UNIVERSITY OF SOUTHAMPTON

STUDIES IN THE COORDINATION CHEMISTRY OF

NICKEL(III) AND NICKEL(IV)

A Thesis Submitted for the Degree of
Doctor of Philosophy

by

Simon Joseph Higgins

- October 1984 -
ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. W. Levason, for his guidance and friendship over the past three years, and his resigned acceptance of my habit of frequently "running round the Common". I am also indebted to all the members of the '6th floor' for friendly discussion, on chemistry and other matters.

This study would have been more inconclusive were it not for the efforts of Dr. M. Webster and Dr. L. Gray in solving the structures of \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_3]\) \(\text{C}_7\text{H}_8\) and \([\text{Ni}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}\text{I}_3]\) \(\text{I}_2\), for which I am very grateful.

I also thank Mrs J. M. Street for n.m.r. work, Dr. D. Pletcher and Mr. D. Pierce for advice and help with the electrochemistry, Dr. M. B. Hurthhouse for X-ray data collection using the QMC/SERC facilities, Dr. S. G. Murray (Royal Military College of Science) for the use of T.G.A. equipment, Dr. D. Rice (Reading University) for some near-infra red spectra, Dr. Annette Lewis and Dr. David Gulliver, my predecessors, for a 'legacy' of multidentate arsine ligands and everyone else who has assisted this work.

This research was funded by the Science and Engineering Research Council.

I finally thank Mrs J. Wright-Green for her accurate and well-presented typing.
To my parents and family
"... of making many books there is no end, and much study wearies the body."

Ecclesiastes 11,12.
Five-coordinate nickel(III) complexes $[\text{Ni}(L-L)\text{Cl}_3]$ (for example, $L-L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2, \sigma^2\text{C}_6\text{H}_4(\text{PPh}_2)_2$) have been obtained by $\text{Cl}_2/\text{CCl}_4$ or $\text{NOCl}/\text{CH}_2\text{Cl}_2$ oxidation of $[\text{Ni}(L-L)\text{Cl}_2]$. The bromides $[\text{Ni}(L-L)\text{Br}_3]$ ($L-L$ as above, plus $\sigma^2\text{C}_6\text{H}_4(\text{AsPh}_2)_2, \sigma^2\text{C}_6\text{H}_4(\text{PPh}_2)(\text{SMe})$) are similarly obtained ($\text{Br}_2/\text{CCl}_4$) - including the first examples of $-\text{AsPh}_2$ and $-\text{SMe}$ coordination to nickel(III). On warming, $[\text{Ni}(L-L)\text{X}_3]$ revert cleanly to $[\text{Ni}(L-L)\text{X}_2]$. Unstable $[\text{Ni}(\sigma^2\text{C}_6\text{H}_4(\text{AsMe}_2)_2)\text{X}_3]$ are prepared by $X_2$ oxidation of $[\text{Ni}(\sigma^2\text{C}_6\text{H}_4(\text{AsMe}_2)_2)(\text{CO})_2]$. The mer- $[\text{Ni}\{\text{PhP}((\text{CH}_2\text{CH}_2\text{PPh}_2)_2)\text{X}_3]$ were also obtained. The synthesis and properties of pseudo-octahedral $[\text{Ni}(L-L)_2\text{X}_2]Y$, (L-L = methyl-substituted bidentate arsine, phosphine or phosphine-stibine; $X = \text{Cl}, \text{Br}$; $Y = \text{ClO}_4$, $\text{BF}_4$) are described and discussed.

The range of nickel(IV) complexes $[\text{Ni}(L-L)_2\text{X}_2]Y_2$ obtainable is restricted to methyl-substituted bidentate arsine and phosphine ligands.

Confusion in the literature over the formulation of "$\text{Ni}^\text{II}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)^2\text{Cl}_3$" is resolved and two forms, viz $[\text{Ni}^\text{II}\text{II}(\text{en})_2\text{Cl}_2]\text{Cl}$ and $[\text{Ni}^\text{II}(\text{en})_2]^\text{II} [\text{Ni}^\text{IV}(\text{en})_2\text{Cl}_2]\text{Cl}_4$, were identified and characterised. Other examples of both nickel(III) and nickel(II)/(IV) complexes are described.

The oxidation of trans-planar $[\text{Ni}(L-L)_2\text{X}_2]$ (for example, $L = \text{PMe}_3$, $\text{Ph}_2\text{PMe}$; $X = \text{Cl}, \text{Br}$) yields very unstable trans-trigonal bipyramidal $[\text{Ni}(L-L)_2\text{X}_3]$. Evidence for the formation of transient nickel(III) complexes of $\text{P(OMe)}_3$, $\text{AsEt}_3$, $\text{PCy}_3$ and $\text{PPPh}_3$ is presented.

Iodine does not oxidise any nickel(II) complex studied, but several nickel(II)-polyiodide complexes were obtained and characterised. Generally, $[\text{Ni}(L-L)\text{I}_4]$ gave $\text{Ni}(L-L)\text{I}_4$, possibly with $I^-$ ..... $I_2$ ..... $I^-$ units, while $[\text{Ni}(L-L)_2\text{I}_2]$ ($L-L = \text{diphosphine}, \text{diarsine}, \text{dithioether}, \text{diselenoether}, \text{diamine}$) gave $[\text{Ni}(L-L)_2][\text{I}_3]\text{I}_2$ or $[\text{Ni}(L-L)_2(\text{I}_2)]_2$.

Preliminary studies indicate that a small number of iron(IV) complexes, $[\text{Fe}(L-L)_2\text{X}_2][\text{BF}_4]_2$, can be synthesised by $\text{HNO}_3/\text{HBF}_4$ oxidation of $D_{2h}$ iron(III) complexes.

All the complexes were characterised by elemental analyses, magnetic, electrochemical and thermogravimetric measurements and infra red, electronic and electron spin resonance spectroscopies. Single crystal X-ray studies of $[\text{Ni}((\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2))\text{Br}_3].\text{C}_7\text{H}_8$ and $[\text{Ni}(\sigma^2\text{C}_6\text{H}_4(\text{PMe}_2)_2)_2][\text{I}_3].2.2(\text{I}_2)$ are reported.
Abbreviations

Ligands and Complexes

M metal
L monodentate ligand, L-L bidentate ligand,
L-L-L tridentate ligand
X halide ion
E Group Vb or Group VIb neutral donor atom
en ethylene diamine (1,2-diaminoethane)
pn 1,2-propylenediamine (1,2-diaminopropane)
tn 1,3-propylene diamine (1,3-diaminopropane)
tmed tetramethylethylediamine (1,2-dimethylaminoethane)

Substituent Groups R (alkyl or aryl)

Me methyl
Et ethyl
Pr\textsubscript{n}, Pr\textsubscript{i} normal propyl and isopropyl respectively
Bu\textsubscript{n}, Bu\textsubscript{t} normal butyl and tertiary butyl respectively
Cy cyclohexyl
Ph phenyl

General

B.P. Boiling point
dr diffuse reflectance (solid state electronic spectroscopy)
I.r. infra red
U.V. ultra violet
n.m.r. nuclear magnetic resonance
$^{31}$P \{\textsubscript{1}H\} - brackets used to indicate broad-band proton decoupling
esr electron spin resonance
SCE Standard Calomel Electrode
TGA Thermogravimetric analysis
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Throughout this study, while Figures of spectra are shown calibrated in wavelength (10⁻⁹ m), Tables usually contain band maxima in reciprocal centimetres. This is because the Perkin Elmer 554 spectrophotometer operates linearly, in wavelength, while for comparison of the energies of maxima in a series of complexes it is convenient to work in reciprocal centimetres as this unit is directly proportional to energy.
CHAPTER 1

INTRODUCTION
INTRODUCTION

1.1 Background

This section is intended to explain the raison d'etre of this study and the difficulties of applying various physical and experimental techniques to complexes of metals in formally high oxidation states.

The chemistry of metal complexes in normal or low oxidation states has expanded rapidly in the last thirty years, aided and accompanied by advances in metal-ligand and metal-metal bonding theory and in physical techniques for the characterisation of complexes. This has been due partly to the industrial importance of organometallic complexes in catalysis and the emerging role of other metal complexes in biological processes, chemotherapy and other processes, some of industrial relevance.

The desire to examine the effects of changing the donor atom, and other ligand properties, on the properties of metal ions, spurred by industrial applications or chemical curiosity, has led to an equally rapid growth in the number and type of ligands available to the co-ordination chemist. In particular, organo-phosphorus, -arsenic and -antimony chemistry has benefitted.\(^3,4\)

However, the co-ordination chemistry of metals in high oxidation states has not expanded at the same rate, particularly that of the later 3d elements with neutral ligands. Such complexes are usually not convenient for study as they often decompose in moist atmospheres, being inherently unstable. Their paucity may be due either to this instability or to previous unwillingness to attempt their study, given the difficulties of handling the known examples. This study was performed with a view to expanding this neglected area.
of chemistry with particular emphasis on iron and nickel, and examining the effect of donor atom, substituents, ligand denticity and geometry on the stability of the complexes made.

Added interest is lent to this field by recent developments in the chemistry of these metals with other ligands, and their biochemistry. Although little industrial application has been found for high oxidation state complexes of iron or nickel, the inherent cheapness of the metals could change this. The oxoanion $\text{K}_2\text{FeO}_4$ is finding use in the treatment of industrial waste waters and "NiO$_2$" is used as an oxidant in organic chemistry. An oxidised form of Ni(OH)$_2$ plays an important role in the nickel-cadmium cell.

Very soon after the discovery that nickel is an essential trace element for certain organisms, it was proposed on the basis of careful e.s.r. experiments that Ni(III) sites exist in a bacterial hydrogenase enzyme. With certain doubly-deprotonated dicarbonyl-substituted pentaamine macrocycles, the redox potential Ni(II)$\rightarrow$Ni(III) + $\Theta$ becomes so low that an (O$_2$) complex of Ni(III) is formed on exposure of solutions of the Ni(II) complex to dioxygen. (See page 75). This complex is probably the intermediate in the oxidation of benzene to phenol, which the Ni(II) complex catalyses.

Iron in a formal oxidation state $+$4 has been suggested as an intermediate in the reaction of various ferroenzymes involved in in vivo electron transfer or peroxidase activity. Synthetic porphyrins containing an $\text{Fe}^{IV}$ unit have been made. A recent textbook, however, is dismissive about the possibility of transient Fe(IV) sites in ferroheme-O$_2$ complexes.

A re-awakening of interest in the features of ligands which will stabilise these high oxidation states, as well as in the
magnetic, structural and spectroscopic properties of their complexes, is therefore likely.

1.2 High Oxidation States

The term 'high' oxidation state is hard to define, since an oxidation state which is quite usual for one 3d element (for example Fe(III), Cr(III)) is considered 'high' for another (for example Ni(III), Cu(III)). 'High' could therefore, rather unhelpfully, be defined as 'higher than usual'.

It is well-known that the higher oxidation states of metals increase in stability in the Periods in the order 3d << 4d < 5d, and also from right to left. For example, whereas the ion PtI\(^{2-}\) is well established, \(^{10}\)Cs\(^{2+}\)Pd\(^{6+}\) has only recently been synthesised\(^{1}\), and Ni\(^{2-}\)(X = I\(^-\), Br\(^-\), Cl\(^-\)) do not exist. Even the \(M\(^{2+}\)NiF\(^{6-}\)(M = alkali metal cation) are very oxidising. \(^{11}\)OsO\(_{4}\) is comparatively stable, even forming adducts such as OsO\(_{4}\).NH\(_{3}\), RuO\(_{4}\) is much more oxidising and FeO\(_{4}\) does not exist, K\(_{2}\)FeO\(_{4}\) being an example of the highest-known oxidation state, Fe(VI)\(^{2-}\). There is, in fact, little similarity between the chemistry of the 4d and 5d elements in their higher oxidation states and that of the 3d elements, except in a few compounds such as MF\(_{6}\)(M = Ni, Pd, Pt) and MO\(_{4}\)(M = Fe, Ru). In spite of the importance of covalent bonding in these complexes, it has been suggested that the enthalpy of formation of the gaseous ions is a reasonable guide to the trends in oxidation state stability.\(^{14}\)

See Table 1.21. (Overleaf.)

On descending each group the formation of \(M^{+}\) and \(M^{2+}\) becomes more unfavourable and the higher ionisation levels become easier to achieve. This trend and the lower polarising power of the heavier elements on account of their larger radii, is
Table 1.21 Enthalpies of Formation of Gas Phase Ions, $M^{n+}(g)$ (kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>$n$</th>
<th>Fe</th>
<th>Ru</th>
<th>Os</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
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<tr>
<td>1</td>
<td>1178</td>
<td>1380</td>
<td>1568</td>
<td>1166</td>
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<td>2918</td>
<td>3059</td>
<td>3000</td>
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<tr>
<td>3</td>
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<td>6407</td>
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<td>10220</td>
<td>9467</td>
<td>11804</td>
<td>10943</td>
<td>9703</td>
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<tr>
<td>5</td>
<td>18,430</td>
<td>16287</td>
<td>14655</td>
<td>19,100</td>
<td>17303</td>
<td>15017</td>
</tr>
<tr>
<td>6</td>
<td>28,000</td>
<td>24111</td>
<td>21224</td>
<td>29,500</td>
<td>25964</td>
<td>22255</td>
</tr>
<tr>
<td>7</td>
<td>40,000</td>
<td>33776</td>
<td>29215</td>
<td>42,300</td>
<td>36549</td>
<td>31125</td>
</tr>
<tr>
<td>8</td>
<td>54,700</td>
<td>?</td>
<td>?</td>
<td>57,900</td>
<td>-</td>
<td>-</td>
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The enthalpies of atomisation contribute to the formation enthalpies of the ions (Figure 1.22) but are relatively more significant for the lower oxidation states. As $\Delta$H$^{\text{EA}}$ increases down the groups, this further promotes the more ready formation of the 4d and 5d higher oxidation states relative to the +1 or +2 states.

Increasing nuclear charge on moving to the right of the transition series and consequent contraction of the d-orbitals is responsible for the relative stabilisation of the higher oxidation states of the 4d and 5d elements relative to their 3d counterparts. The more diffuse, spatially-extended 4d and 5d orbitals have a lower effective nuclear charge acting upon them than the 3d orbitals, thus reducing ionisation potentials.
responsible for the increase in the sums of the ionisation potentials for the higher oxidation states, and the general decrease in stability (Table 1.21 page 4). For the 4d and 5d elements, states with an even number of d electrons tend to be more stable than those with odd numbers and this could account for the lack of Pd(III) and Pt(III) complexes (d^7) compared with Ni(III), which is well-established.

Classically, the ligands most often implicated in stable high oxidation state compounds are F^- and O^2-. For uncharged species, examination of the Born Haber cycle (Figure 1.22 page 6) reveals that the low dissociation energy of F and the greater lattice energy (U) for MF_n (F^- is a small anion and M^{n+} will be small if highly charged) means that the order of ability to promote high oxidation states is F^- > Cl^- > Br^- > I^- . The doubly-charged oxygen anion also leads to high lattice energies in the formation of MO_{n/2}^2-, but the unfavourable process O^- + e^- → O^2- (ΔH and EA in Figure 1.22 suggests, with a purely ionic model, that MF_n should be favoured over MO_{n/2}^2-.

However, the assumption that MF_n consists of discrete M^{n+} and F^- ions is greatly oversimplistic. Generally, these compounds are molecular species, with a high degree of covalency in the M-F and M-O bonds. For example, OsO_4 and RuO_4 are quite volatile. Although fluorine is more electronegative than oxygen, O^2- is better able to stabilise the very highest oxidation states than F-, probably for two reasons. Firstly, OsO_4, for example, is much less sterically crowded than a postulated (molecular) OsF_8. Secondly, O^2- is better able to participate in p^π - d^π ligand-to-metal bonding, reducing the effective charge on the metal.

