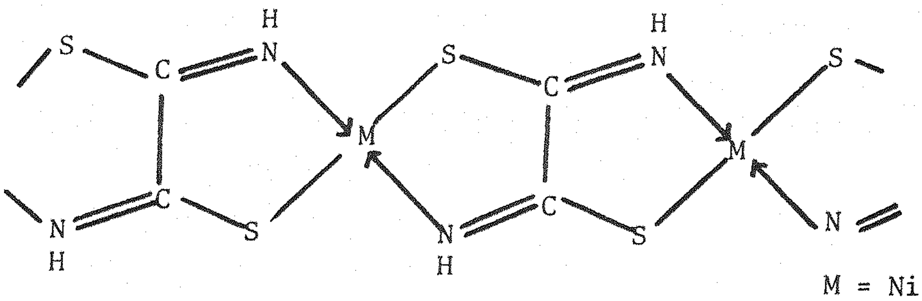
The reaction of copper(II) halides (X = Cl, Br) with the ligand in ethanol in a 1:2 ratio gave white complexes of stoichiometries CuL_3Cl and CuL_2Br respectively. These were diamagnetic and non-electrolytes in 10^{-3} M 1,2-dichloroethane and nitromethane.

The infrared spectrum exhibited bands at 1250 (aryl-O) and 1022 (MeO) attributable to uncoordinated methoxy groups [300].

In the above reaction copper(II) was reduced to copper(I) by the phosphine.

6. Dithiooxamide [366]

This ligand forms insoluble polymers postulated to be as follows:



M = Ni(II), Cu(II)

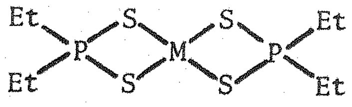
7. Quinoline-2-aldehydethiosemicarbazone [367]

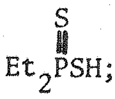
The corresponding isoquinoline ligand gives a NiL_2 monohydrate.

8. Dialkyldithiophosphoric acids

These produce complexes of formulas ML_2 (M = Ni(II), Co(II)) [368,369].

e.g.





$(L = Et_2\overset{S}{\overset{\|}{P}}SH;\ M = Co,\ Ni)$

9. 2-Aminoethanethiol [370]

The ligand forms two types of complexes:

(i) ML_2 (M = Ni, Pd).

(ii) Trinuclear cationic complexes $[M_3L_4]Cl_2$ (M = Co, Ni, Pd).

10. Bis(2-aminoethyl)sulphide [371]

This ligand produces complexes formulated as ML_2 (M = Co(II), Ni(II)).

4.23 THE COBALT(II), NICKEL(II) AND COPPER(I) OR (II) COMPLEXES OF MIXED DONOR LIGANDS IN AQUEOUS SOLUTIONS

The ease of complex formation and extractant capacity of the set of mixed donor ligands in Section 4.22 with nickel(II) in aqueous solutions was investigated. The selectivity of the ligands was studied by comparing with both cobalt(II) and copper(II). This work was carried out at ICI Organics Division at Blakely.

Ligands 1. and 2. were tested for their ability to extract nickel(II) by a titration method using an automatic titrator.

The basic reaction upon such a titration was:

$$M^{2+} + 2LH \rightleftharpoons ML_2 + 2H^+$$

$$\underset{\substack{\text{equilibrium}\\\text{constant}}}{K} = \frac{[ML_2][H^+]^2}{[M^{2+}][LH]^2} \qquad [\ ] = \text{concentration (strictly activity)}$$

$$\underset{\substack{\text{distribution}\\\text{coefficient}}}{D} = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}}$$

$$\underset{\substack{\text{equilibrium}\\\text{constant}}}{K} = \frac{D[H^+]^2}{[LH]^2}$$

$$D = \frac{K[LH]^2}{[H^+]^2}$$

$$\underline{\log D = \log K + 2\log[LH] - 2pH} \qquad (C)$$

ICI provided a patented ligand called L36 known to extract nickel(II) in aqueous solution to test the titration method.

The following experiments were performed:

(a) 25 cm^3 of an aqueous solution of 0.1 M Ni^{2+} in 0.2 M perchloric acid was titrated with 0.1 M NaOH solution.

(b) 25 cm^3 of an aqueous solution of 0.1 M Ni^{2+} ions and the ligand L36 in CH_2Cl_2 (ligand: metal ratio = 3:1) was titrated with 0.1 M NaOH solution.

(c) (b) repeated using diphenylphosphinoacetic acid and o-diphenylphosphinobenzoic acid.

(d) 25 cm^3 solutions of diphenylphosphinoacetic acid and o-diphenylphosphinobenzoic acid in 0.2 M perchloric acid were titrated with 0.1 M NaOH solution.

pH versus sodium hydroxide volume plots were made for (a) to (d).

The type of plot obtained for (a) is shown by curve α in Figure 4.2.

Perchloric acid was used in these titrations in order to keep the initial pH low. However, when this was neutralised by the sodium hydroxide solution, the pH rose sharply. Any further addition of 0.1 M sodium hydroxide then resulted in the formation of $Ni(OH)_2$.

When all the nickel(II) ions had been utilised the pH once again rose steeply.

Titration (b) was shown by curve (β) in Figure 4.2. Here again the perchloric acid was neutralised but this time the pH was kept low by the release of protons from the ligand as it combined with the M^{2+} ions.

When all the ligand was used up and no more protons were being released the pH then rose sharply.

If there happened to be Ni^{2+} ions still present in the system the curve would rise, flatten off and rise again when all the nickel(II) had been precipitated as the hydroxide.

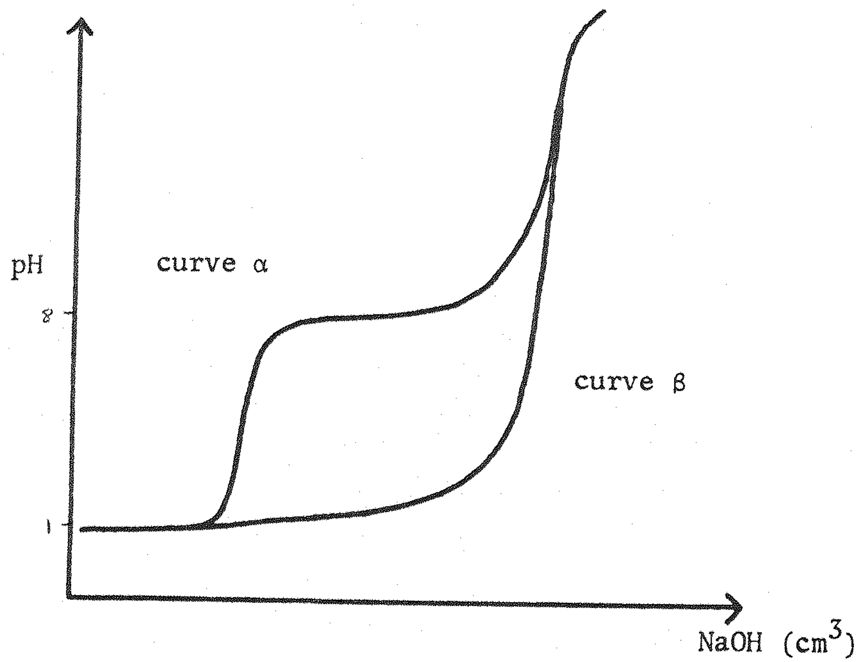


Figure 4.2 pH versus volume of NaOH (cm^3) for (a) and (b)

A plot of extraction versus pH was made. See Figure 4.3 below and equation C.

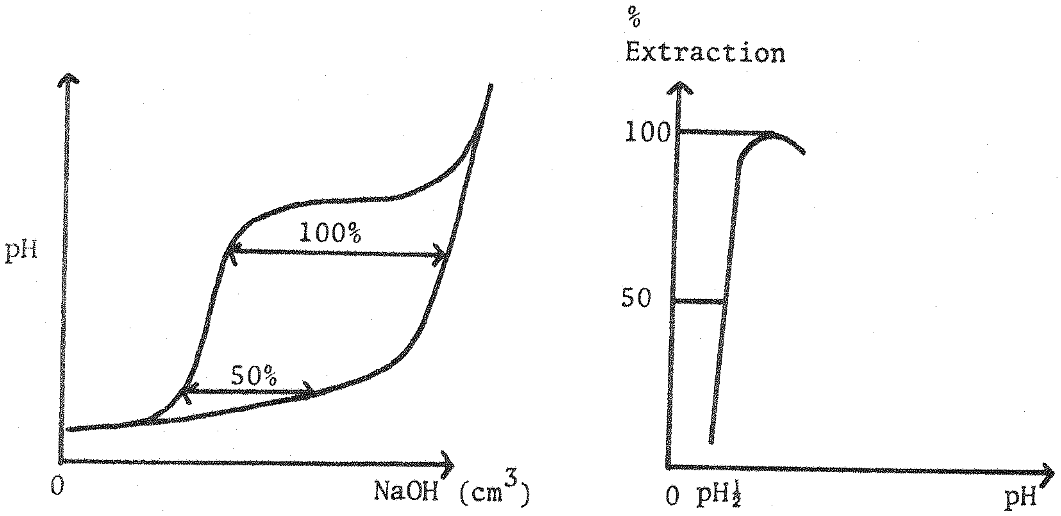
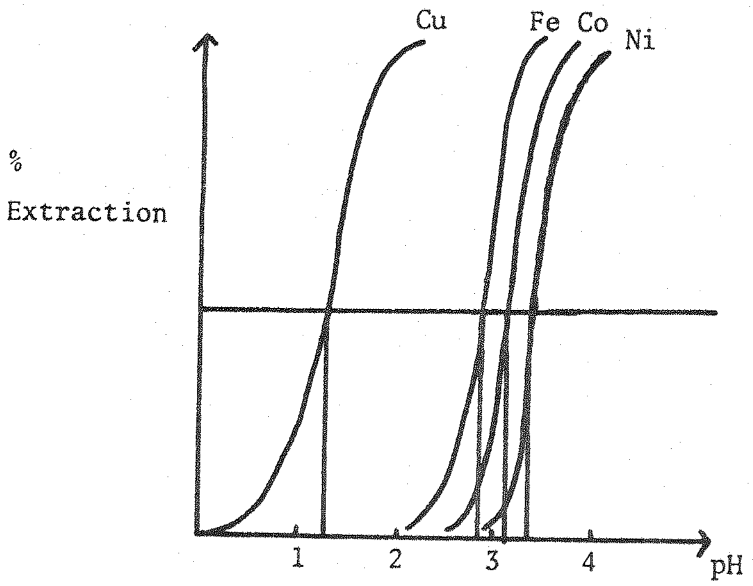