The first direct evidence for covalency in such a complex come with e.s.r. studies on the IrCl_6^{2-} ion (Ir^{17+}, d^5 low spin). It was established that the unpaired spin density was...
Figure 1.22 Born-Haber Cycles for MXₙ and MOₙ/₂

ΔH_{IE} \quad \Delta H_A_M \quad \Delta H_A_{X_2} \quad \Delta H_{f(MX_n)} \quad \Delta H_{f(MO_{n/2})}
delocalised to some extent (ca. 6% for each Cl⁻) onto the ligands, rather than residing, as the ionic model demands, entirely on the metal.

Essentially, then, the bonding in these complexes is intermediate between ionic and covalent and would be best described (although with less convenience) in terms of molecular orbital theory. Such a description has to be used where any precision is required, for example in those complexes where oxidation is possible, but is not centred entirely on the metal. For example, nickel (II) complexes of the 1,2-dithiolenes can be oxidised by halogen, but the products are square planar and their esr and electronic spectra have been interpreted in terms of a nickel (II) - stabilised ligand radical complex. Other authors, however, interpret the results differently, favouring a Ni(III) d⁷ description. Either of these two extremes, however, is unsatisfactory and the best description of the complexes is that the unpaired electron occupies a molecular orbital which has varying degrees of metal d- and ligand-orbital character, depending on the ligand substituents. The current consensus of opinion seems to favour a largely ligand-based oxidation for these ligands. Specific cases will be dealt with in Chapter 2 (page 46).

1.3 The High Oxidation States of the 3d Series.

Complexes with Neutral Ligands

Titanium (IV) (d⁰) is the most stable and common oxidation state for this element, although comparatively few complexes with neutral ligands have been characterised. This is probably because although the compounds are easily formed, they are extremely sensitive to moisture, TiCl₄ itself fuming in atmospheres of > 5 p.p.m. water. Simple adducts TiX₄.L and TiX₄L₂ are formed for a wide variety of L, and the co-ordination geometry is usually octahedral, with bridging halide in the case of the 1:1 complexes. The ligand o-C₆H₄(AsMe₂)₂
forms six co-ordinate TiCl₄(L-L) and the unusual distorted dodecahedral TiCl₄(L-L)₂ (Figure 1.31).

### Vanadium

Vanadium (V), d⁰, does occur in some complexes with neutral ligands, but only with O²⁻ as a co-ligand, for example in [V(0)(H₂O)₄]⁺, formed by the strong acidification of vanadate solutions. The d¹V(IV) species also forms oxo complexes such as [VO(2,2'-bipyridyl)Cl]⁺ and a few non-oxo complexes with Group Vb ligands, such as VCl₄(PMe₃)₂. Reaction of VCl₄ with C₆H₆(AsMe₂)₂ gives dodecahedral VCl₄(L-L)₂ (c.f. Ti(IV)) but only a 1:1 adduct is formed with 4-F C₆H₃(AsMe₂)₂.

### Chromium

The d⁰ Cr(VI) exists only in oxides and oxoanions, and...
few mixed oxide-halides. Chromium (V) has a limited chemistry, tending
to disproportionate to Cr(III) and Cr(VI). Known Cr(V) complexes
invariably involve Cr = O bonds, as for example in (CrO)(N,N'-ethylenbis
(salicylideneaminato))PF₆, recently made by treatment of the
diaoquochromium (III) analogue with PhIO.¹⁹ (Figure 1.32).
The oxide-halide CrOCl₃ is strongly oxidising, being readily
reduced by PPh₃. The N-donor 1,10-phenanthroline catalyses
disproportionation to [CrO₂Cl₂]⁻ and other products, but both 2,2'-
bipyridyl and its 4,4'-dimethyl analogue form genuine octahedral
complexes [CrOCl₃(L-L)].⁴⁵

![Diagram of CrOCl₃](image)

**Figure 1.32.** The structure of [Cr = O(N,N'-ethylenbis
(salicylideneaminato))PF₆ from reference 19, with some
important bond distances (Å), showing the Cr = O unit.
Chromium (IV) is even more unusual, the only complex with neutral ligands to date being \([\text{Cr}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_4]\), made by treating \([\text{Cr}^0(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2(\text{N}_2)_2]\) successively with dry HCl and Cl₂. Further investigation of this system with similar ligands may prove fruitful, although neither \([\text{Cr}(\text{o-C}_6\text{H}_4\text{PMe}_2)_2\text{Cl}_4]^+\) or \([\text{Cr}(\text{o-C}_6\text{H}_4\text{PMe}_2)_2\text{Cl}_4]^-\), for example, could be oxidised, either chemically or electrochemically.

Manganese

Manganese (VII) continues the trend towards decreasing stability of the d° ions, being found only in the oxoanion MnO₄⁻ and in explosively-unstable Mn₂O₇ and MnO₃F. Manganese (VI) only occurs in MnO₄²⁻ and MnO₂Cl₂. The oxoanion readily disproportionates into MnO₄⁻ and MnO₂. Manganese (V) is almost as rare, being restricted to the poorly-characterised MnO₄³⁻ ion and MnOCl₃⁻. Apart from organometallic complexes, outside the scope of this study, Mn (IV) forms a few complexes with neutral ligands and these usually have oxide as co-ligand, for example in the oxide-bridged system \([\{(1,10\text{-phenanthroline)_2MnO}_4^2\_2(1,10\text{-phenanthroline)_2}\}]^{4+}\). Since Mn(II), the highest oxidation state which will not oxidise Group Vb ligands, has a very low affinity for such 'soft' donors, the co-ordination chemistry of Mn (III) and Mn(IV) with such ligands is necessarily restricted. The complex \([\text{Mn}(\text{o-C}_6\text{H}_4\text{PMe}_2)_2\text{Cl}_2][\text{ClO}_4]\) has been made by treatment of the Mn(III) complex with concentrated nitric and perchloric acids, but \([\text{Mn}(\text{o-C}_6\text{H}_4\text{ASMe}_2)_2\text{Cl}_2]\) forms only transient Mn(III) species on treatment with oxidising agents and the Mn(IV) complex is unknown.

Iron

Iron (VIII) and iron (VII) (d⁰ and d¹) are unknown. Iron (VI) is stable only in the oxoanion FeO₄²⁻, which is a powerful
oxidant, stable only in very alkaline solutions. Iron (V) exists only in oxide environments in mixed metal oxide systems. The claimed $\text{FeO}_4^{3-}$ has only poorly been characterised. Recently, iron (IV) complexes of porphyrin ligands, containing an $\text{Fe}=\text{O}$ unit, have been characterised, and a $\mu$-oxo-bridged species has also been made and studied by X-ray diffraction. The only known complexes of neutral ligands are $[\text{Fe}(\alpha-C_6H_4(\text{AsMe}_2)_2)_2X_2][\text{BF}_4]_2$ ($X = \text{Cl, Br}$) and $[\text{Fe}(\alpha-C_6H_4(P\text{Me}_2)_2)_2\text{Cl}_2][\text{ReO}_4]_2$.

Cobalt

There are no complexes yet known of Co(IV) with neutral donors. Attempts at the oxidation of octahedral Co(III) complexes of ligands capable of stabilising Fe(IV) and Ni(IV), for example, $\alpha-C_6H_4(P\text{Me}_2)_2$, have failed. This may be due to the low spin Co(III) complexes having the unusually stable $d^6$ arrangement.

Nickel

Whereas cobalt displays a very wide-ranging co-ordination chemistry in the +3 oxidation state, nickel (III) is regarded as a 'high' oxidation state. While a few complexes of nickel (III) with phosphines and arsines have been known for thirty years or more, the relatively recent development of nickel (III) chemistry with neutral ligands is due to the synthesis of tetraaza macrocycles - 'hard' $N$-donor ligands. Similarly, although nickel (IV) complexes $[\text{Ni}(\alpha-C_6H_4(\text{AsMe}_2)_2)_2X_2][\text{ClO}_4]_2$ ($X = \text{Cl, Br}$) were synthesised by Nyholm in 1951, recent work with nickel (IV) has been restricted to charged ligands of the multidentate amine-oxime and oxime variety.
Copper

Copper (IV) co-ordination chemistry is restricted to \( \text{Cs}_2\text{CuF}_6 \). Copper (III) forms some quite stable complexes with N-donors such as macrocycles and deprotonated peptides. The \([\text{Cu}(L-L)_2][\text{ClO}_4]_2\) and \([\text{Cu}(L-L)_2\text{Cl}][\text{ClO}_4]_2\) (\(L-L = \sigma^2\text{C}_6\text{H}_4(\text{AsMe}_2)_2\), \(\sigma^2\text{C}_6\text{H}_4(\text{PMe}_2)_2\)) have been made by concentrated nitric acid oxidation of the Cu(I) complexes.

1.4 The Preparation of High Oxidation State Complexes

High oxidation state complexes are usually prepared by the oxidation of a previously synthesised complex in a lower oxidation state. Even where a suitable high oxidation state precursor exists, the ligands which are the subject of this study are good reducing agents and the combination of the ligand and precursor would result in ligand oxidation. For example, Pt(IV) complexes of alkyl phosphines cannot be made cleanly from PtCl\(_4\). This can limit the extent of the chemistry of the higher oxidation states. It also means that, in approaching this co-ordination chemistry, due consideration must be given to the stereochemistry and spin states of the starting materials. This will be dealt with for iron and nickel, the main subjects of this study, elsewhere (Chapter 2, page 27).

Although a fairly wide variety of oxidants has been employed, the most common ones are halogens and nitric acid, with hydrohalic acids to provide the appropriate halide anion. The kinetics and mechanisms of these reactions have rarely been studied, but very recent literature reports suggest current activity in the investigation of the reduction of Ni(IV) oxime-imine-amine and Ni(III) macrocyclic amine complexes (see Chapter 2, page 57).
When the term 'stability' is used in this work, it is employed in a qualitative sense, as thermodynamic data does not yet exist.

1.5 The Stabilisation of High Oxidation States in 3d Metal Complexes Containing Neutral Ligands

Inspection of the small number of complexes containing neutral ligands suggests that the formally charged co-ligands $X^{-}(X=Cl, Br)$ and $O^{2-}$ may play a fundamental role in the stability of the complexes, possibly by reducing the effective charge at the metal ion. That is, although the alkyl-substituted phosphines and arsines in particular are good $\sigma$-donors, high in the spectrochemical series, their ability to bind to prospective Ni(III), Ni(IV) or Fe(IV) sites may depend on the halide counter ion reducing the effective charge in these centres.

The nature of the bonding between the metal and Group Vb or VIb donor atom is still a matter of controversy. However, in high oxidation state complexes, the bonds will be dominated by the ligands' $\sigma$-donor ability. Whether or not $\pi$-acceptor ability is significant in their bonding to Fe(II), Fe(III) or Ni(II) centres, it is unlikely to have any importance with the electron-poor high oxidation states, as the contraction of the metal d-orbitals will reduce the possibility of overlap with the ligand orbitals.

Factors of significance in the ability of a given ligand to co-ordinate to a high oxidation state metal ion will include the nature of the donor atom, its substituents and their electronic and steric effects and, for bi- and multidentate ligands, the length and type of the ligand 'backbone'.

Studies of the stability of high oxidation state complexes with a systematic variation of ligand donor atom and
substituent are rare, especially for 3d metals. Warren and Bennett studied some 3d complexes of $\sigma$-C$_6$H$_4$(EMe$_2$)$_2$ (E = P or As) and found little difference, chemically or electrochemically, between the ability of these ligands to stabilise Fe(IV), Ni(III) and Ni(IV) and Cu(III), although the net conclusion drawn was that $\sigma$-C$_6$H$_4$(PMe$_2$)$_2$ was marginally superior. Use of d-d bands in electronic spectra of these complexes to calculate $\Delta$oct is not possible as, for high oxidation states, the much more intense charge transfer bands occur at unusually low energy, masking the d-d bands. This obviates rigorous assessment of the ligand's bonding ability in terms of spectrochemical parameters, and often, qualitative ideas such as shelf life of the complexes and half life in solution have to be used, together, where appropriate, with electrochemical data.

Despite the lack of data, it is possible to make a few predictions about the ligands best suited to bond to high oxidation state metal ions. For the best $\sigma$-donor properties, electron-releasing substituents on the donor atom are necessary. Alkyl groups are suitable, for example, aryl groups less so and alkoxy or aryloxy groups even less, as they are electron-withdrawing.

Alkyl groups, particularly methyl groups, also enjoy steric advantages over aryl groups. As high oxidation state metal centres, especially Fe(IV) or Ni(IV), are likely to be small, co-ordinating ligands must have minimal bulk also.

Rationalisation of the properties of complexes in terms of steric effects due to ligand substituents is not new, but it is only recently that attempts to quantify steric effects have been made, notably by Tolman. A measurement of the steric requirements of ligands is their cone angle, defined as the apex angle of a cylindrical cone centred 2.28 Å from the centre of the phosphorus atom (for a P donor), which just touches the Van der Waals
radii of the outermost atoms of the ligand. The figure 2.28 Å was chosen as the first system tabulated was Ni(CO)$_3$L and the usual Ni$^+$-P bond length is 2.28 Å. Various formulae, based on geometric considerations, were proposed for ligands with mixed substituents, and for bidentate ligands. Although it has been suggested that the relatively small steric requirements of ligands such as $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ are partly responsible for their ability to stabilise unusual co-ordination geometries and oxidation states, no attempts to quantify such effects, for example by examining cone angles, appear to have yet been made.

For ligand backbones, it would be anticipated that these will have a steric and electronic effect on the ligand atoms. A 'C$_2$' backbone is likely to be optimum for complex stability, particularly if rigid (cis-vinyl or o phenyl), because of the favourability of five-membered (P-C-C-P-M) chelate rings. The electronic influence of o-phenylene backbones has been discussed$^{23}$ and it was concluded that $\text{C}_6\text{H}_4(\text{EMe}_2)$ (E = P,As) are essentially "innocent" ligands, and the o-phenylene linkage does not take a significant part in delocalising the additional electron deficiency at the metal on oxidation.