Figure 4.3 Typical pH versus volume of NaOH (cm^3) and extraction versus pH plots for a ligand such as L36

The value of pH at 50% extraction is known as the $pH_{\frac{1}{2}}$ value and is useful for the comparison of different metal ions with a particular extractant, e.g. for L36, $pH_{\frac{1}{2}} = 3.25$ for nickel.

A typical set of extraction versus pH curves are shown in Figure 4.4.

In particular in this work a good separation of cobalt and nickel was required and for this, a large difference in their $pH_{\frac{1}{2}}$ values was necessary.



For Cu, $pH_{\frac{1}{2}} = 1.3$
For Fe, $pH_{\frac{1}{2}} = 2.8$

Figure 4.4 Typical extraction versus pH plots for copper(II), iron(II), cobalt(II) and nickel(II) with the ligand L36

Ligands 1 and 2 were tested similarly to L36. Their pH versus volume of sodium hydroxide plots are shown in Figures 4.5-4.7.

For ligand 1 it appeared from Figure 4.5 that the ligand started to extract and then stopped. Plot (ii) appeared to be displaced a few cm^3 of NaOH in the positive direction. Also the green colour of the aqueous nickel(II) ions remained and the organic layer appeared unchanged.

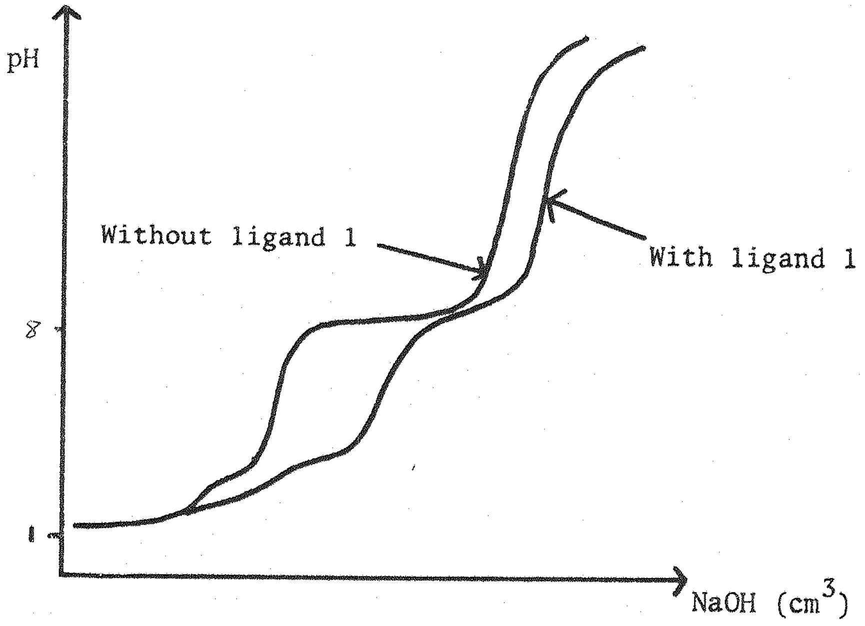


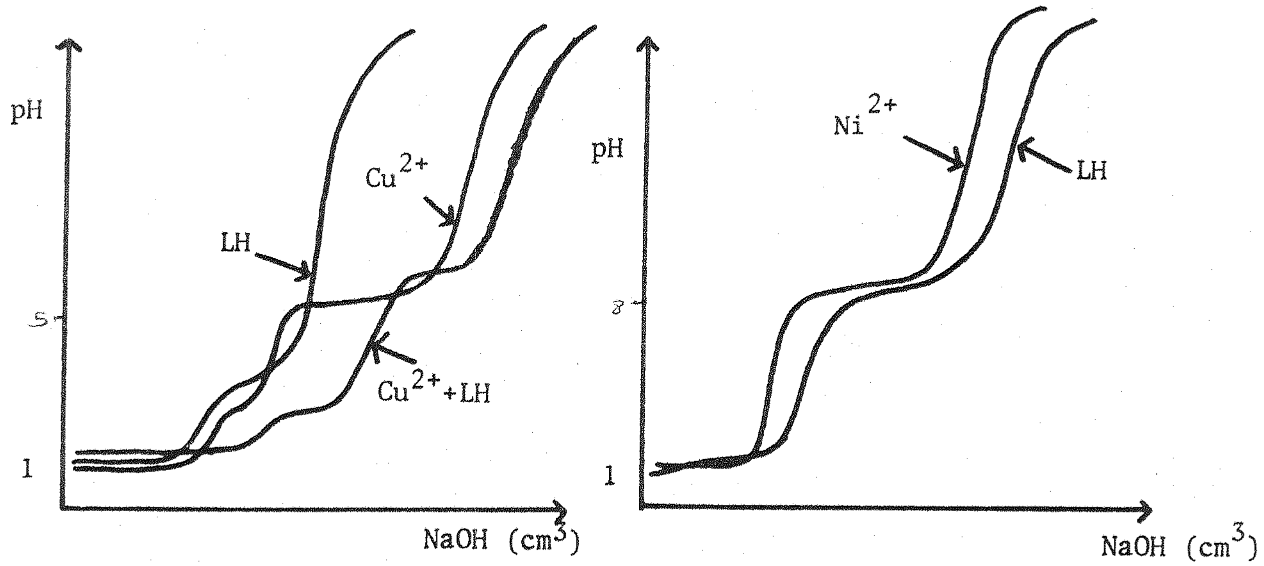
Figure 4.5 pH versus number of cm^3 of 0.1 M NaOH solution for ligand 1. (ϕ_2PCH_2COOH)
(i) Ni^{2+} aqueous solution in 0.2 M $HClO_4$.
(ii)(i)+ligand.

It was concluded that no extraction of ligand 1 by nickel(II) occurred in this aqueous solution.

Ligand 2 was titrated against both acidic Cu^{2+} and Ni^{2+} ions. Here again it appeared that the ligand started to extract the metal ions and then stopped. The hydroxides were then precipitated until the metal ions were exhausted and the pH then rose again.

Ligand 2 also therefore did not extract nickel(II) in aqueous solution. See Figures 4.6 and 4.7.

Ligands 3-13 were tested for their ability both to form cobalt(II) and nickel(II) complexes in aqueous conditions and then to be stripped by strong acid.



Figures 4.6 and 4.7 are pH versus volume of NaOH (cm^3) curves for Cu^{2+} and Ni^{2+} respectively involving the o-diphenylphosphinobenzoic acid ligand

(i) Titration of ligand 2 with 0.1 M NaOH.

(ii) Titration of acidic Cu^{2+} with 0.1 M NaOH.

(iii) Titration of acidic Cu^{2+} and ligand 2 with 0.1 M NaOH.

(i) Titration of ligand 2 with 0.1 M NaOH.

(ii) Titration of acidic Ni^{2+} and ligand 2 with 0.1 M NaOH.

The basic technique involved the shaking up, in a separating funnel, of a cobalt(II) or nickel(II) aqueous (0.5 mmol of the chloride or sulphate in 10 cm^3 water) solution with the ligand (usually a metal: ligand ratio of 1:2) in some suitable solvent. This mixture was mechanically stirred for a five minute duration and then the aqueous and organic phases allowed to disengage and the organic layer than removed.

If the aqueous layer had decolourised and the organic layer had visibly become coloured, the organic layer could be tested for the metal concentration by the atomic absorption technique. The latter was in fact only used in the case of the nickel(II) chloride and tris(2-diphenylphosphinoethyl)amine mixture and here there proved only to be a minimal concentration of nickel.

One of the problems encountered in this procedure was the limited solubility of the ligands and also the precipitation of some of the complexes which formed. In fact only solvents such as dichloromethane and dimethylsulphoxide could be used. These would of course be economically unsuitable in the industrial process. Cheap solvents similar to petroleum ether have usually been adopted and the substituent groups on potential extractants altered to increase their solubility.

Generally, most solvent extraction processes prefer to use the sulphate salts of metals since the chlorides involve the formation of chlorine gas in the system. However, in non aqueous solvents, it is the chlorides which more readily form complexes with the mixed donor ligands.

In the cases where chloride systems have been employed the degree of complexation has been noticed to greatly increase when very high concentrations of chloride ion are present. The equilibrium (equation A) is shifted over to the right.