1.6 Neutral Group Vb and Group VIb Donor Ligands

In addition to the vast range of monodentate tertiary Group Vb ligands E R' R" R"', (E = P,As, Sb), a wide variety of bidentate ligands has been prepared with these donor atoms. Table 1.61 (page 15) shows some of the more important examples. References 34 and 39 give details of the synthetic routes available, including some for 'mixed' donor ligands. Among current limitations in synthetic organo-Group Vb chemistry, the lack of conventional routes to the ligands cis-Me$_2$PCHCHPMe$_2$ and cis-Me$_2$SbCHCHSbMe$_2$ and the failure to incorporate -CH$_2$CH$_2$- backbones into methyl arsine and stibine polydentate ligands are outstanding. For phosphorus and
### Table 161

Bidentate Phosphorus, Arsenic, or Antimony Donor Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>P</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_2\text{ECH}_2\text{CH}_2\text{EMe}_2$</td>
<td>/</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{ECH}_2\text{CH}_2\text{EPh}_2$</td>
<td>/</td>
<td>/</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}_2\text{ECH}_2\text{CH}_2\text{CH}_2\text{EMe}_2$</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{ECH}_2\text{CH}_2\text{CH}_2\text{EPh}_2$</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

![Chemical Structures]
<table>
<thead>
<tr>
<th>Ligand</th>
<th>P</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n R R'</td>
<td>n R R'</td>
</tr>
<tr>
<td>CH₂-ER₂</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>Me-C—CH₂-ER₂</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>R-E [(CH₂)ₙ-ER₂]</td>
<td>2 Me</td>
<td>3 Me</td>
</tr>
<tr>
<td>2 Ph</td>
<td>3 Ph</td>
<td></td>
</tr>
<tr>
<td>R-E [(CH₂)ₙ-ER₂]</td>
<td>Ph</td>
<td>Me</td>
</tr>
<tr>
<td>Ph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-E [(CH₂)ₙ-ER₂]</td>
<td>2 Me</td>
<td>3 Me</td>
</tr>
<tr>
<td>2 Ph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-E [(CH₂)ₙ-ER₂]</td>
<td>2 Ph</td>
<td></td>
</tr>
<tr>
<td>E[(CH₂)ₙ-ER₂]</td>
<td>Ph</td>
<td>Me</td>
</tr>
<tr>
<td>Ph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R'-E — [(CH₂)ₙ — ER₂</td>
<td>2 Me Ph</td>
<td>2 Me Ph</td>
</tr>
<tr>
<td>2 Ph</td>
<td>3 Me Ph</td>
<td></td>
</tr>
<tr>
<td>E(R)—[(CH₂)ₙ—ER₂</td>
<td>3 Me</td>
<td></td>
</tr>
<tr>
<td>E(R)—(o-C₆H₄)—ER₂</td>
<td>Me</td>
<td></td>
</tr>
</tbody>
</table>
arsenic, a wide variety of tri- and tetradeutate ligands are available (Table 1.62) and even some penta- and hexadentate ligands have been made, although the syntheses are often lengthy, tedious and give poor yields. These ligands are less likely to be of use in 3d metal chemistry as, often, some of the donors can be displaced in their complexes by halide ions. As trivalent phosphorus and arsenic moieties are good reducing agents, this is important in attempts at oxidation of complexes, as any 'free' P or As donors would be preferentially oxidised.

The Group VIb donors S and Se have also been incorporated into a number of bi- and tridentate ligands. These, however, are poorer σ-donors than the Group Vb ligands and generally form unstable complexes with the 3d metal ions.

The use of abbreviations for the ligands used in this study has been avoided. Where written formulae are confusing, structures have been drawn. Abbreviations for ligands in the literature are often inconsistent. For example, while the ligand Ph₂PCH₂CH₂PPh₂ has been referred to as diphos, 2-phos, dpe, dppe etc., the name diphos has also been used for cis Ph₂PCH₂CH₂PPh₂ and o-C₆H₄(PMe₂)₂!

1.7 Physical Techniques in High Oxidation State Chemistry of 3d Metals

Magnetism

The magnetic properties of 3d complexes can be useful as a guide to stereochemistry and oxidation state. Although this generally applies to high oxidation states, which for reasons to be discussed later are usually low-spin, the presence of an unpaired electron as revealed by magnetic moment determinations does not give information about the locality of that electron. For Ni(III) (d⁷, low-spin), one would expect a magnetic moment of ca 1.7-2.0 B.M.,
but this also applies to a Ni(II) (d\(^8\), diamagnetic) complex of a cation radical ligand. Another drawback is that Ni(IV) (d\(^6\), low spin) cannot be distinguished from Ni(II) (d\(^8\) square planar or square pyramidal, low spin). However, for distinguishing the stereochemistries of Ni(II) starting materials, especially planar from tetrahedral and square pyramidal from octahedral (d\(^8\), high spin) the bulk magnetic properties are useful. Also, the magnetic moment of a bulk Ni(III) sample is a good guide to its authenticity, where esr spectra and analysis may not distinguish well between pure Ni(III) and Ni(II) - Ni (III) mixtures. For iron (IV) (d\(^4\), low spin) the magnetic properties are still a matter of dispute \(^{23,25}\) but are potentially useful.

**Electron Spin Resonance**

Used in conjunction with X-Ray crystallography, this is potentially the technique **par excellence** for the determination on single crystals, of the distinction between genuine Ni(III) and Ni(II)-stabilised cation radical ligands. The interest in this technique may be gauged from the fact that although \([\text{Ni}(\text{C}_6\text{H}_4(\text{AsMe}_2)_2)^2\text{X}_2]^+\) and \([\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)_2)^{12}\text{X}_2]^+\) \(^{23}\) were, until this study, the only complexes of their type, both have been intensively studied in this way \(^{41,42}\).

However, for complexes of lower symmetry and stability, problems present themselves. A suitable diamagnetic host lattice (of approximately the same geometry) must be available and crystals of the material should be relatively easily grown. If these problems are insurmountable, esr spectra of powders or frozen solutions, and liquid solutions, can also provide some information, but care is required in its interpretation.

**Nuclear Magnetic Resonance**

As Ni(III) and Fe(IV) complexes are paramagnetic this technique is potentially only of use for Ni(IV), but solubility and
solution stability would present problems. No studies have been published to date, whereas extensive work on Pt(IV), and a few papers on Pd(IV), have appeared.

Vibrational Spectroscopy

Use of these techniques require few special comments. The deep colour of high oxidation state 3d complexes restrict the usefulness of laser Raman measurements. Where there are not too many ligand vibrations obscuring them, location of the metal-halogen stretching frequencies can be a useful guide to oxidation state, although for low symmetry complexes the number of metal-halogen vibrations is of little use in assigning stereochemistry, especially when no precedents exist in the literature.

Electronic Spectroscopy

Although, in contrast to 4d and 5d complexes, transitions of d-d character have been observed for some Ni(III)-phosphine complexes, some bands are obscured by charge transfer transitions, which move to lower energies on oxidation. The position of the bands which are observed can establish differences between the stereochemistries in complexes of different ligand types, but cannot be used to determine absolute geometry. The technique does, however, have value in establishing the stereochemistry of Ni(II), Fe(II) and Fe(III) starting materials, since many complexes of these ions are known, and their electronic spectra quite well-understood.

X-Ray Diffraction

The usefulness of this technique for determination of solid state structures needs no comment. However, practical difficulties of growing suitable crystals of unstable or reactive materials and
storing selected crystals before and during data collection without their deterioration need to be overcome.

Electrochemistry (Cyclic Voltammetry)

The technique of cyclic voltammetry is commonly employed to investigate redox systems. The potential is swept linearly with time, between a minimum and maximum value relative to a standard electrode, usually Hg₂Cl₂//HgCl₂ (the so-called calomel electrode) or Ag//Ag⁺, whilst the current flow is monitored. It has the advantages of showing the electrochemical reversibility of a process and can sometimes allow a mechanism to be postulated. However, previous studies have shown that certain restrictive rules apply to the usefulness of the technique. The most important of these is that 'electrochemical' kinetics and/or thermodynamics may prevent a process from occurring in the cell where 'chemical' conditions favour it. For example, whilst Pt(L-L)Cl₄ (L-L = bidentate ligand) could be synthesised by Cl₂/CCl₄ oxidation of Pt(L-L)Cl₂, electrochemical oxidation of Pt(L-L)Cl₂ could not be observed by cyclic voltammetry. ³₂ This could be because in the electrochemical experiment, the reaction was governed by the chemical difficulty of the process \( \text{Pt}(\text{L}-\text{L})\text{Cl}_2 \rightarrow^\text{ne} \text{Pt}(\text{L}-\text{L})\text{Cl}_2^{\text{N}^+} \), which is likely to be unfavourable.

The usefulness of electrochemical measurements is therefore likely to be restricted to systems where there is either a fast equilibrium involving a species with the same co-ordination geometry as the oxidised material, or where the oxidised and reduced species have the same co-ordination number (for example, in the system \( \text{Ir}(\text{L}-\text{L})\text{Cl}_4 \rightarrow^\text{e} \text{Ir}(\text{L}-\text{L})\text{Cl}_4^{52} \)).
Other Techniques

Mossbauer spectroscopy is, of course, applicable to iron (\(^{57}\)Fe), but its potential usefulness is limited by the difficulty of collecting data on samples with the low natural abundance of this isotope, especially where the metal is co-ordinated to strong \(^{37}\)Fe-absorbers like As and Br. Also, as the chemical shift for low-spin Fe(II), Fe(III) and Fe(IV) complexes has been found to be similar, simple measurements are unlikely to be of any assistance in characterisation.
References


CHAPTER 2

THE HIGHER OXIDATION STATES OF NICKEL;

A LITERATURE SURVEY
SECTION 2.1

INTRODUCTION

The aims of this study have been summarised (page 1). In this Chapter, literature pertaining to the study of Ni(III) and Ni(IV) will be reviewed. Particular attention will be paid to systems involving ligands other than phosphines and arsines, which nevertheless involve complexes whose properties bear profitable comparison with those synthesised in the course of this work. Little data is available on the few Ni(III) and Ni(IV) complexes of heavy Group Vb donor atoms, and what is available will be collated and discussed with the results of this study in Chapter 3. Three recent reviews give a fuller treatment of the more exotic organometallic, oxide and fluoride complexes. \(^1\)\(^{11}\)\(^{12}\)\(^2\) as well as a briefer treatment of N-donor macrocycles and other systems discussed in the following pages.

Nickel (II) displays a near-unprecedented range of co-ordination geometries and two common spin states (S = 0 and S = 1). Table 2.11 summarises this range, with specific examples. As the synthesis of Ni(III) and Ni(IV) complexes use Ni(II) complexes as starting materials (page 12), the chemistry of those Ni(II) complexes is of interest and a short review of this is included (Section 2.2).
Table 2.11 Co-ordination Geometries and Spin States Found for Ni (II) - Some Examples

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Spin State ($S =$)</th>
<th>Example</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square planar</td>
<td>0</td>
<td>$[\text{Ni(dimethylglyoxime)}_2]$</td>
<td>11</td>
</tr>
<tr>
<td>Square planar</td>
<td>0</td>
<td>$[\text{Ni(PET}_3)_2\text{Cl}_2]$</td>
<td>2</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>1</td>
<td>$[\text{NET}_4]_2[\text{NiX}_4](X = \text{Cl,Br,I})$</td>
<td>17</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>1</td>
<td>$[\text{NI(PPh}_3)_2\text{Br}_2]$</td>
<td>17</td>
</tr>
<tr>
<td>Trigonal Bipyramidal</td>
<td>0</td>
<td>$[\text{Ni[As(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3]}\text{X}]^+$</td>
<td>51</td>
</tr>
<tr>
<td>Trigonal Bipyramidal</td>
<td>1</td>
<td>$[\text{Ni[MeN(CH}_2\text{CH}_2\text{NMe}_2)_2]}\text{Br}_2$</td>
<td>48</td>
</tr>
<tr>
<td>Square Pyramidal</td>
<td>0</td>
<td>$[\text{Ni[MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2}_2]}\text{Br}_2$</td>
<td>49</td>
</tr>
<tr>
<td>Square Pyramidal</td>
<td>1</td>
<td>$[\text{Ni<a href="NCS">(Et}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{AsPh}_2</a>}_2]_b$</td>
<td>74</td>
</tr>
<tr>
<td>Square Pyramidal</td>
<td>0</td>
<td>$[\text{Ni[O-C}_6\text{H}_4(PPh}_2)(\text{SMe})_2\text{l}]\text{ClO}_4$</td>
<td>1</td>
</tr>
<tr>
<td>Tetragonal$^c$</td>
<td>0</td>
<td>$[\text{Ni[O-C}_6\text{H}_4(AsMe}_2)_2\text{l}_2]$</td>
<td>36</td>
</tr>
<tr>
<td>Octahedral$^c$</td>
<td>1</td>
<td>$[\text{Ni(NH}_3)_6]\text{SO}_4$</td>
<td>11</td>
</tr>
</tbody>
</table>

Notes:  
(a) "Geometry" refers only to co-ordination environment, not symmetry. 
(b) Only the N atoms are co-ordinated in this complex; the As remains non-complexed.  
(c) The term 'tetragonal' is used here to define a complex which is essentially square planar but with weakly interacting axial halide ions. This is common practise in this area of Ni (II) chemistry$^3_6$, where 'octahedral' is used to refer specifically to paramagnetic 6-co-ordinate complexes.
SECTION 2.2

SOME CHEMISTRY OF NICKEL(II)

2.21 Monodentate Phosphine Complexes

The complexes $\text{Ni}(L)_2X_2$ ($L =$ monodentate phosphine, $X =$ Br, Cl) are well-known for a wide variety of $L$ and their spectra, properties and structures are generally well-understood. For $L =$ PR$_3$ ($R =$ Me, Et, nBu)$_2$, $\text{Ni}(L)_2X_2$ are red and diamagnetic. They exhibit low dipole moments in benzene solution$^2$, and an X-ray crystal structure analysis of $\text{Ni}(\text{PET}_3)_2\text{Br}_2$ established a trans-square planar structure.$^4$ The electronic spectra$^3,6,10$ are characteristic, with the first observed band, at ca 25,000 cm$^{-1}$, quite sharp and of moderate molar extinction coefficient. This distinguishes the square planar geometry from tetrahedral complexes, which have absorptions at lower energies and absorbances$^8$ (Figure 2.211). Infra red absorptions of mainly metal halogen and metal-phosphorus character have been assigned by the metal isotope technique, using $^{58}\text{Ni}(\text{PET}_3)_2X_2$ and $^{62}\text{Ni}(\text{PET}_3)_2X_2$ ($X =$ Cl, Br).$^5$

On the basis of their physical and spectroscopic properties, the trialkyl phosphite complexes $\text{Ni}(\text{P(OR)}_3)_2X_2$ ($X =$ Cl, Br; $R =$ Me, Et, Pr$^n$, Pr$^i$)$^9$ were assigned trans-square planar geometry.

Trimethylphosphine is capable of forming five-co-ordinate nickel complexes $\text{Ni}(L)_3X_2$, probably because of its small steric requirements. The crystal structure of $[\text{Ni(PMe}_3)_3\text{Br}_2]$ showed two independent molecules in the crystal, both of distorted trigonal bipyramidal co-ordination, with cis-bromines in the equatorial plane$^{11}$ (Figure 2.212). In solution the complexes exhibit dissociation equilibria which can be reversed by addition of excess ligand.

$$\text{Ni(PMe}_3)_3X_2 \rightleftharpoons \text{Ni(PMe}_3)_2X_2 + \text{PMe}_3.$$
Figure 2.211 Comparison of the electronic spectra of $[\text{Ni(PMe}_3\text{)}_2\text{Cl}_2]$ (square planar; solid line) and $[\text{Ni(PPh}_3\text{)}_2\text{Cl}_2]$ (tetrahedral; broken line). Both are diffuse reflectance spectra, recorded using BaSC₄ as diluent and reference. Vertical scale is absorbance, in arbitrary units.
Some controversy has arisen in the literature over reports that Ni(P(Cyclohexyl)$_3$)$_2$X$_2$ (X = Cl, Br, I) exhibit planar $\rightarrow$ tetrahedral equilibria in solution, as evidenced by electronic spectra and solution magnetic measurements.\textsuperscript{12} Later work\textsuperscript{13} showed that these measurements were in error; in spite of the unusually bulky phosphine and the possibly long M-P bonds, the complexes are trans-planar in the solid and in solution.
The dialkyl aryl phosphines PPhMe₂ and PPhEt₂ also give trans-square planar complexes, but the alkyldiaryl phosphines are unusual. Their complexes exhibit well-established planar and tetrahedral equilibria, and an X-ray study of \([\text{Ni} \{ \text{Ph}_2 \text{P(CH}_2\text{Ph})_2 \} \text{Br}_2]\) showed the presence of both square planar and tetrahedral isomers in the same crystal, evidently as this was the most effective packing arrangement. Proton n.m.r. techniques have been used to examine the position of equilibrium for a number of complexes, and the steric and electronic factors contributing to this.