In the above-mentioned experiment, where extraction appeared to occur, concentrated sulphuric acid (300 $g\ell^{-1}$) (50 cm^3) was added to the system to see whether the complex could readily be stripped of nickel(II).

The viability of a ligand for the solvent extraction process depended not only on the formation of the ML species but also on the kinetics involved. For example a fast rate of phase disengagement was important.

Most of the ligands tested appeared to show no obvious extraction of nickel(II) in aqueous solution (even when excess chloride ion was present in the chloride systems), i.e. PN_ϕ, PO_ϕ, 2,2'-diaminodiphenyldisulphide, o-thiomethylbenzoic acid, bis(2-aminoethyl)sulphide and dioctadithiophosphoric acid. See Table 4.5.

The ligands dithiooxamide and quinoline-2-aldehydethiosemicarbazone formed not only nickel but also cobalt complexes. These all however tended to precipitate out and were not further investigated.

The 2-aminoethanethiol ligand appeared to show some extraction of nickel(II) and not cobalt(II). The organic layer was also readily stripped of nickel by sulphuric acid. This N-S ligand and other similar ligands thus warrant further work [370].

It was the didodecyldithiophosphoric acid $(C_{12}H_{25}O)_2PSSH$ which appeared to be the most promising of these ligands.

The sulphate solutions of both cobalt(II) and nickel(II) produced mauve and turquoise complexes which could then readily be stripped of metal by sulphuric acid.

Sabot et al [368] have studied a series of the dialkyldithiophosphoric acids and have found that their extractant capacity towards nickel(II) is high compared with cobalt(II), ($\sim$1 mole of nickel(II) per litre of solvent). The stripping reaction of nickel is however slow but this could be enhanced by the addition of octanol to the organic phase.

These dialkyldithiophosphoric acids seem to distinguish between nickel(II) and cobalt(II), more readily forming complexes with the former. This is probably a result of the ligand being a 'soft' base and thus prefering to bond with the 'softer' nickel(II).

Table 4.1 Analytical data and physical measurements of the complexes of PO_ϕ

Complex	Colour	Elemental Analysis[a] C	H	X	$\Lambda^b{}_M(\Omega^{-1}cm^{-1})$	$\chi_{corr}{}^f$/ $\mu_{corr}{}^g$(BM)	Infrared Data (cm^{-1})
NiL_2Br_2	dark-green	56.76(55.6)	4.1(4.0)		1.89 (d)[c] 23.6 (N)[d]	$5.786x10^{-8}$/ 3.3	213 270 ν(Ni-Br)
NiL_2I_2	brown	50.6(50.8)	3.8(3.79)		48.82 (N)	-	204 238 ν(Ni-I)
$NiL_2(NCS)_2$	reddish-brown	63.4(63.3)	4.2(4.48)	X=N 3.4(3.69)	insol (d) e (N)	-	2090 ν(C-N)
CoL_2Cl_2	turquoise	63.1(63.9)	4.7(4.76)	X=Cl 10.4(9.9)	27.06 (N)	$1.056x10^{-7}$/ 4.47	303 350 ν(Co-Cl)
CoL_2Br_2	turquoise	56.0(56.8)	4.3(4.22)	X=Br 20.3(19.92)	3.24 (d) 16.88 (N)	$1.212x10^{-7}$/ 4.79	278 222 ν(Co-Br)
CoL_2I_2	green	50.3(50.8)	3.5(3.79)		7.49 (d) 44.5 (N)	$1.112x10^{-7}$/ 4.73	204-222 br ν(Co-I)
$CoL_2(NCS)_2$	blue	64.0(63.24)	4.5(4.5)	X=N 3.3(3.6)	31.77 (N)	$8.63x10^{-8}$/ 4.01	2062 ν(C-N)
CuL_3Cl	white	69.8(70.15)	5.1(5.2)		2.25 (d) 16.88 (N)	D[m]	-
CuL_2Br	white	62.68(62.5)	4.6(4.67)		2.77 (d) 19.1 (N)	D	-
$Pd_2L_2Cl_4$	red	48.6(48.6)	3.8(3.62)		0.28 (d) 4.75 (N)	D	270 303 350-365 br ν(Pd-Cl)

** For footnotes see Page 174.

Table 4.2 Analytical data and physical data of the complexes of PN_ϕ, NP_3, HB[j] and HAc[k]

Complex	Colour	Elemental Analysis[a] C	H	X	$\Lambda^b_M(\Omega^{-1}cm^{-1})$	Infrared Data (cm^{-1})
$Co(PN_\phi)Cl_2$	Royal blue	55.0(55.17)	4.8(4.6)	X=N 3.2(3.2)	32.4 (N)[d]	-
$Co(PN_\phi)Br_2$	Royal blue	45.5(45.8)	3.6(3.8)	X=N 2.7(2.7)	32.1 (N)	-
$Co(PN_\phi)I_2$	green	38.8(38.8)	2.3(3.2)	X=N 2.2(2.2)	2.0 (d)[c] 38.9 (N)	204 216 ν(Co-I)
$[Co(PN_\phi)_2Cl]B\phi_4$	blue	74.3(75.0)	5.4(5.86)	2.5(2.7)	51.3 (N)	-
$[Co(PN_\phi)_2Br]B\phi_4$	blue	72.0(71.9)	5.3(5.6)	X=N 2.3(2.6)	60.5 (N)	-
$[Ni(PN_\phi)Br_2]$	green	45.0(45.9)	4.0(3.9)	X=N 2.3(2.67)	e (N)	-
$Ni_2(NP_3)Cl_4$	light orange-brown	56.5(55.23)	3.9(4.6)	X=N 1.33(1.5)	0.57 (d) 12.87 (N)	290(?) 334 ν(Ni-Cl)
$Ni_2(NP_3)Br_4$	long brown needles	46.4(46.22)	3.6(3.85)	X=N 1.3(1.28)	0.26 (d) 22.49 (N)	209 270 ν(Ni-Br)
$[Co(NP_3)Cl]_2[CoCl_4]$	green	58.8(59.4)	5.2(5.0)	X=N 1.8(1.65)	15.15 (d) 47.3 (N)	290 326 ν(Co-Cl)
$[Co(NP_3)Br]_2[CoBr_4]$	green	50.8(51.3)	4.0(4.2)	X=N 1.5(1.4)	25.7 (d) 69.55 (N)	215 257 ν(Co-Br)
$Co(HB)_2Br_2$	turquoise	56.0(55.0)	3.6(3.6)		1.36 (d) 19.4 (N)	-
$Co(HAc)_2I_2$	green	41.0(41.9)	3.2(3.2)		9.97 (d) 60.1 (N)	220br

** For footnotes see Page 174.

Table 4.3 Electronic spectral data of the complexes of PO_ϕ

Complex	E_{max}^{n} (ε^P) x 10^{-3} cm^{-1}	E_{max} x 10^{-3} cm^{-1}
NiL_2Br_2	(d)^c 11.15(154) 15.1(174) 16.3sh(163) 17.7(157) 24.4(11100)	7.0sh 8.8sh 10.8 16.35sh 17.75 23.7sh
NiL_2I_2	(N)^d 11.0(8) 15.0(18) 19.0(65)	10.8 15.0 20.0sh 26.25br
$NiL_2(NCS)_2$	(N) insoluble	19.35brsh 24.4br
CoL_2Cl_2	(d) 15.7(72) 16.7(73) 28.4(48)brsh	5.7 10.4 12.8sh 14.0 16.0 17.7sh 25.7sh 28.3sh
CoL_2Br_2	13.75(77) 14.1(83) 15.1(38) 15.4(37) 15.7sh(48)	5.75 9.75 14.0 15.25 15.85sh 17.0sh 18.0sh 21.5 24.4sh 27.75
CoL_2I_2	(N) 11.0w(5) 14.5(117) 15.2(134) 16.2sh(72) 22.25(725) 24.7(338) 24.85(338)	5.5 7.5sh 11.7 14.5 15.8sh 22.7sh 25.0sh
$CoL_2(NCS)_2$	(d) 16.1(251) 17.8sh(128) (N) 6.9(111) 8.5sh(96) 15.8(446) 17.2sh(293) 24.7brsh	6.3sh 15.9br 30.7sh
$Pd_2L_2Cl_4$	(d) 25.25(650)	24.7br 17.9sh

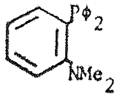
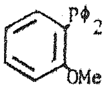
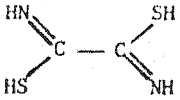
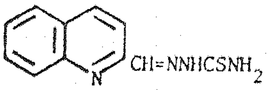
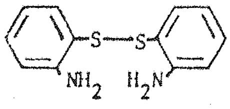
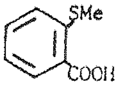
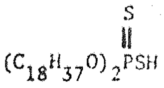
** For footnotes see Page 174.