The triaryl phosphines (including PPh₃) form tetrahedral complexes \(\text{NiL}_2\) when the ligand and nickel (II) salts are combined in a poor donor solvent such as n-butanol or glacial acetic acid.

The complex \([\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]\) when recrystallised from cold, concentrated \(\text{CH}_2\text{Cl}_2\) solution, appears to form the trans square planar isomer as a red powder. This spontaneously rearranges to the blue tetrahedral form on storage. No spectral data was obtained, however.

A wide variety of triaryl phosphine complexes has been synthesised together with some anions of type \(\text{R}_4\text{N}[\text{Ni}(\text{PPh}_3)\text{X}_2]\). They have magnetic moments of 3.0 - 3.4 B.M., consistent with tetrahedral, high-spin geometry, and this has been confirmed by X-ray crystallography in a number of cases. Electronic spectral data has been obtained for many of these complexes. In particular, the absorbance at ca 11,000 cm⁻¹, with a shoulder at ca 8500 cm⁻¹, is of diagnostic value. Additionally, far infra-red spectra have been obtained which are characteristic of the tetrahedral isomers and enable easy distinction from the trans-planar complexes.

2.22 Miscellaneous Monodentate Ligands

Monodentate tertiary arsines and stibines, by contrast with phosphines, show little tendency to co-ordinate to the
relatively 'hard' nickel (II). The few complexes that have been made are stable in solution only in the presence of a large excess of ligand and are sensitive to moisture. They decompose in donor solvents. Monodentate thio- and selenoethers show no inclination to co-ordinate to nickel (II).

While the octahedral ammine complex [Ni(NH₃)₆]²⁺ is well-known, much less attention has been paid to primary, secondary and tertiary amine-nickel (II) co-ordination chemistry. Uhlig and Staiger synthesized a few complexes of Me₃N, Me₂NH and Et₂NH, but could only make tentative structural assignments. The secondary amines formed complexes of stoichiometry Ni(L)₂X₂ (X = Cl, Br, I) and these were thought to be tetrahedral or octahedral with, presumably, bridging halogens. Phosphate- and arsine-oxide complexes of nickel (II) have been obtained, and shown to be tetrahedral monomers, [Ni(R₃P=O)₂X₂] (R = aryl group; X = Cl, Br, I).

2.23 Aryl-Substituted Bidentate Ligands

The binding of bidentate phosphate and arsine chelate ligands in square planar complexes has received some coverage in a recent review. The complexes [Ni(L-L)X₂] (L-L = Ph₂PCH₂PPh₂; n = 1-4; X = Cl, Br, I) have all been investigated to a varying extent.

Contrary to an earlier report, chelate complexes of nickel (II) with Ph₂PCH₂PPh₂ can be obtained and are stable, although with excess ligand, [Ni(Ph₂PCH₂PPh₂)₂X₂] form, with the ligands behaving as monodentates. The [Ni(Ph₂PCH₂CH₂PPh₂)X₂] are diamagnetic and square planar in the solid state and in solution, but [Ni(Ph₂P(CH₂)₃PPh₂)X₂] display a cis square planar to tetrahedral isomerisation in solution which has been evaluated by ¹H nmr measurements. The solid complexes, however, are diamagnetic, as indicated by Gouy measurements and diffuse reflectance spectra.
The ligand $\text{Ph}_2\text{P}^\cdot(\text{CH})_4\text{PPh}_2$ forms 1:1 complexes with nickel (II) halides, and these are reportedly of distorted pseudo-tetrahedral geometry. Once formed, the complexes are extremely insoluble, as are those of $\text{Ph}_2\text{P}^\cdot(\text{CH})_5\text{PPh}_2$. This may indicate the presence of bridging ligands, as the complexes of $\text{Ph}_2\text{P}^\cdot(\text{CH})_2\text{O(CH)}_2\text{PPh}_2$ (in which the oxygen is unco-ordinated) are soluble, and X-ray crystallography has revealed that $[\text{Ni(Ph}_2\text{P}^\cdot(\text{CH})_2\text{O(CH)}_2\text{PPh}_2]_\text{Cl}_2$ is a pseudo tetrahedral monomer.

Studies of nickel (II) complexes with bidentate phosphines containing long backbones, sometimes incorporating potential donor atoms such as O or N, appear to be continuing.

Other bidentate ligands, with the more rigid cis-vinyl or cis-phenylene backbones, form cis planar nickel (II) complexes whose behaviour in solution is wholly conventional, uncomplicated by geometrical isomerism. Among these complexes $[\text{Ni(cis-Ph}^\cdot\text{PCHCHPPh}^\cdot)\text{X}_2]$ ($X = \text{Cl,Br,I}$) and $[\text{Ni(o-C}_6\text{H}_4\text{(EPh}_2\cdot)(E'^\cdot\text{Ph}_2)]_\text{X}_2$ ($E = E' = \text{P}^\cdot$, $E = \text{P}$, $E' = \text{As}^\cdot$, $X = \text{Cl,Br,I}$) are well-characterised and their electronic spectra are distinctive. Tentative assignments of some far infra-red bands to vibrations of predominantly $\nu_{\text{M-X}}$ character have been made for some examples.

Ligands containing phenyl-substituted arsine and stibine donors are more reluctant to co-ordinate to nickel (II) and poor $\sigma$-donor solvent mixtures, especially n-butanol/dichloromethane, have to be used to isolate complexes. The $\text{Ni(L-L)}\text{X}_2$ ($L-L = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$, $\text{cisPh}_2\text{AsCHCHAsPh}_2$, $\text{o-C}_6\text{H}_4\text{(AsPh}_2\cdot)$ $X = \text{Br,I}$) are conventional diamagnetic planar complexes.

A limitation of importance to attempts at formation of nickel (III) complexes is that nickel (II) chloride will not form complexes with these ligands. The ligand $\text{o-C}_6\text{H}_4{(\text{PPh}_2\cdot)}_2\text{SbPh}_2$ reacts with $\text{NiBr}_2$ in n-butanol to give a 1:1 complex which electronic spectral and magnetic data suggested was probably a mixture of planar and pseudo-octahedral isomers, although once formed the
complex was insoluble in all solvents in which it did not decompose.

Whereas the planar \([\text{Ni}(L-L)X_2]\) and (to a lesser degree) the tetrahedral \([\text{Ni}(L-L)Br_2]\) \((L-L = \text{Ph}_2\text{P(CH}_2)_4\text{Ph}_2, \text{trans-Ph}_2\text{PCHCHPPPh}_2)\) are well-documented, \(\text{Ni}(L-L)_2X_2\) \((L-L = \text{aryl-substituted bidentate ligand}; X = \text{Cl}, \text{Br}, \text{I})\) are still the subject of controversy.

Booth and Chatt first isolated \(\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X_2\) \((X = \text{Br}, \text{I})\) although no spectroscopic data was recorded. Later, it was suggested on the basis of electronic spectral, magnetic and conductivity data that the complexes are probably planar \([\text{Ni}(\text{ligand})_2]X_2\) in the solid state, with weak axial Ni-X interaction. In solution, the equilibrium (a) was proposed in \(\text{CH}_3\text{NO}_2\) and

\[
\begin{align*}
\text{(a) } [\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X_2] & \rightleftharpoons \text{[Ni(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X]_2 + \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \\
\end{align*}
\]

\(\text{CH}_2\text{Cl}_2\) solution, on the grounds of electronic spectroscopic data, while equilibrium (b) was thought not to occur. However, Morassi examined

\[
\begin{align*}
\text{(b) } [\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X_2] & \rightleftharpoons [\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X]X \\
\end{align*}
\]

the conductivity and electronic spectrum of solutions of \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X_2]\) in the presence of varying concentrations of free ligand, and concluded that, in nitroethane, equilibrium (b) occurred to a measurable extent.

The cis vinyl ligand cis-\(\text{Ph}_2\text{PCHCHPPh}_2\), by comparison, does not form yellow \([\text{Ni}(L-L)_2]X_2\) \((X = \text{halide})\), but in the presence of the bulky \(\text{BPh}_4^-\) anion, pentaco-ordinate
[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X]B\text{Ph}^+ (X = \text{Br}, \text{I} \text{ only}) \ can \ be \ isolated. \ \text{Attempts} \ to \ isolate \ [\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2X]B\text{Ph}^+, \ however, \ failed. \ With \ non-co-ordinating \ anions \ (Y = \text{BF}_4^-, \text{ClO}_4^-), \ planar \ 2:1 \ complexes \ [\text{Ni}(\text{L-L})_2]Y_2 \ can \ be \ obtained \ readily \ (L-L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \ \text{cis}-\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \ \text{o-C}_6\text{H}_4(\text{PPh}_2)_2)^{31} \ and \ these \ maintain \ their \ integrity \ in \ solution.

The electronic effects of substituents upon a donor atom can be varied without significantly altering the steric requirements of the ligand by substitution of -F for -H in the substituent. The ligand \(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2\) has been synthesised and its complexes compared with those of the unfluorinated analogues.\(^{76}\)

While \(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2\) was capable of giving square pyramidal \(\text{[Ni(ligand)]_2X]ClO}_4\) on refluxing a 1:1:4 mixture of \text{NiX}_2, \text{Ni(C1O}_4)_2, \text{6H}_2\text{O} \ and \text{ligand} \text{in ethanol-dichloromethane}, \text{the fluorinated ligand would not yield isolable five-co-ordinate complexes.}\(^{76}\) Despite this the spectra of the \(\text{[Ni(ligand)]_2}^{2+}\), and \(\text{[Ni(ligand)]X}_2\), were very similar for the fluorinated and non-fluorinated ligands.\(^{31}\)

\section*{2.24 Methyl-Substituted Bidentate Ligands}

Methyl-substituted phosphines and arsines behave very differently to the phenyl analogues. Nyholm\(^{35}\) found that the chelate \(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\) gave exclusively 2:1 complexes in alcoholic solutions, of type \(\text{[Ni(L-L)]_2X}_2\), \(\text{[Ni(L-L)]_2X}^+Y\) and \([\text{Ni(L-L)]_2}Y_2 (X = \text{Cl}, \text{Br}, \text{I} ; Y = \text{ClO}_4^-)\). It was later suggested that the \(\text{[Ni(L-L)]_2X}_2\) complexes are in fact five-co-ordinate in solution,\(^{37}\) but X-ray data on \(\text{Ni(L-L)}_2I_2\) shows that this, at least, is six co-ordinate in the solid phase, although with a very large tetragonal distortion (very long Ni-I bonds). The weakness of the Ni-X interactions in these (nominally) six co-ordinate species is responsible for the observed diamagnetism.\(^{37}\) The related ligands \(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\), \(\text{o-C}_6\text{H}_4(\text{AsMe}_2)(\text{PMe}_2)\),\(^{38,39}\) and \(\text{o-C}_6\text{H}_4(\text{AsMe}_2)(\text{SbMe}_2)\),\(^{78}\), give similar complexes, with closely similar spectral properties. On replacing a 'soft'-EMe_2
(E = P, As, Sb) group with a 'hard'-NMe2 group, however, different behaviour is observed. The ligand \( \sigma-C_6H_4(PMe_2)(NMe_2) \) formed only square planar \([Ni(L-L)X_2]\), whatever Ni:ligand ratio was chosen. Use of a 1:1:4 mole ratio of nickel (II) halide, nickel (II) perchlorate and ligand, however, yielded the square pyramidal \( (P_2N_2X) \) donor set \([Ni(ligand)_2X]ClO_4\) and nickel (II) perchlorate alone gave planar \([Ni(ligand)_2](ClO_4)_2\). In contrast was the behaviour of \( \sigma-C_6H_4(NMe_2)(AsMe_2) \), which gave only 2:1 complexes, \([Ni(\sigma-C_6H_4(NMe_2)(AsMe_2)]_2X_2\). These were green, paramagnetic and therefore octahedral. The single infrared band of \( \nu_{Ni\cdot\cdot\cdotX} \) character suggested trans \( X \) groups and in solution, spectra similar to those of pseudotetrahedral \([Ni(diamine)X_2] \) were observed, suggesting dissociation of the \(-AsMe_2\) groups. Infra red criteria and electronic spectra suggested that the \([Ni(\sigma-C_6H_4(AsMe_2)(NMe_2)]X_2\)ClO_4\) are not, in fact, square pyramidal, but square planar with one \(-AsMe_2\) group unco-ordinated. The preferential achievement of \(-NMe_2\) co-ordination in these complexes is interesting. No evidence for \(-OMe\) co-ordination in the nickel (II) complexes of \( \sigma-C_6H_4(PMe_2)(OMe) \) could be found and the ligand behaved as a simple dialkylaryl monodentate phosphine, forming trans planar \( Ni(L)_2X_2 \) (\( X = Cl, NCS \)).

As already stated, of the series P, As, Sb, antimony is the most reluctant to co-ordinate to Ni (II). However, bidentate, methyl-substituted antimony ligands \( \sigma-C_6H_4(SbMe_2)_2 \) and \( Me_2Sb(CH_2)_3SbMe_2 \) do form nickel (II) complexes. The \( \sigma \)-phenylene ligand gives \([Ni(ligand)_2Cl]Cl \) (by analogy with the corresponding arsine complex). The ligand 1,3-bis(dimethylstibino) propane also gives five-co-ordinate \([Ni(ligand)_2X]ClO_4\) (\( X = Cl, Br, I \)) and with nickel (II) perchlorate, the increased tendency of antimony to promote five-co-ordination is shown by the formation of purple \([Ni(ligand)_2(H_2O)]ClO_4\).

The effect of fluorine substitution in ligand backbones
was mentioned earlier. In a brief study of $\sigma$-C$_6$F$_4$(AsMe$_2$)$_2$, it was found that the $\sigma$-donor properties of this arsine were significantly weaker than those of $\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$, since green high-spin [Ni$\sigma$-C$_6$F$_4$(AsMe$_2$)$_2$X$_2$] (X = Cl, Br, I) were formed on treatment of NiX$_2$·nH$_2$O in ethanol with the ligand. In nonpolar solvents the stereochemistry apparently remained pseudo-octahedral, but in dilute nitromethane solution, pink [Ni(ligand)$_2$X]$^+$, analogous to [Ni($\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$ X]$^+$, formed. These could be isolated as perchlorate salts by treating solutions of [Ni(ligand)$_2$] (ClO$_4$)$_2$ with one equivalent of LiX.

Although in hot, concentrated ethanol solution, it is possible to make the [Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)X$_2$] from the 2:1 complex and NiX$_2$, this cannot be done for $\sigma$-C$_6$H$_4$(EMe$_2$)$_2$ complexes (E = P, As). Nyholm did succeed in making [Ni$\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$] (X = Br, I) by treating [Ni$\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$(CO)$_2$] with X$_2$ or, better, HX (X = Cl, Br, I). These cis-planar complexes rearrange in polar solvents (acetone, ethanol) to Ni(ligand)$_2$X$_2$ and NiX$_4$²⁻, their instability being in the order Cl > Br > I. In one of the first reports of the properties of $\sigma$-C$_6$H$_4$(EMe$_2$)$_2$, the carbonyl [Ni(CO)$_2$($\sigma$-C$_6$H$_4$(EMe$_2$)$_2$)] was made, but as the diphosphine was only accessible in very low yield at that time, no nickel (II) derivatives were reported.