Table 4.4 Electronic spectral data of the complexes of PN_ϕ, NP_3, HAc and HB ligands

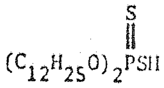
Complex	E_{max} (ε) $(cm^{-1}) \times 10^{-3}$	E_{max} $(cm^{-1}) \times 10^{-3}$
$[Co(PN_\phi)Cl_2]$	(d) 23.9sh 16.6(238) 15.25(291) (N) 6.9(43) 15.2(78) 16.7(63) 20.7wbr	-
$[Co(PN_\phi)Br_2]$	(d) 15.25(216) 16.1sh(176) 24.9wsh (N) 6.9(94) 15.0(211) 16.1(211) 17.2sh 20.1brsh	6.2sh 15.4br
$[Co(PN_\phi)I_2]$	(d) 14.7 15.7 17.4 21.6wsh	6.8sh 14.7 15.7sh 16.45sh 17.2sh 22.7sh 27.0sh
$[Co(PN_\phi)_2Cl]B\phi_4$	(d) 15.4(173) 17.1(168) 21.0sh 23.0sh (N) 6.9(122) 15.0(278) 16.2(251) 17.2 (163) 21.0brsh 23.2sh 24.9brsh	6.1sh 15.35 24.0sh
$[Co(PN_\phi)_2Br]B\phi_4$	(N) 6.8(54) 15.0(395) 16.15(355)	7.25wsh 15.7 24.0wsh 29.75sh
$[Ni(PN_\phi)Br_2]$	(N) 8.7wsh 13.9 17.0br 21.9br	-
$[Ni_2(NP_3)Cl_4]$	(d) 21.5(81)br	21.6br
$[Ni_2(NP_3)Br_4]$	(d) 20.9(62) 25.75(140)	21.05br 24.85sh 26.75brsh
$[CoLBr]_2[CoBr_4]$	(d) 6.5(187) 14.0(117) 14.4(121) 14.9 (126) 15.7(118) 22.6sh(56) 24.7(46)	6.8 8.4 14.0sh 15.4sh 15.65 15.8 21.85sh 22.5sh 24.1 29.0
$[CoLCl]_2[CoCl_4]$	(d) 14.7(149) 15.1(252) 17.775(180) 19.1sh 23.225(481) 29.0(1657)	6.7 8.3 14.7sh 16.2 15.7sh 16.8 22.7 28.7br
$[Co(HB)_2Br_2]$	(d) 14.6(207) 15.25sh 16.225(142)	6.4sh 8.7sh 15.6br 19.0wsh 22.75wsh
$[Co(HAc)_2I_2]$	(N) 14.5(127) 15.15(127) 15.7sh 22.5sh	6.7 14.35 15.0sh 17.0sh 21.8sh

** For footnotes see Page 174.

Table 4.5 The 'shake up' tests for various mixed donor ligands with nickel(II) and cobalt(II) aqueous solutions

Ligand	Solutions used[a,c]	Results
3. $N(CH_2CH_2P\phi_2)_3$	$NiCl_2/H_2O$ L/CH_2Cl_2	Aqueous layer decolourised organic phase became reddish-brown
4. 	$NiCl_2/H_2O$ L/CH_2Cl_2	No apparent nickel extraction even with excess chloride ions
5. 	$NiCl_2/H_2O$ L/CH_2Cl_2	No apparent nickel extraction even with excess chloride ions
6. 	$NiCl_2/H_2O$ L/DMSO	Immediate brown-black precipitate
	$CoCl_2/H_2O$ L/DMSO	Immediate orangey-brown organic phase
7. 	$NiCl_2/H_2O$ L/DMSO	Immediate single intense brown layer which partially extracted into DM. This layer could be acid[b] stripped.
	$CoCl_2/H_2O$ L/DMSO	Immediate brown colouration of the organic phase. A yellow solid precipitated. The organic phase could be acid stripped.
	$Ni(Co)SO_4/H_2O$ L/DMSO	Intense deep brown organic phase which could readily be acid stripped
8 	$NiCl_2/H_2O$ L/CH_2Cl_2	No apparent extraction of nickel even with excess chloride ions
9. 	$NiCl_2/H_2O$ L/DMSO	No apparent extraction of nickel even with excess chloride ions
10.  $(C_{18}H_{37}O)_2\overset{\overset{S}{\|}}{P}SH$	$NiSO_4/H_2O$ $L/CHCl_3$ or DMSO	No obvious nickel extraction
	$CoSO_4/H_2O$ $L/CHCl_3$ or DMSO	A mauve-pink intense organic phase which could be acid stripped

/continued.....

11.	 $(C_{12}H_{25}O)_2P(S)SH$	$NiSO_4/H_2O$ L/CH_2Cl_2	A mauve organic layer which could be acid stripped
		$CoSO_4/H_2O$ L/CH_2Cl_2	A turquoise organic layer which could be acid stripped
12.	$NH_2(CH_2)_2SH$	$NiCl_2/H_2O$ L/DMSO	Deep-pink organic layer
		$CoCl_2/H_2O$ L/DMSO	No apparent cobalt extraction
		$NiSO_4/H_2O$ L/DMSO + CH_2Cl_2 $Ni^{2+}:L > 1:2$ (slight excess Ni^{2+} ion)	Deep-brown organis phase which could be acid stripped
		$CoSO_4/H_2O$ L/DMSO + CH_2Cl_2	No apparent Co^{2+} extraction
13.	$S(CH_2CH_2NH_2)_2$	$NiCl_2/H_2O$ L/DMSO	No apparent Ni^{2+} extraction

[a] $NiCl_2/H_2O$ and L/DMSO = nickel(II) chloride dissolved in water and the ligand in dimethylsulphoxide respectively.

[b] 30 cm^3 of sulphuric acid (300 $g\ell^{-1}$).

[c] Metal:ligand = 1:2.

APPENDIX

APPENDIX

A. PHYSICAL MEASUREMENTS

(i) Infrared spectra

Routine infrared spectra were obtained either in nujol or in hexachlorobutadiene using sodium chloride or caesium iodide plates in the range 4000-500 cm^{-1} on a Perkin-Elmer 225 or a Perkin Elmer 580 Grating infrared spectrometer.

Far infrared spectra were obtained in nujol using polythene plates from a Beckman IR11 Spectrometer.

(ii) ^1H nuclear magnetic resonance

These spectra were measured in deuterochloroform using tetramethylsilane as internal standard on a Perkin-Elmer R12 NMR spectrometer.

(iii) Electronic spectra

These were obtained in both the 10^{-3} M solution (1,2-dichloroethane, dichloromethane, nitromethane, acetone, N,N-dimethylformamide) and solid states using a double beam instrument the Unicam SP700 spectrophotometer.

In the solution state the solution and solvent were contained in 1 cm silica cells and the spectra obtained over the following ranges:

1,2-Dichloroethane	36-5000 cm^{-1}
Dichloromethane	36-5000 cm^{-1}
Nitromethane	25-5000 cm^{-1}
Acetone	35-5000 cm^{-1}
N,N-Dimethylformamide	35-5000 cm^{-1}

The solid state spectra were obtained by mulling the samples with nujol, smearing them onto a strip of filter paper and then placing them in the front of the cell holder. The reference used was filter paper smeared with nujol.

Values of the energy maxima (E_{max}) in cm^{-1} were determined from these spectra and their molar extinction coefficients calculated using the Beer-Lambert Law.

i.e. $\log_{10}\frac{I_o}{I} = A = \varepsilon c l$

where c = concentration (mol l^{-1})
l = pathlength of sample (cm)
A = absorbance
I_o = intensity of incident radiation
I = intensity of transmitted radiation.
The units of ε are litre mol^{-1} cm^{-1}.

(iv) Molar conductivity

Conductivities were measured in 10^{-3} M nitromethane and 1,2-dichloroethane at 293K using a Pye Conductance Bridge, Cat No 11700. A glass cell fitted with platinised electrodes (1 cm^2) was used and whose cell constant was determined by measuring the conductance ($^1/R$) (R = resistance) of various concentrations of aqueous potassium chloride. The specific conductance of potassium chloride in water is known for various temperatures [372].

$$\text{Cell constant} = \text{conductance } (\tfrac{1}{R}) \times \text{specific conductivity (K)}$$

Molar conductivity of 10^{-3} M solutions of samples

$$\Lambda_M = \text{conductivity}(\tfrac{1}{R}) \times \text{cell constant} \times \frac{1000}{\text{molarity of solution}}$$

(v) Molecular weights

These were obtained using a Machrolab Inc Vapour Pressure Osmometer Model 30A which has been calibrated using naphthalene.

(vi) Elemental Analyses

Carbon, hydrogen, halogen and nitrogen analyses were obtained from an F amd M Carbon, Hydrogen and Nitrogen Analyzer Model 185 and also the Microanalytical services of University College London, UMIST and ICI Organics Division at Blackely.

(vii) Magnetic measurements

Solid state measurements of magnetic susceptibility and hence magnetic moment at 293K were obtained using a Gouy balance.

The following equation was used to calculate the magnetic moment (μ) in Bohr Magnetons

$$\mu = 797.5\sqrt{\chi_M T} \qquad (D)$$

where χ_M = molar susceptibility $(\frac{\chi}{\rho} \times M)$

T = temperature in degrees Kelvin

χ = magnetic susceptibility

ρ = density of sample

M = molecular weight

Diamagnetic corrections were made to these magnetic moments [373].

The variable temperature magnetic studies were performed by Dr S M Nelson of Queen's University, Belfast.

Magnetic susceptibilities in the solution state were obtained using the Evans' NMR method [352].

A sealed melting point tube containing the solvent is placed in an nmr tube containing a 1% solution of the sample and the shift in frequency (Hz) between the two measured. The following equation is used to calculate the magnetic susceptibility:

$$\chi = \frac{3\Delta f}{2\pi m f} + \chi_o$$

where χ, χ_o = mass susceptibility of sample solution and solvent respectively.

$\Delta f, f$ = shift in frequency (Hz) and frequency (Hz) respectively. $f = 60 \times 10^6$ Hz.

m = mass of solute (g) per cm^3 of solution.