Although conventional syntheses cannot be used to prepare Me$_2$AsCH$_2$CH$_2$AsMe$_2$, treatment of cis-1,2 dichloroethylene with NaAsMe$_2$ in THF yields a 90% trans-10% cis mixture of 1,2-bis (dimethylarsino) ethylene. By irradiating solutions of NiX$_2$ with this mixture with UV light, the cis/trans ratio can significantly be improved, and reasonable yields of [Ni(cis-Me$_2$AsCHCHAsMe$_2$)$_2$X$_2$] can be obtained. These complexes are closely similar to analogous complexes of $\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$ in all respects.
2.25 Hybrid Group Vb - Group VIb Donors

The substitution of a Group VIb donor atom for a Group Vb donor in a given ligand results in interesting changes in the properties of normal oxidation state complexes. For example, the ligands \( \text{C}_6\text{H}_4(\text{PPh}_2)(\text{EMe}) \) (E = S, Se) \(^{46}\) give four-, five- and six-co-ordinate complexes. The \([\text{Ni}(\text{C}_6\text{H}_4(\text{PPh}_2)(\text{XMe}))\text{Cl}_2]\) is planar and diamagnetic, \([\text{Ni}(\text{C}_6\text{H}_4(\text{PPh}_2)(\text{SMe}))_2\text{Br}]\text{ClO}_4\) is square pyramidal and also diamagnetic, but the six-co-ordinate \([\text{Ni}(\text{C}_6\text{H}_4(\text{PPh}_2)(\text{SMe}))_2\text{Cl}_2]\) is paramagnetic and bright green, and its electronic spectrum is consistent with pseudo-octahedral coordination. \(^{46}\) Nickel (II) perchlorate gives the planar, yellow, diamagnetic \([\text{Ni}(\text{ligand})_2\text{ClO}_4]\) as expected. On addition of \(X^-\), this is instantly converted to the purple, five-co-ordinate \([\text{Ni}(\text{ligand})_2\text{X}\text{ClO}_4]\). The selenoether-phosphine ligand is similar, although electronic spectra indicate that the Se donor exerts a lower ligand field than S. The dimethylphosphine-sulphur analogue \(\text{C}_6\text{H}_4(\text{PMe}_2)(\text{SMe})\) has been synthesised \(^{47}\); however, to date, no metal complexes have been reported.

2.26 Multidentate Ligands

The interest in five-co-ordination in transition metal complexes \(^{48}\) has led to a wide variety of tri- and tetradentate P and As donor ligands being synthesised. Early work was confined to tri- and tetradentate alkyl arsines. The ligand \(\text{Me}_2\text{As(CH}_2)_3\text{As(Me)}(\text{CH}_2)_3\text{AsMe}_2\) (TAS) was found to give square pyramidal, diamagnetic \([\text{Ni}(\text{TAS})\text{Br}_2]\). X-ray crystallography showed that, as expected on steric grounds, the three As donors occupy the basal plane (Figure 2.261) \(^{49}\), and the axial Ni-Br bond is long. This weak bond is attributed to the occupancy of the \(\sigma\)-antibonding \(d^2_2\) orbital by two electrons (low spin \(d^8\)).
which is also advanced as an explanation for the weak axial Ni-X interactions in the [Ni(L-L)\_2X]\(^+\) species (L-L = bidentate phosphine or arsine). A pure complex of TAS with NiCl\(_2\) could not be obtained. The corresponding tetra-arsine As(CH\(_2\)CH\(_2\)CH\(_2\)AsMe\(_2\))\(_3\) was at first thought to form only Ni(III) derivatives [Ni\{As(CH\(_2\)CH\(_2\)CH\(_2\)AsMe\(_2\))\(_3\}\}X\(_2\)]\(^+\)\(_2\), but later workers found that the complexes were actually the deep blue, diamagnetic trigonal-bipyramidal [Ni(tetradentate)X]\(^+\), better isolated as their perchlorate or tetrphenylborate salts, and the original complexes were probably [Ni(tetradentate)X]\(_2\)NiX\(_4\). The electronic spectra were recorded and discussed in terms of spectrochemical and nephelauxetic effects (Figure 2.262 shown overleaf).

More recently, the triphosphines Ph\(_2\)PCH\(_2\)CH\(_2\)P(Ph)CH\(_2\)CH\(_2\)PPh\(_2\) and MeC(CH\(_2\)PPh\(_2\))\(_3\) have become available commercially. An early report suggested that the latter formed five-co-ordinate square pyramidal [NiMeC(CH\(_2\)PPh\(_2\))\(_3\}]Br\(_2\)], with one -PPh\(_2\) group loosely co-ordinated and comparatively easily displaced by quaternisation with Mel. It has since been suggested that it is possible to

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**Figure 2.261**

*a\(^1\) = 2.27, a\(^2\) = 2.26, a\(^3\) = 2.26, b\(^1\) = 2.37, b\(^2\) = 2.69 Å.
Angles: b\(^1\)\(^a\) = 92°, b\(^2\)\(^a\) = 93°, b\(^3\)\(^a\) = 93°, b\(^1\)\(^b\) = 111°, b\(^2\)\(^b\) = 88°, b\(^1\)\(^a\) = 154°, b\(^2\)\(^a\) = 88°, a\(^1\)\(^c\) = 90°, a\(^2\)\(^c\) = 175°, a\(^3\)\(^c\) = 91°.
Figure 2.262. Electronic spectrum of two trigonal-

bipyramidal Ni (II) complexes;

\[ \text{[Ni}\{\text{P(\text{CH}_2\text{CH}_2\text{AsMe}_2)}_2\}\text{Cl}\}\text{ClO}_4 \quad \text{and} \quad \text{[Ni}\{\text{As(\text{CH}_2\text{CH}_2\text{AsMe}_2)}_2\}\text{Cl}\}\text{ClO}_4 \]

isolate the complexes in a square planar form with one -\text{PPh}_2 group
unco-ordinated. 53

The linear triphosphine forms square pyramidal complexes
with Ni(II) halides, similar to those with TAS. However, in
solution in polar solvents, the complexes are 1:1 electrolytes,
indicating dissociation of the weakly-bonded axial halide.
This is confirmed by electronic spectroscopy.
Tetradentate phosphines \([\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(Ph)CH}_2]_2\) \((P_4)\) and \(\text{P(CH}_2\text{CH}_2\text{PPh}_2)_3\) \((P-P_3)\) can be synthesised by extensions of the routes used for \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(Ph)CH}_2\text{CH}_2\text{PPh}_2\). Their nickel (II) complexes have been the subject of some investigation. Upon recrystallisation from acetone in presence of excess \(\text{NH}_4\text{PF}_6\), \(\text{Ni}(P_4)\text{Cl}_2\) gave square planar \([\text{Ni}(P_4)](\text{PF}_6)_2\)\(^{54}\), but square pyramidal complexes \([\text{Ni}(P_4)X]^+\) were later found to be stabilised by the large \(\text{BPh}_4^-\) counterion.\(^{55}\) The tripodal \(P-P_3\) gives trigonal bipyramidal \([\text{Ni}(P-P_3)\text{Cl}]\text{PF}_6\) on recrystallising the product of the reaction of \(\text{NiCl}_2\) and the ligand from an acetone solution of \(\text{NH}_4\text{PF}_6\).\(^{54}\) No further work with this ligand appears to have been reported.

### 2.27 Amines and Other Donors

The well-known 1,2-ethanediarnine and its C-substituted analogues 1,2-propanediarnine and 1,2-cyclohexanediarnine, and 1,3-propanediarnine, form octahedral \([\text{Ni(diamine)}]_2\)\(^{2+}\) with nickel (II) halides in aqueous solution.\(^{56}\) Electronic spectra typical of high-spin octahedral nickel (II) \((d^8, S = 1)\) are observed for these complexes\(^{11}\) and their properties are unremarkable. Upon recrystallisation from methanol in the presence of one mole equivalent of \(\text{NiX}_2\), \(\text{Ni(diamine)}_2\text{X}_2\) are obtained.\(^{57}\) These have pseudo-octahedral co-ordination. On the basis of preliminary X-ray data, a dimeric structure \([\text{Ni}_2(\text{diamine})_4\text{X}_2]_2\)\(^{80}\) with bridging \text{cis} halides, was proposed, but later work showed that \(\text{Ni}, \text{X} \text{and N atoms lay on 2-fold axes in the crystal (P2}_1/c, Z = 4)\). Hence a \text{trans}-pseudo-octahedral structure was likely.\(^{81}\) With suitable non-co-ordinating anions, planar \([\text{Ni(diamine)}]_2\)\(^{2+}\) can be obtained.\(^{62}\)

The N-substituted diarnines form different complexes. In particular, on reaction of \(\text{N, N, N', N'-tetramethyl-1,2-ethanediarnine with nickel (II) halides in n-butanol, only 1:1 complexes are obtained.\(^{58}\)
These are pseudo-octahedral, with bridging halogens, in the solid state, but in solution in non-polar solvents display an octahedral-tetrahedral equilibrium, as evidenced by electronic spectroscopy. A very similar ligand, \( \text{C}_6\text{H}_4(\text{NMe}_2) \), gives complexes which are pink, monomeric and tetrahedral, but achieve octahedral co-ordination on reaction with atmospheric moisture, yielding green \( \text{NiC}_6\text{H}_4(\text{NMe}_2)_3(\text{H}_2\text{O})_2\text{X}_2 \).  

Complexes of heterocyclic amines such as 1,10-phenanthroline and 2,2'-bipyridyl have been extensively studied for many years and have been reviewed. Nickel (II) halides yield pink high spin octahedral \( \text{Ni}(L-L)_3\text{X}_2 \) (\( L-L = 1,10\)-phenanthroline, 2,2'-bipyridyl) on combination with the ligands in aqueous solution. On heating in vacuo or, better, in an inert high-boiling solvent (dichlorobenzene, xylene) the cis pseudo-octahedral pale green \( \text{Ni}(L-L)_2\text{X}_2 \) are produced.

Although monodentate thioethers will not co-ordinate to nickel (II) even under anhydrous conditions, bidentate alkyl-substituted thioethers react with anhydrous butanol solutions of nickel halides to give yellow, unstable complexes \( \text{Ni}(L-L)_2\text{X}_2 \) (\( L-L = \text{MeSCH}_2\text{CH}_2\text{SMe}, (\text{Me}_2\text{CH})\text{SCH}_2\text{CH}_2\text{S(CHMe}_2) ; \text{X} = \text{Cl}, \text{Br}, \text{I} \)). These are high spin and pseudo-octahedral; their electronic and infra red spectra are consistent with this description.

2.3 Complexes of Nickel (III) and Nickel (IV)

2.31 Oxide and Fluoride Complexes

In common with many metal oxide systems, nickel oxides containing nickel in a higher valence state than +2 have been claimed in numerous reports over the years, but it is doubtful whether stoichiometric oxides such as \( \text{Ni}_2\text{O}_3, \text{Ni}_3\text{O}_4 \) and \( \text{NiO}_2 \) have been prepared pure. This is despite the widespread application of
"NiO₂" in organic oxidation reactions, recently reviewed. The importance of NiO(OH) in the nickel-cadmium cell has already been mentioned (page 2).

Several ternary oxides of composition \( \text{MNI}^{\text{III}} \text{O}_2 \) \( (M = \text{Li, Na}) \) and \( \text{MNI}^{\text{IV}} \text{O}_2 \) \( (M = \text{Ba,Sr}) \), \( \text{MNI}^{\text{III}} \text{O}_3 \) \( (M = \text{La,Y}) \), have been examined, but this area remains undeveloped. Nickel (IV) has also been stabilised in heteropolyanions and the first report, by Hall in 1907, of nickel (IV) was in \( \text{Ba}_2\text{NiMo}_9\text{O}_{32} \cdot \text{nH}_2\text{O} \). Heteropolyniobates, such as \( \text{Na}_{12}\text{Ni}^{\text{IV}}\text{Nb}_{12}\text{O}_{38} \cdot \text{nH}_2\text{O} \) \( (n = 48-50) \) are also known, in which the nickel atom is octahedrally co-ordinated by oxygen atoms from two Nb₆O₁₉ groups and the Ni-O distances are all 1.87 Å. The periodate anion \( \text{IO}_4^- \) gives such structures as \( \text{MNI}^{\text{IV}}\text{IO}_6 \cdot \text{nH}_2\text{O} \) \( (M = \text{Na,K}) \), which are weakly paramagnetic owing to the presence of some nickel (III) atoms in the lattice.

Binary nickel (III) or nickel (IV) fluorides have not been obtained. Although \( \text{NiF}_3 \) has been estimated to have marginal thermodynamic stability, it could not be prepared in a pure form either by high pressure fluorination or solvolysis of \( \text{NiF}_6^{n^-} \) \( (n = 2,3) \) in anhydrous HF. Complex fluorides \( \text{M}_3\text{NiF}_6 \) \( (M = \text{alkali metal, typically K}) \) and \( \text{M}_2\text{NiF}_6 \) have been fairly well characterised and synthetic procedures resulting in pure samples of Ni(III) or Ni(IV) have now been developed; in the past, samples contaminated with the other oxidation state gave problems in characterisation. See Figure 2.311 overleaf.

While the red \( \text{NiF}_6^{2^-} \) ion is diamagnetic, and generally agreed to be strictly octahedral, \( \text{NiF}_6^{3^-} \) exhibits the expected Jahn-Teller distortion. It has a low spin \( (S = \frac{1}{2}) \) ground state and magnetic and molecular orbital studies together support the existence of a low-lying triplet state which is significantly populated at room temperature.
Figure 2.311 Syntheses of Nickel (III) and (IV)

Oxides and Fluorides - Some Examples

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni + MOH (molten) + O₂</td>
<td>2-4 days</td>
<td>MNiO₂</td>
</tr>
<tr>
<td>NiO + BaO (intimate mixture)</td>
<td>O₂, 500°C, 4 days</td>
<td>BaNiO₃</td>
</tr>
<tr>
<td>NiSO₄ + 2Na₇H₂NbO₁₉ + NaOBr</td>
<td>H₂O, 50°C, 40 minutes</td>
<td>Na₁₂NiIV Nb₁₂O₃₈·5H₂O</td>
</tr>
<tr>
<td>NiSO₄·₆H₂O + 3KCl</td>
<td>200-250°C, F₂ in N₂ (1:1) stream</td>
<td>K₃NiIII F₆</td>
</tr>
<tr>
<td>K₂Ni(CN)₄</td>
<td>1:1 F₂/N₂, 250°C, flow system</td>
<td>K₂NiIV F₆</td>
</tr>
<tr>
<td>Na₂Ni(CN)₄·₃H₂O</td>
<td>300°C, 300 bar F₂</td>
<td>Na₂NiIV F₆</td>
</tr>
<tr>
<td>Li₂Ni(CN)₄·₃H₂O</td>
<td>300°C, 300 bar F₂</td>
<td>Li₂NiIII F₅</td>
</tr>
<tr>
<td>BaNi(CN)₄·₄H₂O</td>
<td>300°C, 140 bar F₂</td>
<td>BaNiIV F₆</td>
</tr>
</tbody>
</table>

Recently, the development of apparatus for handling fluorine at quite high pressures and temperatures has enabled the synthesis of the previously inaccessible Na₂NiF₆, Li₂NiF₅ and
BaNiF$_6$ and preliminary X-ray data was reported for these compounds. Upon attempting the synthesis of BaAuF$_6$ in a Monel-metal autoclave, single crystals of BaNiF$_6$ were unexpectedly obtained. X-ray crystal structure analysis confirmed the previous powder data, which ascribed the BaGeF$_6$ structure (that is, a CsCl-like arrangement of Ba$^{2+}$ and NiF$_6^{2-}$ ions) to the compound.

2.32 Group VIb Donor Ligands

Neutral sulphur and selenium donor atoms are relatively poor $\sigma$-donors and form only weak complexes with nickel (II). Consequently it is not surprising that attempts to oxidise these complexes with halogen resulted only in decomposition, except with iodine, which gave nickel (II) polyiodides (q.v. Chapter 5, page 234).