From χ, χ_M, the molar susceptibility is calculated, corrections being made for diamagnetism. The magnetic moment is then calculated using the equation D.

B. SOLVENTS

Tetrahydrofuran (THF) was dried by refluxing with freshly extruded sodium wire until the addition of a few drops of benzophenone produced a blue colouration. The dry THF was then distilled (bpt = 66°C) as required.

Absolute ethanol was prepared [374] from commercially bought ethanol (∿99.5% purity). The latter was refluxed with quicklime for three to six hours and then allowed to cool. Subsequently the ethanol was refluxed for 30 minutes with magnesium, a little iodine being added. In the latter only a small volume of ethanol was used initially in order to convert all the magnesium into the ethylate and the rest of the ethanol then added. The ethanol was then distilled and stored over molecular sieves.

Diethyl ether was dried using sodium wire and best commercial grade 1,2-dichloroethane over molecular sieves. The other solvents used, dichloromethane, nitromethane, acetone, N,N-dimethylformamide, dimethyl sulphoxide, n-butanol, propan-2-ol, chloroform, acetonitrile and carbon tetrachloride were of the best grades commercially available.

REFERENCES

1. F A Cotton and G Wilkinson, 'Advanced Inorganic Chemistry', 3rd Edition, Interscience, J Wiley and Sons Inc, New York, (1972).

2. F R Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Ltd, (1973).

3. R N Goldberg and L G Hepler, Chem Rev, (1968), 68, 229.

4. R M Izatt, D J Eatough, C E Morgan, J J Christenson, J Chem Soc (A), (1970), 2514.

5. J P Birk, J Halpern, A L Pickard, J Amer Chem Soc, (1968), 90, 4491.

6. S Ahrland, J Chatt, N R Davies, Quart Rev, (1958), 12, 265.

7. R G Pearson, J Amer Chem Soc, (1963), 85, 3533.

8. C K Jorgensen, Inorg Chem, (1964), 3, 1201.

9. R G Pearson, Science, (1966), 151, 172; Chemistry in Britain, (1967), 3, 103.

10. R J P Williams, J D Hale, Structure and Bonding, (1966), 1, 249.

11. F Basolo and R G Pearson, 'Mechanisms of Inorganic Reactions', J Wiley and Sons Inc, New York, (1958), 172.

12. D M Adams, J Chatt, J Gerratt, A D Westland, J Chem Soc, (1964), 734.

13. L E Orgel, J Inorg Nuclear Chem, (1956), 2, 137.

14. L Cattalini, M Cusamaro, S Degetto, J Chem Soc Dalton, (1978), 12.

15. R Gosling and M L Tobe, Inorg Chim Acta, (1980), 42, 223.

16. L Cattalini, G Marangoni, S Degetto, M Brunelli, Inorg Chem, (1971), 10, 1545.

17. L Cattalini, G Marangoni, J S Coe, M Vidali, M Martelli, J Chem Soc (A), (1971), 593.

18. L Cattalini, 'Inorganic Reaction Mechanisms', ed J O Edwards, Wiley, New York, (1971).

19. B P Kennedy, R Gosling, M L Tobe, Inorg Chem, (1977), 16, 1744.

20. J Chatt and R G Wilkins, J Chem Soc, (1956), 525.

21. R J Goodfellow, J G Evans, P L Goggin, D A Duddell, J Chem Soc (A), (1968), 1604.

22. R J Cross, T H Green, R Keat, J Chem Soc Dalton, (1976), 382.

23. J M Jenkins and B L Shaw, J Chem Soc (A), (1966), 770.

24. G K Anderson and R J Cross, Chem Soc Rev, (1980), 185.

25. F R Hartley, Chem Soc Rev, (1973), 2, 63.

26. S E Livingstone, Quart Rev, (1965), 19, 386.

27. C A McAuliffe, 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', The Macmillan Press Ltd, (1973).

28. C A McAuliffe and W Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Elements', Elsevier, (1979).

29. G Booth, Adv Inorg Chem Radiochem, (1964), 6, 1.

30. L M Venanzi, Chem In Britain, (1968), 4, 162.

31. C A McAuliffe, Adv Inorg Chem Radiochem, (1975), 17, 165.

32. E W Abel, M Booth, K G Orrell, J Chem Soc Dalton, (1979), 1994.

33. R Ugo, G La Monica, S Cenini, A Segre, F Conti, J Chem Soc (A), (1971), 522.

34. J Chatt and D M P Mingos, J Chem Soc (A), (1970), 1243.

35. R J Cross and F Glockling, J Chem Soc, (1965), 5422.

36. F Glockling and E H Brooks, Preprints Div Petr Chem 14, (1961), 2, B135.

37. F G Mann and D P Purdie, J Chem Soc, (1935), 1549.

38. G E Hunter, R A Krause, Inorg Chem, (1970), 9, 537.

39. T A Stephenson, S M Morehouse, A R Powell, J P Heffer, G Wilkinson, J Chem Soc, (1965), 3632.

40. T Boschi and G Crociani, Inorg Chem, (1970), 9, 532.

41. R G Hayter and F S Humiec, J Inorg Nucl Chem, (1964), 26, 807.

42. R S Nyholm, J F Skinner, M H B Stiddard, J Chem Soc (A), (1968), 38.

43. J Chatt and F A Hart, J Chem Soc, (1953), 2363.

44. J Chatt and F A Hart, J Chem Soc, (1960), 2807.

45. J Chatt and F G Mann, J Chem Soc, (1938), 1949.

46. L A Tschugaev and W Subbotin, Chem Ber, (1910), 43, 1200.

47. K A Jensen, Z Anorg Chem, (1935), 225, 97.

48. K A Jensen, Z Anorg Chem, (1935), 225, 115; Chem Abs, (1936), 30, 132.

49. J E Fritzmann, Z Anorg Chem, (1911), 73, 239; Chem Abs, (1912), 6, 839.

50. E Fritzmann and V V Knnitzkiv, J Appl Chem Russ, (1939), 11, 1610.

51. 'Gmelin's Handbuch Der Anorganischen Chemie', achte auflage, editor E H Erich Pietsch, Volume 68 (Platinum).

52. 'Gmelin's Handbuch Der Anorganischen Chemie', achte auflage, editor E H Erich Pietsch, Volume 65 (Palladium).

53. J R Allkins and P J Hendra, J Chem Soc (A), (1967), 1325.

54. R J H Clarke, G Natile, U Belluco, L Cattalini, C Filippin, J Chem Soc (A), (1970), 659.

55. G B Kaufman and D O Cowan, Inorg Synth, (1960), 6, 211.

56. E A Allen, N P Johnson, D T Rosevear, W Wilkinson, Chem Comm, (1971), 171.

57. E Fritzmann, J Russ Chem Soc, (1915), 47, 588.

58. E Fritzmann, Z Anorg Chem, (1924), 133, 119, 133.

59. P E Skakke and S E Rasmussen, Acta Chem Scand, (1970), 24, 2634.

60. B E Aires, J E Fergusson, D T Howarth, J M Miller, J Chem Soc (A), (1971), 1144.

61. P L Goggin, R J Goodfellow, S R Haddock, F J S Reed, J G Smith, K M Thomas, J Chem Soc Dalton, (1972), 1904.

62. R Roulet, C Barbey, Helv Chim Acta, (1973), 56, 2179.

63. K Nakamoto, J Fujita, R A Condrate, Y Morimoto, J Chem Phys, (1963), 39, 423.

64. A Sabatini and I Bertini, Inorg Chem, (1965), 4, 959.

65. D M Adams, 'Metal Ligand and Related Vibrations', Edward Arnold, London, (1967).

66. G E Coates and C Parkin, J Chem Soc, (1963), 421.

67. K Nakamoto, 'IR spectra of Inorganic and Coordination Compounds', Wiley, New York, (1963).

68. J R Durig, R Layton, D W Sink, B R Mitchell, Spectrochim Acta, (1965), 21, 1367.

69. P L Goggin, R J Goodfellow, D L Sales, J Stokes, P Woodward, Chem Comm, (1968), 31.

70. J Chatt and L M Venanzi, J Chem Soc, (1957), 2351.

71. J Chatt and L M Venanzi, J Chem Soc, (1955), 2787.

72. J Chatt, L A Duncanson, L M Venanzi, J Chem Soc, (1955), 4461.

73. D L Sales, J Stokes, P Woodward, J Chem Soc (A), (1968), 1852.

74. R J Goodfellow, P L Goggin, L M Venanzi, J Chem Soc (A), (1967), 1897.

75. V N Ipatieff and B S Friedman, J Chem Soc, (1939), 61, 684.

76. E W Abel, A K S Ahmed, G W Farrow, K G Orrell, J Chem Soc Dalton, (1977), 47.

77. E W Abel, G W Farrow, K G Orrell, V Šik, J Chem Soc Dalton, (1977), 42.

78. G M Bennett, A N Moses, F S Statham, J Chem Soc, (1930), 1668.

79. G T Morgan and W Ledbury, J Chem Soc, (1922), 2882.

80. L A Tschugaev and A K oblinskii, Z Anorg Chem, (1913), 83, 14.

81. D Goodall, J Chem Soc (A), (1967), 1298.

82. L A Tschugaev and A Koblinskii, Z Anorg Chem, (1913), 83, 8; (1913), 83, 159.

83. H D K Drew, G H Preston, W Wardlaw, G H Wyatt, J Chem Soc, (1933), 1294.

84. Yu N Kukushkin, G S Krylova, S I Bakhireva, Russ J Inorg Chem, (1974), 19, 922 and references therein.

85. M Atoji, I W Richardson, R F Rundle, J Amer Chem Soc, (1957), 79, 3017.

86. J Plusec and A D Westland, J Chem Soc, (1965), 5371.

87. S E Livingstone and B Wheelahan, Austral J Chem, (1964), 17, 219.

88. C M Harris and R S Nyholm, J Chem Soc, (1956), 4375.

89. C M Harris, R S Nyholm, D J Phillips, J Chem Soc, (1960), 4379.

90. J A Brewster, C A Savage, L M Venanzi, J Chem Soc, (1961), 3699.

91. A D Westland, J Chem Soc, (1965), 3060.

92. A D Westland, and J Plusec, Can J Chem, (1968), 46, 2097.

93. M Schmidt and G G Hoffman, Z Anorg Chem, (1978), 445, 167.

94. W Levason, C A McAuliffe, S G Murray, J Chem Soc Dalton, (1975), 1566.

95. W Levason, C A McAuliffe, S G Murray, Inorg Chim Acta, (1976), 17, 247.

96. C A McAuliffe and S G Murray, Inorg Nucl Chem Letts, (1976), 12, 897.

97. T N Lockyer, Austral J Chem, (1974), 27, 259.

98. D C Goodall, J Chem Soc (A), (1967), 1387.

99. C A McAuliffe, Inorg Chem, (1973), 12, 2477.

100. L Tschugaev, Chem Ber, (1908), 41, 2222.

101. R J Cross, T H Green, R Keat, J F Paterson, J Chem Soc Dalton, (1976), 1486.

102. R J Cross, T H Green, R Keat, J Chem Soc Dalton, (1976), 1150.

103. R J Cross, T H Green, R Keat, J Chem Soc Chem Comm, (1974), 207.

104. R J Cross, T H Green, R Keat, J F Paterson, Inorg Nucl Chem Letts, (1975), 11, 145.

105. P Haake and P C Turley, J Amer Chem Soc, (1967), 89, 4611, 4617.

106. W B Jennings, Chem Rev, (1975), 75, 307.

107. E W Abel, G W Farrow, K G Orrell, J Chem Soc Dalton, (1979), 1994.

108. E W Abel, G W Farrow, K G Orrell, J Chem Soc, (1976), 1160.

109. R J Cross, I G Dalgleish, G J Smith, R Wardle, J Chem Soc Dalton, (1972), 992.

110. E W Abel, R P Bush, F J Hopton, C R Jenkins, Chem Comm, (1966), 992.

111. G Hunter and T C Massey, J Chem Soc Dalton, (1976), 2007.

112. R Donaldson, G Hunter, R Keat, J Chem Soc Dalton, (1974), 288.

113. G Hunter and R C Massey, J Chem Soc Chem Comm, (1973), 797.

114. E W Abel, A Rauf Khan, K Kite, K G Orrell, V Šik, J Chem Soc Dalton, (1980), 1169.

115. E W Abel, A Rauf Khan, K Kite, K G Orrell, V Šik, J Chem Soc Dalton, (1980), 1175.

116. E W Abel, A Rauf Khan, K Kite, K G Orrell, V Šik, J Organomet Chem, (1978), C18, 145.

117. G Binsch, J Amer Chem Soc, (1969), 91, 1304.

118. D R Rayner, A J Gordon, K Mislow, J Amer Chem Soc, (1968), 90, 4854.

119. D Darwish, R L Tomlinson, J Amer Chem Soc, (1968), 90, 5938.

120. F Colleta, R E Horre, A Gambaro, Inorg Nucl Chem Letts, (1972), 8, 667.

121. J E Fergusson, K S Loh, Austral J Chem, (1973), 26, 2615.

122. M P Brown, R J Puddephatt, C E Ellpton, J Chem Soc Dalton, (1976), 2490.

123. See Reference [26].

124. D A Rowley and R S Drago, Inorg Chem, (1968), 7, 795.

125. W Rosen and D H Busch, J Amer Chem Soc, (1969), 91, 4694.

126. W Levason, C A McAuliffe, S G Murray, S M Nelson, Inorg Chim Acta, (1976), 19, L51, L16.

127. D O Hall, K K Rao, R Commack, Sci Prog, (1975), 62, 285.

128. R Backhouse, M E Foss, R S Nyholm, J Chem Soc, (1957), 1714.

129. W K Musker and N L Hill, Inorg Chem, (1972), 11, 710.

130. R A Walton and D A Edwards, Spectrochim Acta, (1968), 24A, 833.

131. B L Wilson and J B Hamilton, Inorg Nucl Chem Letts, (1976), 12, 59.

132. W Levason, C A McAuliffe, F P McCullough, S G Murray, C A Rice, Inorg Chim Acta, (1977), 22, 227.

133. M Schaeffer-King and R E McCarley, Inorg Chem, (1973), 12, 1972.

134. E W Ainscough, A M Brodie, K C Palmer, J Chem Soc Dalton, (1976), 2375.

135. R A Walton, Prog Inorg Chem, (1972), 16, 1.

136. J Chatt, G J Leigh, A P Storace, J Chem Soc (A), (1971), 1380.

137. D C Goodall, J Chem Soc (A), (1967), 887.

138. F A Cotton and R A Walton, Inorg Chem, (1966), 5, 1802.

139. D A Rice and R A Walton, Spectrochim Acta, (1971), 27A, 279.

140. D J Gulliver, W Levason, K G Smith, S G Murray, M J Selwood, J Chem Soc Dalton, (1980), 1872.

141. R A Walton, J Chem Soc (A), (1967), 1852.

142. J Chatt, G J Leigh, A P Storace, D A Squire, B J Starkey, J Chem Soc (A), (1971), 899.

143. J E Fergusson, J D Karran, S Seevaratnam, J Chem Soc, (1967), 2627.

144. F P Dwyer and R S Nyholm, Proc Roy Soc, New South Wales, (1944), 78, 67.

145. S J Anderson, J R Barnes, P L Goggin, R J Goodfellow, J Chem Res, (1978), 3601.

146. G B Kauffman, J H S Tsau, R C Fay, C K Jørgensen, Inorg Chem, (1963), 2, 1233.

147. H R Hays, E F Lutz, S Searles, J Org Chem, (1962), 27, 2828.

148. P P Perkins and M A Youtz, J Amer Chem Soc, (1929), 51, 3508.

149. R Adams, W Reifschneider, A Ferretti, Org Synth, (1962), 42, 22.

150. S E Livingstone, J Chem Soc, (1956), 437.

151. C A McAuliffe, S G Murray, R D Sedgwick, Inorg Chim Acta, (1975), 14, 49.

152. W Levason, C A McAuliffe, S G Murray, J Chem Soc Dalton, (1976), 269.

153. P W Allen, P N Baunton, I T Millar, J C Tebby, J Chem Soc (C), (1971), 3454.

154. W Autenrieth and A Brurung, Ber, (1903), 36, 183.

155. L Brandsma, P Vermeer, J G A Kroijam, H Boelens, J T Maessen, Rec Trav Chim, (1972), 91, 729.

156. Z Rappaport, Adv Phys Org Chem, (1969), 7, 1.

157. W E Truce, R J McManimie, J Amer Chem Soc, (1954), 76, 5745.

158. W E Parham and J Herberling, J Amer Chem Soc, (1955), 77, 1175.

159. C A McAuliffe, F P McCullough, R D Sedgewick, W Levason, Inorg Chim Acta, (1978), 27, 185.

160. W J Geary, Coord Chem Rev, (1971), 7, 81.

161. L Tschugaev and W Chlopin, Z Anorg Chem, (1914), 86, 241.

162. F R Hartley, S G Murray, W Levason, H E Soutter, Inorg Chim Acta, (1979), 35, 265.

163. J Chatt and R G Wilkins, J Chem Soc, (1951), 2532.

164. G B Kauffman and L A Teter, Inorg Synth, (1963), 7, 245.

165. H D K Drew, F W Pinkard, G H Preston, W Wardlaw, J Chem Soc, (1932), 1895.

166. R A Walton, D A Walton, Spectrochim Acta, (1968), 24A, 833.

167. W Levason and C A McAuliffe, Inorg Chim Acta, (1976), 16, 167.

168. A R Sanger, J E Weiner-Fedorak, Inorg Chim Acta, (1980), 42, 101.

169. H B Gray, Trans Met Chem, (1965), 239 and references therein.

170. B G Anex and N Takeuchi, J Amer Chem Soc, (1974), 96, 4411 and references therein.

171. R M Rush, D S Martin, R G Legrand, Inorg Chem, (1975), 14, 2543 and references therein.

172. K K Chow, W Levason, C A McAuliffe, Inorg Chim Acta, (1974), 15, 79.

173. K P Beaumont, C A McAuliffe, M J Cleare, Chem Biol Interact, (1976), 14, 179.

174. W Levason, C A McAuliffe, Inorg Chem, (1974), 13, 2765.

175. D W Meek, P E Nicpon, V I Meek, J Amer Chem Soc, (1970), 92, 5351.

176. P L Goggin, R J Knight, L Sindellari, L M Venanzi, Inorg Chim Acta, (1971), 5, 62.

177. D A Duddell, P L Goggin, R J Goodfellow, M G Norton, J G Smith, J Chem Soc (A), (1970), 545.

178. W Levason, C A McAuliffe, S G Murray, J Organomet Chem, (1976), C25, 110.

179. A Pryde, B L Shaw, B Weeks, J Chem Soc Dalton, (1976), 332.

180. S F Pavkovic and D W Meek, Inorg Chem, (1965), 4, 1091.

181. W Levason and C A McAuliffe, J Chem Soc Dalton, (1974), 2238.

182. D Gulliver, personal communication, (1981).

183. A J Pryde, B L Shaw, B Weeks, J Chem Soc Chem Comm, (1973), 947.

184. F C Marsh, R Mason, K M Thomas, B L Shaw, J Chem Soc Chem Comm, (1975), 584.

185. W Levason, C A McAuliffe, S G Murray, J Chem Soc Dalton, (1976), 2321.

186. A R Sanger, J Chem Soc Dalton, (1977), 1971.

187. W L Steffen and G J Palenik, Inorg Chem, (1976), 15, 2432.

188. C Ercolani, J V Quagliano, L M Vallarino, Inorg Chim Acta, (1973), 7, 413.

189. G M Bancroft, M J Mays, P E Prater, J Chem Soc (A), (1970), 956.

190. S A Cotton, Coord Chem Rev, (1972), 185.

191. J Lewis, R S Nyholm, G A Rodley, J Chem Soc, (1965), 1483.

192. R D Feltham and W Silverthorn, Inorg Chem, (1968), 7, 1154.

193. R D Feltham and W Silverthorn, Inorg Chem, (1970), 9, 1207.

194. R D Feltham, H G Metzger, W Silverthorn, Inorg Chem, (1968), 7, 2003.

195. A H Ewald, R L Martin, E Sinn, A H White, Inorg Chem, (1969), 8, 1837.

196. J S Griffith, Discuss Faraday Soc, (1958), 26, 81.

197. R L Martin and A H White, Inorg Chem, (1967), 6, 712.

198. B N Figgis, Trans Faraday Soc, (1961), 57, 199.

199. B N Figgis, M Gerloch, R Mason, Proc Roy Soc of London (A), (1969), 309, 91.

200. N N Greenwood, 'Physical Chemistry, An Advanced Treatise', Volume 4, Chapter 12, Academic Press, (1970),; N N Greenwood and T C Gibb, 'Mössbauer Spectrometry', Chapman Hill, (1971).