1,2-Dithiolenes

It is well-known that the square-planar nickel complexes of the 1,2-dithiolenes (Figure 2.32) undergo a series of facile one-electron transfers. While it is generally agreed that the dianion (C) is best described as a nickel (II) complex, some controversy has arisen over the description of the monoanion (b) and the neutral species (a) (alternative descriptions in the Figure). Indeed, it has even been suggested on the basis of X-ray photoelectron spectroscopy that the neutral species and the monoanion and dianion are Ni(0) complexes; their Ni(2p$^{3/2}$) binding energies are similar to those in metallic nickel and in [Ni$^0$(Ph$_2$PCH$_2$CH$_2$P(Ph)Et)(CO)$_2$], rather than those of NiO and K$_2$[Ni(CN)$_4$]. However, difficulties have been encountered in XPES studies with surface decomposition due to the high vacuum, and photoreduction of the sample.

It is now generally accepted that it is unrealistically naive to describe 'a' as a Ni(IV) complex, in view both of the expected reducing character of the dianionic ligands and the spectral
Figure 2.321. Electron Transfer Series for Ni/1,2-Dithiolene Complexes

Alternatively 'a' can be represented as:

\[
\begin{align*}
\text{R} & \quad \text{S} & \quad \text{Ni} & \quad \text{S} & \quad \text{R} \\
\text{R} & \quad \text{S} & \quad \text{Ni} & \quad \text{S} & \quad \text{R}
\end{align*}
\]

and 'b' can be represented as:

\[
\begin{align*}
\text{R} & \quad \text{S} & \quad \text{Ni} & \quad \text{S} & \quad \text{R} \\
\text{R} & \quad \text{S} & \quad \text{Ni} & \quad \text{S} & \quad \text{R}
\end{align*}
\]
and structural properties of the complexes. Specifically, X-Ray crystallography performed on [Ni(S₂C₂Ph₂)₂], [Ph₃PMe][Ni(S₂C₂(CN)₂)₂] and [NMMe₂][Ni(S₂C₂(CN)₂)₂] reveal bond length changes consistent with additional electrons entering a molecular orbital of primarily ligand-based character. (Table 2.322). This conclusion is supported by esr measurements on ⁶¹Ni-enriched samples of [Ni(S₂C₂CN₂)₂]. The ⁶¹Ni has a nuclear spin (I = 3/2). The small observed ⁶¹Ni hyperfine coupling in this complex supports a predominantly ligand-based unpaired electron. This data suggests that the oxidation state of the nickel in all the one-electron transfer-related species is best described as +2. Several reviews of this contentious area of chemistry have been written. 

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ni-S (Å)</th>
<th>C-S (Å)</th>
<th>C=C (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(S₂C₂Ph₂)₂]</td>
<td>2.101(2)</td>
<td>1.715(10)</td>
<td>1.370(14)</td>
<td>82</td>
</tr>
<tr>
<td>[Ni(S₂C₂(CN)₂)₂]⁻</td>
<td>2.146(1)</td>
<td>1.714(4)</td>
<td>1.356(7)</td>
<td>84</td>
</tr>
<tr>
<td>[Ni(S₂C₂(CN)₂)₂]²⁻</td>
<td>2.16</td>
<td>1.75</td>
<td>1.30</td>
<td>104</td>
</tr>
</tbody>
</table>

Less work has been performed with 1,2-diselenolates, probably because of difficulties encountered in preparing the ligands. Esr data suggested greater delocalisation of the unpaired
electron onto the ligand in the monoanion than in the corresponding 1,2-dithiolenes.

Analogues of the 1,2-dithiolenes with O or N substituents form similar nickel complexes, and have also been rather intensively studied.

Controversy over the bonding descriptions has not hindered efforts to use the unusual redox properties of these complexes for other studies. The planar $[\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]^-$ moieties are ideal anions for planar cations in one-dimensional conducting materials. High levels of conductivity in the sodium and ammonium salts may suggest that the anion plays a significant role in the conduction mechanism in these materials. Recently, attempts have been made to use bulky cations, such as $[(\text{C}_6\text{H}_5)\text{NMMe}_3]^+$, to promote ordering of the anion stacks in the crystal in, for example, $[(\text{C}_6\text{H}_5)\text{NMMe}_3][\text{Ni}(\text{S}_2\text{C}_2\text{CN})_2]_2$, in the hope that such structures might display interesting electrical properties. Attempts to synthesise one-dimensional conductors analogous to $\text{Li}_{0.75}[(\text{S}_2\text{C}_2\text{CN})_2]_2.2\text{H}_2\text{O}$ have failed, however.

(ii) 1,1-Dithiolenes and 1,1-Diselenolenes

It has been noted that for the redox system involving 1,2-dithiolene-nickel complexes, the two five-membered unsaturated (M-S-C-C-S) rings are necessary. The 1,1-dithiolenes chelate with nickel (II), forming four-membered (M-S-C-S) rings, in a square-planar fashion. However, upon oxidation in acetonitrile with excess iodine, the colour of the complexes changes from red to dark green, and black materials are isolated. Only for the 1,1-diselenolene ligand Se$_2$CC(CN)$_2$ was a pure product obtained. This was isolated as its tetraphenyl-arsonium salt, (Ph$_4$As)$_2$.
The oxidation was thought to proceed via a Ni(III) intermediate; cautious iodine oxidation of the Ni(II) chelate, or combination of the Ni(II) and Ni(IV) chelates in a 1:1 mole ratio in situ in an e.s.r. tube, produced olive green solutions with an e.s.r. spectrum of rhombic symmetry, \( g_1 = 2.045, g_2 = 2.149, g_3 = 2.232 \), which differs from spectra observed for the \([\text{Ni}(1,2\text{-dithiolene})]^-\) anions. An X-ray crystal structure analysis of the Ni(IV) complex revealed a slightly distorted octahedral co-ordination, with the average Ni-Se distance 2.387(1) Å. The C=C and C=N distances were very similar to those found in \((\text{H}_3\text{CS})_2\text{C} = \text{C}(\text{CN})\text{C}_6\text{H}_4\text{-p-Br}\), indicating that extensive delocalisation of charge from the NiSe_6 unit does not occur. Octahedral co-ordination in tris(dithiolene) complexes is rather unusual; most are best described as distorted trigonal prisms.

(iii) Dithiocarbamates and Diselenocarbamates

The dithiocarbamates \((\text{S}_2\text{CNR}_2)\) form discrete complexes of nickel (III) and, more importantly, nickel (IV), as might be expected from their structural similarity to 1,1-dithiolenes.

The nickel (III) complexes so far proposed are limited to \([\text{Ni}^{\text{III}}(\text{Et}_2\text{dtc})_3]\), reportedly produced upon treating \([\text{Ni}^{\text{II}}(\text{Et}_2\text{dtc})_3]\) with a thirty-fold excess of thiuram disulphide in situ in an e.s.r. tube, and characterised only by low-temperature e.s.r. and to \([\text{Ni}(\text{Bu}_2\text{dtc})_2]^-\). The latter complex was described in a short report as the product obtained upon careful iodine oxidation of \([\text{Ni}(\text{Bu}_2\text{dtc})_2]\) at -30°C in diethyl ether. In ethanol, it disportionates to \([\text{Ni}(\text{Bu}_2\text{dtc})_2]\) and \([\text{Ni}^{\text{IV}}(\text{Bu}_2\text{dtc})_3]\).

* For explanation of dithio- and diselenocarbamate nomenclature, see Figure 2.323, page 51.
Its esr spectrum showed axial symmetry but was uninformative as to the co-ordination geometry. The low magnetic moment, 1.33BM, could indicate some decomposition. Further work on this system is necessary before structural assignments can be made. Russian workers studying the reaction of halogens with $\left[\text{Ni}(R_2\text{dtc})_2\right]$ in benzene and toluene have claimed the existence of $\left[\text{Ni}(R_2\text{dtc})_2\right]X$ ($R = \text{Et, Bu}; X = \text{Cl, Br, I}$), and have assigned a tetrahedral structure to the 'Ni(III)' cation - a most unusual complex.

Better-established are the tris-dithiocarbamate complexes of Ni (IV). These have been included in two comprehensive and recent reviews. Halogen oxidation of $\left[\text{Ni}(R_2\text{dtc})_2\right]$ at room temperature yields $\left[\text{Ni}(R_2\text{dtc})_3\right]X$ ($X = \text{I, Br, Cl}$). By using the appropriate iron (III) salt as oxidant, non-co-ordinating counter ions may be incorporated in place of halide ions, as in $\left[\text{Ni}(\text{Bu}_2\text{dtc})_3\right]\text{ClO}_4$.

Figure 2.32A 3 Dichalcogenocarbamate Structure and Nomenclature

(Above) Canonical forms of the dithiocarbamates ($X = Y = \text{S}$) and diselenocarbamates ($X = Y = \text{Se}$), $R_2\text{dtc}$ and $R_2\text{dsc}$ respectively.

(Below) Tetraethylthiuram disulphide ($\text{Et}_4\text{tds}$).
X-ray crystallography has revealed the co-ordination geometry of \([\text{Ni}(\text{Bu}_2\text{dtc})_3]\)Br to be distorted octahedral, with the \(\text{NiS}_6\) core 'twisted' by 45.5° from the idealised trigonal prismatic structure. The molecular parameters (Table 2.324) are consistent with a ligand-stabilised Ni(IV) system, and established that ligand oxidation (formation of S-S bonds) had not occurred. Figure 2.324 (i) (page 53) shows a view of the cation. The Ni-S distance is not significantly different to that observed for the planar Ni(II) species; this may be due to the increase in co-ordination number compensating for the higher oxidation state.

<table>
<thead>
<tr>
<th>Bond Distances (Å) and Angles (deg) for ([\text{Ni}(\text{Bu}_2\text{dtc})_3])Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-S</td>
</tr>
<tr>
<td>S-Cl</td>
</tr>
<tr>
<td>Cl-N</td>
</tr>
<tr>
<td>N-C2</td>
</tr>
<tr>
<td>S-Ni-S</td>
</tr>
<tr>
<td>Ni-S-Cl</td>
</tr>
<tr>
<td>S-Cl-S</td>
</tr>
<tr>
<td>C2-N-C2'</td>
</tr>
</tbody>
</table>
Figure 2.324 (i). An ORTEP view of the 
[Ni(Bu$_2$dtc)$_3$]$^+$ unit (A), and some important 
interatomic distances and angles (B). Information 
in Table 2.324 and Figure 2.324 (i) from reference 104

The selenium analogue [Ni(Bu$_2$dsc)$_3$]Br has been the subject of another crystal structure determination, in spite of 'twinning' of the crystal. The Ni-Se distance was 2.391 (5) Å similar to that found in the analogous, 1,1-diselenolene complex [Ni$^{IV}$Se$_2$C=C(CN)$_2$]$_2$- 98 (page 49) and the co-ordination geometry is similar to the dithiocarbamate complex.

Spectroscopically these complexes are well-characterised, and changes in the infra red spectra on oxidation to nickel (IV) ($\nu$ C-N; 1505 cm$^{-1}$ (Ni(II)), 1545 cm$^{-1}$ (Ni(IV))) have been rationalised as due to a greater contribution to the overall structure of the resonance hybrid (ii) (Figure 2.323 i, page 51) in the nickel (IV) complex. The bond lengths (Table 2.324 page 52) support
this view, as does the $^4$H nmr data; as expected, the resonance values of the methylene protons in \([\text{Ni}((\text{PhCH}_2)_2\text{NCS})_2\text{Br}]\) are shifted downfield from those in \([\text{Ni}((\text{PhCH}_2)_2\text{NCS})_2]\). ($\delta = 4.88$, from $\delta = 4.70$).

The electronic spectra of the tris dichalcogenocarbamate complexes are not easy to measure as they are photochemically (and thermally) degraded in solution, in certain solvents, according to the reversible reaction:

\[
\text{Ni}(\text{R dtc})_3^+ + \text{hv or } \Delta, \text{CH}_3\text{CN} \rightarrow \text{Ni}(\text{R dtc})_2 + \text{R dtc} + \text{NiBr}_2
\]

The dependence of the reaction on R, and on the anion, has recently been studied.

In basic solvents, which can presumably co-ordinate to the NiBr$_2$ produced (e.g. pyridine, triethylamine-CHCl$_3$) the process is irreversible, while in chlorinated hydrocarbons (e.g. CH$_2$Cl$_2$, CH$_2$Br$_2$) it does not occur. In fact, in dry CHCl$_3$ solution, [Ni(R$_2$dtc)$_2$] is converted into [Ni(R$_2$dtc)$_3$]Cl on irradiation, while in diethyl ether, [Ni(R$_2$dtc)$_2$] can be oxidised to [Ni(R$_2$dtc)$_3$]Cl by ZnCl$_2$.

While Pt (IV) and Pd (IV) complexes \([\text{M}(\text{R dtc})_2\text{X}_2]\) (X = Cl, Br, I) are known, claims to have isolated corresponding nickel complexes have been questioned by Steggerda et al. who found the spectral data consistent with a mixture of [Ni(R$_2$dtc)$_3$]X and NiX$_2$. They also found that the electronic spectrum of [Ni(R$_2$dtc)$_3$]$^+$ was similar to that of the isoelectronic [Co(R$_2$dtc)$_3$]. Assuming a low-spin d$^6$Ni (IV) arrangement and $O_h$ symmetry, the ligand field splitting energy and the Racah parameter $B$ were calculated from the two low-energy weak absorptions found at ca 17,500 and 19,500 cm$^{-1}$. However, too much reliance
cannot be placed on the values found because of the gross 107 distortion from perfect $O_h$ symmetry.

Recently, some Ni (III) complexes of a ligand type analogous to the dithiocarbamates, namely xanthates ($S_2COR$), have been claimed as the product of the reaction of the square planar $[\text{Ni}(S_2COR)_2]$ with NO$_2$. The $[\text{Ni}(S_2COR)_2]$ have esr spectra of axial symmetry at 77K, but no solid complexes could be isolated.

In conclusion, the stabilisation of high formal oxidation states in all the complexes of charged S and Se donors is due to the effectiveness of the ligands at neutralising the charge at the metal atom, and the description of the complexes as nickel (III) or nickel (IV), or nickel (II) with radical anion ligands, depends on the extent to which the charge is delocalised onto the ligand frame. In the 1,2-dithiolene complexes, this extent is so great that the monoanion and neutral complexes are best described as Ni (II), whilst in the $[\text{Ni}(L)_3]^{n+}$ ($L = 1,1$-dithiolene, $R_2dtc, R_2dsc$, xanthate; $n = 0,1$) the Ni (III) and Ni (IV) descriptions are more appropriate.

2.33 Nitrogen-donor Ligands, Excluding Amine Macrocycles

Amine donors No isolated complexes of nickel (III) or nickel (IV) containing ammine ligands, or monodentate amines, has been reported. Pulse radiolysis has been used to generate Ni(NH$_3$)$_n^{3+}$, with a half-life of the order of milliseconds in aqueous solution, and Ni(1,2-ethane-diamine)$_n^{3+}$ with a longer half-life (ca 1 second). The second order rate constants for the decay of these transients has been related to a possible disproportionation (Equation 2.33 i).