201. D Rininger, J B Zimmerman, N V Duffy, D L Uhrich, J Inorg Nucl Chem, (1980), 42, 689.

202. T Fujita, A Ito, K Ono, J Chem Phys Soc Japan, (1966), 21, 1734.

203. C E Johnson, W Marshall, G J Perlow, Phys Rev, (1962), 126, 1503.

204. P R Edwards, C E Johnson, R J P Williams, J Chem Phys, (1967), 47, 2074.

205. S Debenedetti, G Lang, R Ingalls, Phys Rev Letts, (1961), 6, 60.

206. T Birchall, Can J Chem, (1969), 47, 1351.

207. L Maier, 'Organic Phosphorus Compounds', editors, L Maier and G M Kosolapoff, Wiley, New York, (1972), 1, 1.

208. L Maier, Prog Inorg Chem, (1963), 5, 27.

209. G O Doak and L D Freedman, 'Organometallic compounds of arsenic, antimony and bismuth', Wiley, New York, (1970).

210. M Dub, 'Organometallic compounds', 2nd Edition, Volume III, Springer-Verlag, New York, (1968).

211. Reference [207] p289.

212. G O Doak and L D Freedman, Synthesis, (1974), 328.

213. B Buchner and L B Lockhardt, Org Synth, (1951), 31, 88.

214. L D Quin and J S Humphrey, J Amer Chem Soc, (1961), 83, 4124.

215. B Chiswell and L M Venanzi, J Chem Soc (A), (1966), 417.

216. G W Parshall, J Inorg Nucl Chem, (1960), 12, 372.

217. S A Butler and J Chatt, Inorg Synth, (1974), 15, 185.

218. L Horner, P Beck, V G Toscano, Chem Ber, (1961), 94, 2122.

219. F A Hart, J Chem Soc, (1960), 3324 and references therein.

220. W Levason, K G Smith, C A McAuliffe, F P McCullough, R D Sedgwick, S G Murray, J Chem Soc Dalton, (1979), 1718.

221. I T Millar, H Heaney, D M Heinekey, W C Fernelius, Inorg Synth, (1960), 6, 113.

222. R L Barker, E Booth, W E Jones, A F Millidge, F N Woodward, Chem Ind, (1949), 68, 285, 289, 295.

223. E R H Jones and F G Mann, J Chem Soc, (1955), 4472.

224. W Levason, C A McAuliffe, A I Plaza, S O Grim, Inorg Synth, (1976), 16, 184.

225. F G Mann and F C Stewart, J Chem Soc, (1955), 1269.

226. W Levason and C A McAuliffe, Inorg Synth, (1976), 16, 188.

227. A M Aguiar, J Beister, A Miller, J Org Chem, (1962), 27, 1007.

228. W Levason, C A McAuliffe, R C Barth, S O Grim, Inorg Synth, (1976), 16, 188.

229. W Hewertson and H R Watson, J Chem Soc, (1962), 1490 and references therein.

230. K Issleib and A Tzschach, Chem Ber, (1959), 92, 1118.

231. A M Aguiar and T G Archibald, J Org Chem, (1967), 32, 2627.

232. A Tzschach and W Lange, Chem Ber, (1962), 95, 1360.

233. J Ellerman and K Dorn, Chem Ber, (1967), 100, 1230.

234. K Issleib, Pure App Chem, (1964), 9, 205.

235. S O Grim and R P Molenda, Phosphorus, (1974), 4, 189.

236. J R Phillips and J H Vis, Can J Chem, (1967), 45, 675.

237. R D Feltham, A Kasenally, R S Nyholm, J Organomet Chem, (1967), 7, 285.

238. R D Feltham and W Silverthorn, Inorg Synth, (1967), 10, 159.

239. F Basolo, Inorg Synth, (1976), 16, 153 and references therein.

240. K Issleib and A Brack, Z Anorg Chem, (1954), 277, 258.

241. F G Mann and E J Chaplin, J Chem Soc, (1937), 527.

242. J Meisenheimer, J Casper, M Höring, W Lanter, L Lichtenstadt, W Samuel, Annalen, (1926), 449, 213.

243. R L Schriner, C N Wolf, Org Synth, (1950), 30, 95.

244. C E Wymore, and J C Bailar, J Inorg Nucl Chem, (1960), 14, 42.

245. K Issleib and D W Müller, Chem Ber, (1959), 92, 3175.

246. K Issleib and G Döll, Chem Ber, (1963), 96, 1544.

247. L Sacconi and J Gelsamini, Inorg Chem, (1968), 7, 291.

248. R B King and P N Kapoor, J Amer Chem Soc, (1971), 93, 4158.

249. A M Aguiar and J Beisler, J Org Chem, (1964), 29, 1660.

250. G R Van Hecke and W deW Horrocks, Inorg Chem, (1966), 5, 1960.

251. A M Aguiar and D Daigle, J Amer Chem Soc, (1964), 86, 2299.

252. G Kordosky, B R Cook, J C Cloyd, D W Meek, Inorg Synth, (1973), 14, 14.

253. L F Warren and M A Bennett, Inorg Chem, (1976), 15, 3126.

254. R J H Clark, R H U Negrotti, R S Nyholm, Chem Comm, (1966), 486.

255. A M Aguiar, J T Mague, H J Aguiar, T G Archibald, B Prejean, J Org Chem, (1968), 33, 1681.

256. K Sommer, Z Anorg Chem, (1970), 376, 150.

257. K K Chow, W Levason, C A McAuliffe, J Chem Soc Dalton, (1976), 1429.

258. A Tzschach and H Nindel, Z Anorg Chem, (1970), 10, 118.

259. D J Thornhill and A R Manning, J Chem Soc Dalton, (1973), 2086.

260. M A Bennett, G J Erskine, J D Wild, Inorg Chim Acta, (1968), 2, 379.

261. R D Feltham and H G Metzger, J Organomet Chem, (1971), 33, 347.

262. J Chatt and F G Mann, J Chem Soc, (1939), 610.

263. G Booth and J Chatt, J Chem Soc, (1962), 2099.

264. L H Pignolet, D Forster, W D Horrocks, Inorg Chem, (1968), 7, 828.

265. K A Jensen, Z Anorg Chem, (1936), 229, 282.

266. K Issleib and G Döll, Z Anorg Chem, (1960), 305, 1.

267. L Naldini, Gazz Chim Ital, (1960), 90, 391.

268. D Forster and D M L Goodgame, J Chem Soc, (1965), 455.

269. F A Cotton, O D Faut, D M L Goodgame, R H Holm, J Amer Chem Soc, (1961), 83, 1780.

270. P P Singh and R Rivest, Can J Chem, (1968), 46, 1773.

271. M Baker and J Lutz, Inorg Chim Acta, (1976), 16, 5.

272. M H Jones, W Levason, C A McAuliffe, S M Nelson, unpublished work, 1975-1977.

273. J Chatt and R G Hayter, J Chem Soc, (1961), 5507.

274. W Levason, C A McAuliffe, M M Khan, S M Nelson, J Chem Soc Dalton, (1975), 1778.

275. L F Warren and M Bennett, J Amer Chem Soc, (1974), 96, 3340.

276. B N Figgis and J Lewis, Prog Inorg Chem, (1964), 6, 164.

277. G S Hazeldean, R S Nyholm, R V Parish, J Chem Soc (A), (1966), 162.

278. E Verdonk and L G Vanquickenborne, Inorg Chem, (1974), 13, 762.

279. R S Nyholm, J Chem Soc, (1950), 851.

280. R V Parish, and P J Rowbotham, J Chem Soc Dalton, (1973), 37.

281. H L Nigam, R S Nyholm, R V Rao Ramano, J Chem Soc, (1959), 1397.

282. T E Nappier, R D Feltham, J H Enemark, A Kruse, M Cooke, Inorg Chem, (1975), 14, 806.

283. W Silverthorn and R D Feltham, Inorg Chem, (1967), 6, 1662.

284. R D Feltham, W Silverthorn, H Wickman, W Wesolowski, Inorg Chem, (1972), 11, 676.

285. P J Pauling, D W Porter, G B Robertson, J Chem Soc, (1970), 2728.

286. R J H Clark and T M Dunn, J Chem Soc, (1963), 1198.

287. R H Petty, E V Dose, M F Tweedle, L J Wilson, Inorg Chem, (1978), 17, 1064.