(Eq. 2.33 i) $2\text{Ni(III)} \rightarrow \text{Ni(IV)} + \text{Ni (II)}$

Direct evidence, however, is unavailable.
Russian workers isolated some oxidised nickel-diamine complexes, of formula Ni(diamine)$_2$X$_3$ (diamine = 1,2-ethanediamine and C-substituted analogues; X = Br, Cl), by X$_2$ oxidation of the Ni(II) complex in methanol. Depending upon the ligand, these were either green yellow, μ$_{\text{eff}}$ = 1.8 B.M., or dark green and essentially diamagnetic. Metathesis with dilute mineral acids yielded [Ni(diamine)$_2$X$_2$]Y (X = Cl, Br, Y = NO$_3$, ClO$_4$) while with concentrated acids, Ni(diamine)$_2$X$_2$Y were obtained. Later, Japanese workers suggested that the light-coloured, paramagnetic materials were genuine Ni(III) complexes and the dark coloured complexes were mixed valence (Ni(II)/Ni(IV)) complexes of formula [Ni$^{\text{II}}$(diamine)$_2$][Ni$^{\text{IV}}$(diamine)$_2$Cl$_2$]Y (Y = Cl, ClO$_4$, NO$_3$, HSO$_4$). This explanation fitted with available electronic spectral, infra red and e.s.r. data. However, Greek workers denied these results, claiming that the Ni(III) complexes were, in fact, ligand-deficient materials and that they had synthesised both Ni(1,2-ethanediamine)$_2$X$_3$ (X = Cl, Br) as dark green complexes with similar resonance Raman spectra to the other mixed valence species. Very recently, Indian workers have claimed the synthesis of [Ni(1,2-propanediamine)$_2$Cl$_2$]Cl as a genuine Ni(III) complex.

All the complexes are insoluble in organic solvents and decompose in water. Spectroscopically, the "Ni(III)" complexes show similar diffuse reflectance spectra to those of the Ni(III) tetraazamacrocycle complexes, whilst the fairly intense band at ca 15,200 cm$^{-1}$ found for all the mixed valence species has been assigned to Ni(IV)$\rightarrow$Ni(II) charge transfer. It occurs at lower energies than the corresponding Pd and Pt compounds, as might be expected given the claim of Ni(III) species for some of the ligands. Resonance Raman spectroscopy (excitation into the charge transfer band) gave a spectrum with a long progression of overtones in the symmetric Cl-Ni$^{\text{IV}}$-Cl stretch, in common with that observed for the better-characterised Pt compounds, with $v_1$ at 263 cm$^{-1}$.  


Di-imine Ligands

A recent development in Ni(III) chemistry has been the synthesis by electrochemical methods of [Ni(L-L)]\(^{3+}\) (L-L = 2,2'-bipyridyl, 4,4'-methyl-2,2'-bipyridyl, 1,10-phenanthroline etc.).

The complex [Ni(2,2'-bipyridyl)\(^3+\)] was synthesised by anodic oxidation of the nickel (II) complex in strongly acidic (2.0 mol dm\(^{-3}\) HCIO\(_4\)) conditions, as a lime-green solution. Later, in common with analogues with 5-methyl-1,10-phenanthroline, 4,4'-dimethyl 2,2'-bipyridyl, 5-chloro- and 5-nitro-1,10-phenanthroline, it was isolated as a dark green solid from CH\(_3\)CN solution after anodic oxidation.

E.s.r. data (Figure 2.331) confirmed the d\(^7\) Ni(III) formulation (axial spectrum; \(g_{||} = 2.027, g_{\perp} = 2.137\) with coupling to \(^14\)N). Cyclic voltammetry in CH\(_3\)CN(1M NaClO\(_4\)) showed that electron-withdrawing groups greatly increased the redox potential (Figure 2.331). The electronic spectra showed a weak absorbance at 16,130 cm\(^{-1}\), often observed for pseudo-octahedral d\(^7\) Ni (III) complexes.

The principle interest in these unusual complexes is in their redox reactions. They are powerful oxidants in aqueous solution. Initial studies with [Ni(2,2'-bipyridyl)\(^3+\)] showed that the reactions with H\(_2\)O\(_2\) and Br\(^-\) were first order in both reagents, and pH-independent over the range measured, indicating an outer-sphere one-electron transfer mechanism. Recent work has concentrated on the study of the kinetics of the Ni(II)/Ni(III) couple.

Oximes and Related Ligands

The co-ordination chemistry of nickel (III) and (IV) with oxime ligands has provided a fruitful area of research for many
Electron spin resonance spectra of frozen solutions at 77 K; Ni(bipy)(ClO₄)₂ in CH₃CN (0.1 M NaClO₄),—binary mixture CH₃CN/5% H₂O.

Platinum sphere cyclic voltammetry of Ni(II) (bipy)₂(ClO₄)₄ in CH₃CN (0.1 M NaClO₄), recorded at 2 mV/s using S.C.E./NaCl (satd) reference.

### Electrochemical data on complexes (in CH₃CN, I = 0.1 M (NaClO₄), T = 25°C)

<table>
<thead>
<tr>
<th>Complex</th>
<th>E (V)²</th>
<th>ΔmVᵇ</th>
<th>Scan rate (Vs⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(phen)₃²⁺</td>
<td>0.937</td>
<td>74</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe(5-Me phen)₃²⁺</td>
<td>0.911</td>
<td>77</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe(bipy)₃²⁺</td>
<td>0.918</td>
<td>63</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni(phen)₃²⁺</td>
<td>1.641</td>
<td>104</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni(bipy)₃²⁺</td>
<td>1.625</td>
<td>107</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni(4,4'-Me₂ bipy)₃</td>
<td>1.507</td>
<td>(208)</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni(5-Cl phen)₃²⁺</td>
<td>1.747</td>
<td>98</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni(5-NO₂ phen)₃²⁺</td>
<td>1.820</td>
<td>(170)</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni(5-Me phen)₃²⁺</td>
<td>1.609</td>
<td>150</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Determined by cyclic voltammetry at the scan speed shown. [Ni(II)] ≈ 4 x 10⁻⁴ M.
* Peak to peak separation indicating reaction reversibility.

---

**Figure 2.331.** E.s.r. and electrochemical data obtained for Ni(LL)₃³⁺ complexes (L-L = di-imine ligand). Hyperfine coupling in the e.s.r. spectrum is seen only in 'wet' CH₃CN solution (A); another indication of the sensitivity of Ni (III) e.s.r. spectra to conditions (Chapter 3, Page 167). All data from Reference 121.
years, with controversy over the oxidation state actually present in the oxidised complexes. It is now clear that Ni(III) or Ni(IV) complexes may be present, depending on the reaction conditions. For example, while pulse radiolysis of a basic solution of NiSO₄ and H₂dmg* in presence of N₂O gave, by a pseudo-first order process, a solution whose electronic spectrum was consistent with Ni(III), the red solution formed by lead dioxide oxidation of a similar solution was postulated to contain Ni(IV), as electrochemical experiments suggested a two-electron reversible polarogram. However, these authors did find an anomalous magnetic moment for their complex, tentatively ascribed to a thermally accessible triplet state for the Ni(IV), but more likely due to the presence of Ni(III).

Genuine Ni(IV) complexes of oxime ligands can be isolated. The product of iodine oxidation of nickel (II) salts in the presence of KOH and H₂dmg is K₂[Ni(IV)(dmg)₃]. Most unusually, this complex is also the product of the treatment of "NiO₂".

Figure 2.332 Oxime Nomenclature

For details of oxime nomenclature, see Figure 2.332.
with dmg in alkaline conditions - the only known case of a higher-valent state of nickel being used in the preparation of a complex. It exhibits metal-nitrogen stretching frequencies around 500 cm⁻¹, \( \nu_{\text{C=N}} \) at 1560 cm⁻¹ and \( \nu_{\text{NO}} \) at 1240 and 1093 cm⁻¹. No bands assignable to intramolecular H-bonding could be observed, confirming that the ligand is doubly deprotonated. Older reports of esr signals produced on combining aqueous solutions of NiSO₄ and H₂dmg in base, then rapidly freezing to 123K, were substantiated by the observation that esr signals could be seen when insufficient oxidant was employed in the Ni(IV) synthesis. The kinetics of formation of Ni(dmg)₂⁺⁻ have been examined using 10⁻⁷ as oxidant, but on the data obtained no clear mechanism could not be proposed. The acid decomposition of the complex to Ni(II) was thought to proceed by a mechanism involving double protonation of the Ni(IV) complex followed by a rate determining Ni-N bond cleavage, intramolecular electron transfer and dissociation. No suggestion of the intermediacy of a Ni(III) complex was made.

It was at first assumed that the complexes "Ni(Hdpg)₂X" made by reaction of Ni(Hdpg)₂ with X₂ (X = Br, I) were of Ni(III). However, X-ray crystallography revealed that the halogen atoms are 'sandwiched' between the layers of Ni(Hdpg)₂ moieties and do not interact with the metal (see Chapter 4, page 192). Genuine Ni(III) complexes of Hdpg are obtained in the presence of a good co-ordinating base, for example pyridine, and [Ni(Hdpg)₂(py)₂]⁺ has been isolated. This provides another example of the need for Ni(III) complexes to be stabilised by good axial donor ligands. The pyridine ligands interact strongly with the \( dz^2 \) orbital, as evidenced by the large ¹⁴N coupling constant in the \( g_{||} \) region of the esr spectrum.

In view of the relative ease with which [Ni(Hdpg)₂(py)₂]⁺ is formed, it is unsurprising that multidentate amine-oxine ligands can stabilise nickel (III) and, in certain cases, Ni(IV).
In an attempt to rationalise some of the factors influencing the stability of these oxidation states with various donor sets, Drago and Baucom synthesised two specially-designed ligands (A and B in Figure 2.333, this page). The Ni (III) complex [Ni(A)] has an electronic spectrum typical of pseudooctahedral low-spin Ni (III) complexes, with a weak transition at 13,850 cm\(^{-1}\) and a shoulder at 18,500 the most distinctive features. The e.s.r. spectrum of the polycrystalline powder was of rhombic symmetry with g values similar to those observed in [Ni(\(\text{C}_6\text{H}_4\text{AsMe}_2\))\(_2\text{Cl}_2\)]\(^+\)\(^{133}\). The ligand BH\(_2\) on the other hand, reacts with nickel (II) salts in the presence of ammonium persulphate in basic conditions to give [Ni\(^{IV}\)(B)\(_2\)] as a deep purple material, stable as a solid and in aqueous solution.

**Figure 2.333** 2-acetylpyridineoxime (HA) and 2,6-diacetylpyridine dioxime (H\(_2\)B)

(\(\text{the hydroxyl protons are lost on complexation to Ni (III) and (IV).}\))

These have been the subject of X-ray crystallographic study.\(^{134}\) The structure consists of discrete [Ni(B)\(_2\)] molecules with a pseudo-octahedral co-ordination sphere. The ligand is considerably deformed by the requirements of octahedral co-ordination. The average Ni-N distance (1.98 Å) in this complex is much shorter.
than that normally found in octahedral Ni(II)-N chelate complexes. Interestingly, no nickel (III) intermediate could be detected by cyclic voltammetry, or by the use of weaker oxidants, while all attempts to prepare a Ni(IV) complex of HA or A failed.

Recent studies on a series of related dialkylglyoxime complexes [Ni(dRg)_3]^{2-} show a stability order corresponding to the spectrochemical series of the ligands. Various kinetic studies using [Ni(dmg)_3]^{2-} as an oxidant have been reported.

Multidentate amine-imine-oximes also stabilise Ni(III) and Ni(II). Concentrated nitric acid oxidation of [Ni^{II}(H,C)(ClO_4)_2} (Figure 2.334) yielded dark violet [Ni^{IV}(C)(ClO_4)_2, stable in dry air.

![Figure 2.334](H_2C)

On exposure to moisture, progressive reduction to [Ni^{III}(HC)]^{2+} occurs, and this has been examined by e.s.r. The Ni(III) complex can also be produced by controlled-potential electrolysis of the Ni(II) complex. Interest in the factors determining preferential formation of Ni(III) or Ni(IV) complexes of HC or C have led to detailed electrochemical and kinetic investigation of these complexes. The great solution stability of the Ni(IV) complex is well illustrated by the fact that it has recently been optically resolved by elution through Sephadex with potassium (+) antimonyl tartrate solution. The enantiomers are solution-stable, and are being investigated as enantiospecific oxidants.
Electronic spectroscopic data has been obtained for some Ni (IV)-oxime complexes, and this is summarised in Table 2.335.

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT</th>
<th>ABSORBANCES (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Me₂L)(ClO₄)₂</td>
<td>Water</td>
<td>20,000 (6300); 23,260 (5960)</td>
</tr>
<tr>
<td></td>
<td>Nitromethane</td>
<td>18,940 (6560); 23,260 (6030)</td>
</tr>
<tr>
<td>Ni(Me₂L)(ClO₄)₂</td>
<td>0.001 N HClO₄</td>
<td>20,000 (5430); 23,260 (5310)</td>
</tr>
<tr>
<td>Ni(MeEtL)(ClO₄)₂</td>
<td>Water</td>
<td>20,000 (6150); 23,260 (6000)</td>
</tr>
<tr>
<td>Ni(MeEtL)(ClO₄)₂</td>
<td>Water</td>
<td>20,000 (5440); 23,260 (5440)</td>
</tr>
<tr>
<td>Ni(MePhL)(NO₂)(ClO₄)</td>
<td>Water</td>
<td>19,420 (3360); 23,530 (3200)</td>
</tr>
<tr>
<td>Ni(PhMeL)(NO₂)(ClO₄)</td>
<td>6 N HNO₃</td>
<td>19,230 (2850); 22,730 (2510)</td>
</tr>
</tbody>
</table>

Table 2.335. Electronic absorption spectra of complexes of Ni (IV) with ligand type C (Figure 2.334).

(a) Figures in parentheses are molar extinction coefficients (ε, dm²M⁻¹ cm⁻¹)

(b) Ligand nomenclature is as in Figure 2.334 with the 'R' groups indicated in the order R, R'.

Hexadentate amine-imine-oxime ligands containing only one deprotonated oxime function can stabilise only Ni(III). The complex [Ni(D)(ClO₄)]₁₃₆ has been isolated as dark red crystals (Figure 2.336).

![Figure 2.336](image-url)
As a 'rule of thumb' it has been suggested that at least two deprotonated oxime functions are necessary to yield Ni(IV) complexes.

In conclusion, the charged oxime function is unusually proficient at stabilising Ni(III) and Ni(IV), and this is probably due to the good \( \sigma \)-donor unsaturated \( N \) atom. The proximity of the oxygen anion will improve this donor ability and it probably plays an important role in neutralising the charge at the metal centre, without leading to a redox process whereby a ligand anion radical and nickel (II) are generated. Recently, a complex of a ligand related to the dioximes, viz. 3(hydroxyamino)-3-methyl-2-butanone, has been synthesised (Figure 2.337) where, in a Ni(IV) description, two negative charges are required to be localised on the \( N \)-donors. The properties of the complex lead to its formulation as a Ni(II)-di (anion radical),\(^{143}\) emphasising the importance of the negative charge on the oxime being localised at \( O \), for Ni(IV) formation.

Figure 2.337. The complex discussed in Reference 143

Deprotonated Peptides and Amides

Recently, nickel has become established as a necessary trace element in biochemical systems,\(^ {145} \) and by \(^ {62} \)Ni labelling studies
and ESR measurements, Ni(III) sites have been discovered in some bacterial dehydrogenase enzymes. This is likely to spur efforts at the characterisation of Ni(III)-peptide and amide complexes, which have been known for slightly longer.

One of the first such complexes to be made was the biuret (H₂bi) complex K[Ni(bi)₂]. Only analytical data, and the magnetic moment (2.4 BM) were determined. Although alkyl-substituted biuret complexes were also synthesised later, no ESR data has been reported, so that the precise nature of these materials remains open to question.