288. See Reference [279].

289. M R Fernardopulle, D A Gillespie, W R McWhinnie, Inorg Chim Acta, (1978), 29, 197.

290. K S Murray, Coord Chem Rev, (1974), 12, 1.

291. M G B Drew, V McKee, S M Nelson, J Chem Soc Dalton, (1978), 80.

292. W Levason and K G Smith, Inorg Chim Acta, (1980), 41, 133.

293. L Sacconi and R Morassi, J Chem Soc (A), (1969), 2904.

294. M Ciampolini and N Nardi, Inorg Chem, (1966), 5, 41.

295. H Gilman and I Banner, J Amer Chem Soc, (1940), 62, 344.

296. P Nicpon and D W Meek, Inorg Chem, (1967), 6, 145.

297. W Levason and C A McAuliffe, Inorg Chim Acta, (1974), 11, 33.

298. H P Fritz, I R Gordon, K E Schwarzhaus, L M Venanzi, J Chem Soc, (1965), 5210.

299. G Dyer and D W Meek, J Amer Chem Soc, (1967), 89, 3983.

300. T B Rauchfuss, F T Patino, D M Roundhill, Inorg Chem, (1975), 14, 652.

301. W Levason and K G Smith, J Organomet Chem, (1979), 169, 283.

302. K Issleib and G Thomas, Chem Ber, (1960), 93, 803.

303. T Jarolim and J Podlahova, J Inorg Nucl Chem, (1976), 125.

304. K Issleib and H Zimmerman, Z Anorg Chem, (1967), 353, 197.

305. H C Brown and K Le Roi Nelson, J Amer Chem Soc, (1953), 75, 24.

306. L Sacconi and I Bertini, J Amer Chem Soc, (1968), 90, 5443.

307. L Sacconi, J Chem Soc (A), (1970), 248.

308. L Sacconi, M Ciampolini, G P Speroni, Inorg Chem, (1965), 4, 1116.

309. W V Dahlhoff, T R Dick, G H Ford, S M Nelson, J Inorg Nucl Chem, (1971), 33, 1799.

310. E Uhlig and M Schäfer, Z Anorg Chem, (1968), 359, 67.

311. E Uhlig and M Maaser, Z Anorg Chem, (1967), 349, 300.

312. E Uhlig and M Schäfer, Z Anorg Chem, (1968), 359, 178.

313. M Schäfer and E Uhlig, Z Anorg Chem, (1974), 407, 23.

314. B Chiswell, R Plowman, K Verrall, Inorg Chim Acta, (1971), 5, 579.

315. S S Sandhu and S S Parmar, J Chem Soc (A), (1971), 111.

316. S S Sandhu, B S Manhas, M R Mittal, S S Parmar, Ind J Chem, (1969), 7, 286.

317. R S Nyholm, J Chem Soc, (1950), 2071.

318. G A Rodley and P W Smith, J Chem Soc (A), (1967), 1580.

319. F W B Einstein and G A Rodley, J Inorg Nucl Chem, (1967), 29, 347.

320. F H Burstall and R S Nyholm, J Chem Soc, (1952), 3570.

321. T M Dunn, R S Nyholm, S Yamada, J Chem Soc, (1962), 1564.

322. S Yamada, Coord Chem Rev, (1967), 2, 89.

323. P Bernstein, G A Rodley, R Marsh, H B Gray, Inorg Chem, (1972) 11, 3041.

324. D Taylor and G B Robertson, reported as a private communication in reference [253].

325. L Sacconi, I Bertini, F Mani, Inorg Chem, (1967), 6, 262.

326. P C Mitchell and R J P Williams, J Chem Soc, (1960), 1912.

327. F A Cotton, D M L Goodgame, R H Soderberg, Inorg Chem, (1963), 2, 1162.

328. E J Duff, J Chem Soc (A), (1968), 434.

329. P L Oriolli and L Sacconi, Chem Comm, (1969), 1012.

330. L Sacconi, M Di Vaira, A Bianchi, J Amer Chem Soc, (1970), 92, 4465.

331. W Haase, Z Anorg Chem, (1974), 404, 273.

332. E Uhlig and M Maaser, Z Anorg Chem, (1966), 344, 205.

333. R E Christopher, I R Gordon, L M Venanzi, J Chem Soc (A), (1968), 205.

334. B Chiswell, R A Plowman, K Verrall, Inorg Chim Acta, (1972), 6, 113.

335. J F Sieckhaus and T Layloff, Inorg Chem, (1967), 6, 2185.

336. A H Norbury, Adv Inorg Chem Radiochem, (1975), 17, 231.

337. L Sacconi, Trans Met Chem, (1968), 4, 199.

338. J R Preer and H B Gray, J Amer Chem Soc, (1970), 92, 7306.

339. T D Dubois and D W Meek, Inorg Chem, (1967), 6, 1395.

340. R S Nyholm, J Chem Soc, (1952), 2061.

341. N C Stephenson, Acta Cryst, (1964), 17, 592.

342. M J Hudson, R S Nyholm, M H B Stiddard, J Chem Soc (A), (1968), 40.

343. J Chatt and B L Shaw, J Chem Soc, (1961), 285.

344. F A Cotton, D M L Goodgame, M Goodgame, J Amer Chem Soc, (1961), 83, 4161.

345. J Bradbury, K P Forest, R H Nuttall, D W A Sharp, Spectrochim Acta (A), (1967), 23, 2701.

346. N F Curtis and Y M Curtis, Inorg Chem, (1965), 6, 804.

347. B M Gatehouse, S E Livingstone, R S Nyholm, J Inorg Nucl Chem, (1958), 8, 75.

348. B M Gatehouse, J Inorg Nucl Chem, (1958), 8, 79.

349. A B P Lever and E Mantovani, Inorg Chim Acta, (1971), 5, 429.

350. A B P Lever and E Mantovani, Inorg Chem, (1971), 10, 817.

351. W Hatfield and C Piper, Inorg Chem, (1964), 3, 841.

352. D F Evans, J Chem Soc, (1959), 2003.

353. K K Chow and C A McAuliffe, Inorg Chim Acta, (1975), 14, 121.

354. J K Stalick, P W R Corfield, D W Meek, Inorg Chem, (1973), 12, 1668.

355. G Dyer and D Meek, Inorg Chem, (1967), 6, 149.

356a. F A Cotton, D M L Goodgame, M Goodgame, A Sacco, J Amer Chem Soc, (1961), 83, 4157.

356b. E Uhlig, Coord Chem Rev, (1973), 10, 227.

357. D S Flett, 'Solvent Extraction in Metallurgical Processes', International Symposium, Antwerp, 4-5th May (1972), and references therein.

358. R C Weast, 'Handbook of Chemistry and Physics', 55th edition, CRC Press Inc, (1974-75).

359. A W Chester, Adv Chem Ser, (1967), 62, 78.

360. J C Bailar Jr, Inorg Synth, (1946), 2, 222.

361. D S Flett, Reports on the Progress of Applied Chemistry, (1972), 57, 284.

362. D S Flett and D R Spink, Hydrometallurgy, (1976), 1, 207.

363. A K De, S M Khopkar, R A Chalmers, 'Solvent Extraction of Metals', Van Nostrand Reinhold Co, London, (1970), 174.

364. F A Cotton, O D Faut, D M L Goodgame, J Amer Chem Soc, (1961), 83, 344.

365. G Garton, D E Henn, H M Powell, L M Venanzi, J Chem Soc, (1963), 3625.

366. R V G Ewens and C S Gibson, J Chem Soc London, (1949), 431.

367. A V Ablov, N V Gerbeleu, B T Oloi, Russ J Inorg Chem, (1971), 16, 99.

368. J L Sabot and D Bauer, J Inorg Nucl Chem, (1978), 40, 1129.

369. D E C Corbridge, 'Phosphorus', Elsevier, (1978).

370. M Akbar Ali and S E Livingstone, Coord Chem Rev, (1974), 13, 101.

371. E Gonick, W C Fernelius, B E Douglas, J Amer Chem Soc, (1954), 76, 4671.

372. G M Barrow, 'Physical Chemistry', 3rd edition, McGraw-Hill Kogakusha Limited, Tokyo, (1973),

373. F E Mabbs and D J Machin, 'Magnetism and Transition Metal Complexes', Chapman Hall Limited, (1973), page 5.

374. A I Vogel, 'A Textbook of Practical Organic Chemistry including Qualitative Organic Analysis', 3rd edition, (1966), page 166.