More recently, electrochemical oxidation of nickel (II) perchlorate and peptide-amides has been found to yield nickel (III) complexes, Figure 2.33, with characteristic electronic and ESR spectra (d⁷: unpaired electron in d⁷ orbital), but these have only been studied in solution. They are thought to be of D₄h symmetry with water occupying axial sites. This theory is supported by substitution of aqueous ammonia as the solvent, when hyperfine coupling is observed in the g₉z region of the ESR spectrum. In accord with expectation, successive substitution of

**Figure 2.33.** The complex \[\text{[Ni}^{II}_{\text{glycylglycylglcylamide}^3}] \]
\[(L = \text{H}_2\text{O or NH}_3)\]
NH₂ for H₂O in the axial positions leads to successively lower redox potentials for Ni(II) \( \rightarrow \) Ni(III) + e, and greater solution stability. The related ligands biguanide and amidinourea (Figure 2.339) also stabilise nickel (III) when axial donors, particularly halide ions, are available, as in \([\text{Ni(Hbiguanide)}\text{Cl}_2]X\) (X = Cl, F).\(^{150}\)

**Figure 2.339**

![H.B. biguanide and H. Amidinisourea](image)

2.34 **Aza-Macrocycles**

Interest in the properties of naturally-occurring macrocycle-metal complexes, for example in haems and Vitamin B12, led to the study of methods by which simpler, but similar, metal complexes could be made artificially.

It was discovered that in the presence of certain metal ions, methyl ketones and short, linear α, γ-diamines could be induced to condense around the metal ion, yielding metal-(unsaturated tetraazamacrocycle) complexes.\(^{152}\) Further developments and refinements of the method have led to the synthesis of a wide variety of these macrocycles.
Macrocyclic complexes exhibit properties that make them well-suited to the study of metal complexes in unusual oxidation states. The "core size" (roughly, the total radius of the atoms arranged around the chelate ring) can be tailored to fit a particular ionic radius. The donor atoms cannot easily dissociate from the metal centre because of the rigidity of the macrocycle, and the metal ion can co-ordinate anions in a tetragonal arrangement to reduce its effective charge. Finally, it has been noted that the ligand field exerted on nickel (II) by these ligands can be very high, raising the energy of the antibonding orbitals such that removal of an electron (oxidation) becomes feasible chemically. Spectrochemical and kinetic data related to these properties have been recently reviewed.

The first Ni(III) complex of such a macrocycle was \([\text{Ni}^\text{III}(\text{Me}_6(14)\text{-ane N}_4)(\text{NO}_3)_2]\text{ClO}_4\) \(^{153}\), produced upon nitric acid oxidation of an aqueous solution of \([\text{Ni}(\text{Me}_6(14)\text{-ane N}_4)](\text{ClO}_4)_2\).

Olson and Vasilevskis \(^{154}\) obtained \([\text{Ni}(L)(\text{CH}_3\text{CN})](\text{ClO}_4)_3\) (where \(L = \text{cis or trans-Me}_6(14)\text{-4,11-diene-N}_4\)) by electrolytic oxidation at +1.7V (vs. Standard Hydrogen Electrode) of the Ni (II) complex in aqueous perchloric acid. Although such electrolyses have since proved to be of widest application in the preparation of similar complexes, (no difficulties with separating the products of oxidation arise) chemical oxidants (for example \((\text{NH}_4)_2\text{S}_2\text{O}_8\), \([\text{NO}^+]\ [\text{ClO}_4^-]\), \(\text{HNO}_3\) and \(\text{Na}_2\text{IrCl}_6\)) have also been of value.\(^{122}\) In particular, \((\text{NO})(\text{ClO}_4^-)\) can be used to generate bis (solvento) complexes \([\text{Ni}(L)(\text{solvent})_2]^{3+}\) in non-aqueous media.

* The full names of these macrocycles in IUPAC nomenclature are tedious both to write and to interpret. Therefore, abbreviations are used, the logic of which is explained in Figure 2.\(^{341}\)
Figure 2.341 (opposite page). Some representative examples of tetraaza macrocycles synthesised in recent years, and their nomenclature.

Figure 2.342 (below). Oxidation potentials for Ni (II) - macrocycle complexes, showing their variation with ligand core size, substituents and unsaturation.

All data from reference 151.

### Electrochemical Behavior of Macrocyclic Complexes of Nickel

<table>
<thead>
<tr>
<th>Neutral ligand</th>
<th>Oxidation potential (V) Ni(L)²⁺ → Ni(L)³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[13]aneN₄</td>
<td>+0.7 → +0.9 (^b)</td>
</tr>
<tr>
<td>[14]aneN₄</td>
<td>+0.67</td>
</tr>
<tr>
<td>Me₄[14]aneN₄</td>
<td>+0.68</td>
</tr>
<tr>
<td>Me₄[14]aneN₄</td>
<td>+0.71</td>
</tr>
<tr>
<td>Me₄[14]aneN₄</td>
<td>+0.87</td>
</tr>
<tr>
<td>Me₄[14]aneN₄,11-dieneN₄</td>
<td>+0.98</td>
</tr>
<tr>
<td>Me₄[14]aneN₄,4,8,11-tetraeneN₄</td>
<td>+1.05</td>
</tr>
<tr>
<td>[15]aneN₅</td>
<td>+0.90</td>
</tr>
<tr>
<td>Me₄[16]aneN₅</td>
<td>+1.3</td>
</tr>
<tr>
<td>Me₄[16]aneN₅,12-dieneN₄</td>
<td>+1.3</td>
</tr>
<tr>
<td>Me₄[16]aneN₅,4,12-trieneN₄</td>
<td>+0.86</td>
</tr>
<tr>
<td>CR + 4H</td>
<td>+0.89</td>
</tr>
<tr>
<td>CR + 2H</td>
<td>+0.93</td>
</tr>
<tr>
<td>CR</td>
<td>+1.03</td>
</tr>
<tr>
<td>CR – 2H</td>
<td>+1.05</td>
</tr>
<tr>
<td>Me₄[14]aneN₅,3,7,11-tetraeneN₄</td>
<td>+1.05</td>
</tr>
<tr>
<td>Me₄[14]aneN₅,3,8,10-tetraeneN₄</td>
<td>+1.00</td>
</tr>
<tr>
<td>Me₄[14]aneN₅,4,7-dieneN₅</td>
<td>+0.72</td>
</tr>
<tr>
<td>Me₄[15]aneN₅,8,11-dieneN₅</td>
<td>+0.94</td>
</tr>
<tr>
<td>Monoanionic ligand</td>
<td>Ni(L)⁺ → Ni(L)²⁺</td>
</tr>
<tr>
<td>(Me₄[13]dienoN₄)⁻</td>
<td>+0.27 (J) (^b)</td>
</tr>
<tr>
<td>(Me₄[14]dienoN₄)⁻</td>
<td>+0.23 (J) (^b)</td>
</tr>
</tbody>
</table>

* In acetonitrile solution, 0.1 M (n-Bu)₄NBF₄, volts vs. Ag/Ag⁺ (0.1 M) reference electrode.

\(^b\)
In general, co-ordinated solvent in these complexes cannot be removed even on warming in vacuo, an indication of the strong tendency of the low spin $d^7$ configuration in this high oxidation state to co-ordinate potential donors in the axial positions.

Most of the interest in nickel (III)-macrocycle complexes has been in their electrochemistry. In particular, the variation in the redox potential (for $\text{Ni(II)} \rightleftharpoons \text{Ni(III)} + e^-$) in acetonitrile with variation in the macrocycle type (Figure 2.342 page 69) has been well studied. The variation in redox potential for one particular macrocycle type (Figure 2.342, page 69) with substituent R has also been examined. In short, it was found that the ideal size of the tetraaza macrocycle was the 14-membered ring; increasing the size to [15] or [16]-ane-$N_4$ rings progressively increased the redox potential, and hence the unfavourability of oxidation. Concurrently, the ease of reduction to Ni(I) was increased. Unsaturation in the macrocycle also increased the redox potential for $\text{Ni(II)} \rightleftharpoons \text{Ni(III)} + e^-$, while aiding the formation of Ni(I).

Although dianionic macrocycle complexes (e.g. 23-26, Figure 2.341) were found to exhibit lower redox potentials than the saturated macrocycles, the nature of the products formed is somewhat doubtful; they show no tendency to axial co-ordination in acetonitrile. Also their esr spectra show $g_{II} < g_L$ greater than 2.00, when for $d^7$ low spin complexes one predicts $g_{II} \simeq 2.0$, $g_L \simeq 2.2$. Although it was suggested that the complexes are Ni (III), with a $(d_2^2 - y^2)^1$ ground state, it is possible on the basis of the data that they are nickel (II)-stabilised anion-radicals, similar to the $[\text{Ni(l,2 dithiolene)}_2]^-$ species.

As most of the complexes of nickel (III) have been generated and studied electrochemically, characterization has often been entirely by solution esr spectroscopy. The usual spectrum for $D_{4h}$ $d^7$ low spin systems ($g_{II} \simeq 2.00$, $g_L \simeq 2.20$) is
observed for most of the complexes. The resolution of hyperfine splitting due to the $^{14}N$ or the axial donors is sometimes possible,

![E.S.R. spectra](image)

**Figure 2.34**. E.S.R. spectra (at -196°C) of solutions containing

(a) $[\text{Ni} (\text{Me}^-14[\text{ane}]N_2)^+ Cl_2]^+$,
(b) a mixture of $[\text{Ni} (\text{Me}^-14[\text{ane}]N_2)^+ Cl_2]^+$ and $[\text{Ni} (\text{Me}^-14[\text{ane}]N_2)^Cl]^2^+$, and
(c) $[\text{Ni} (\text{Me}^-14[\text{ane}]N_2)^3^+]$.

From reference 161.

but can depend on solution environment. For example, Lovecchio, Gore and Busch found that the observation of hyperfine coupling in their solutions of electrochemically-generated nickel (III) complexes depended on the cation of the support electrolyte, but
not on the anion. For $[\text{Ni}(L)X_2]^+ (X = \text{Cl,Br})$ coupling to axial halides is often observed in the $g_{\perp}$ region, and on solution, one $X^-$ may dissociate, lowering the symmetry so that three $g$-values are observed.

However, when $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is used as an oxidant in the absence of a good donor ligand, and complexes $[\text{Ni}(L)\text{SO}_4]^+$ are synthesised, these exhibit one broad line ($g = 2.16$) in the esr, consistent with a cis-bidentate sulphato arrangement as earlier suggested on the basis of conductivity measurements for such complexes. Here, the macrocycle is forced to 'fold' to accommodate the sulphate anion.

As well as electrochemical and esr studies, the properties of macrocyclic ligand complexes lend themselves well to the investigation of the kinetics of various reactions. For nickel (III), naturally, these most often involve reduction. Early in their study, it was noticed that solvents more basic than acetonitrile (e.g. water at pH > 2.0, pyridine) induced decomposition, with reduction to nickel (II) \cite{122}. Barefield and Mocella found that base (pyridine,Et$_3$N,H$_2$O)-catalysed decomposition involved a ligand radical intermediate;

$$\text{Ni}^{III} + \text{BCD} \rightarrow \text{Ni}^{II} + \text{BH}.$$ 

Some controversy over the reaction of Ni (II) macrocycle complexes with such potential oxidants as $\cdot \text{OH}$ \cite{122} and Br$_2$ \cite{160} exists. In particular, Br$_2^-$ is reported to both oxidise Ni(II) to Ni(III) and then to decompose the product by a different route.

Other spectral data on nickel (III)-macrocycle complexes is rather sparse, possibly because few appear to have been isolated as solids. In particular, no X-ray crystal structure determinations have been performed. Gore and Busch \cite{159} isolated some complexes of Me$_2$(14)-ane(N$_4^-$) (Figure 2.341) by persulphate or nitric acid
oxidation, followed by precipitation, and reported some preliminary magnetic and electronic spectral data. Olsen and Vasilevskis also isolated nickel (III) complexes, of $\text{Me}_6(14)$-ane $N_4$ (cis and trans isomers of the ligand) and $\text{Me}_6(14)$-4,11-diene $N_4$, and reported detailed electrochemical and electronic spectral results.

Figure 2. The electronic spectrum of $[\text{Ni(Me}_6(14)\text{aneN}_4)]^{n+}$ (n = 2,3) in CH$_3$CN solution (n = 3; generated electrochemically) - from reference 154.
The general shift of bands due to charge transfer to lower energies on oxidation is typical, as for nickel (III), is the appearance of a low energy d-d band at $\lambda 16,700 \text{ cm}^{-1}$ ($\lambda 600 \text{ nm}$).

Chan and Poon isolated nickel (III) complexes of (14) a-n-N$_4$, [Ni((14) a-n-N$_4$)$_2$X$_2$]ClO$_4$ ($X = \text{Cl, Br}$) and on the basis of their ir spectra assigned to them trans stereochemistry ($D_{4h}$).

A halide-dependent vibration at 220 cm$^{-1}$ ($X = \text{Cl}$) was recorded - the first time had been reported for these complexes.

The low value was rationalised as due to the ($d^8$) configuration - the antibonding electron weakens the Ni-Cl bond. (This is consistent with data on the (bis)diarsine-Ni(III) complexes, considered in Section 2.35(page82).

Recently, advances in macrocycle synthesis and interest in factors which produce nickel (II) complexes with a low redox potential without giving ligand-radical species has led to the investigation of rather more exotic macrocycle complexes. For example, the oxidation of nickel (II) halide complexes of tetra-, penta- and hexadentate saturated amine macrocycles of different ring sizes has been examined. Whereas nickel (III) complexes of (12) a-n-N$_4$ (Figure 2.345, page75) were found to be of the 'folded' ligand (i.e. cis arrangement, N$_4$X$_2$ donor set), with an esr spectrum characteristic of this arrangement ($g_{\|} = 2.17$, $g_{\perp} = 2.06$), the corresponding (13)-ane-N$_4$ complex was of conventional, $D_{4h}$ symmetry ($g_{\perp} = 2.20$, $g_{\|} = 2.02$; 5 lines; 2 x CH$_3$CN).

These spectra are compared in Figure 2.346. Incorporation of an 'extra' N-donor into the macrocycle did not aid oxidation as it would have to occupy an axial site in the resulting complex, and this would distort the planar N$_4$ arrangement of the other donors. Hexadentate macrocycles gave octahedral, axially-compressed, nickel (III) trications, the first known examples with such stereochemistry.
Figure 2.345. Nomenclature of some novel macrocycles studied in reference 162.

1, asym-(14)ane $N_4$; 2, (12)ane$N_4$; 3, (16)ane$N_4$; 4, 15(ane)$N_5$; 5, (16)ane $N_5$; 6, (17) ane $N_5$; 7, (18) ane $N_6$. 
Figure 2.346. (below) The effect of changing stereochemistry on the esr of Ni (III) macrocycle complexes. (A) is a 'folded' species, (B) is a conventional, D₄h complex.

X-Band (9 GHz) ESR spectrum of Ni(II)(aneN₄)²⁺ in acetonitrile solution, 0.1 M in Bu₄NBF₄, frozen at 77 K.

Q-Band (35 GHz) ESR spectrum of Ni(II)(aneN₄)²⁺ in acetonitrile solution, 0.1 M in Bu₄NBF₄, frozen at 77 K.

More success in lowering the Ni(II)-Ni(III) redox potential occurs when carbonyl groups adjacent to the N-donors are incorporated, and the ligand is deprotonated upon complexation. While this does not lower the redox potential of [Ni(dioxo-14-aneN₄)] (Figure 2.347) significantly, relative to the 14-ane-N₄ analogue, upon incorporation of a fifth N-donor remarkable effects occur. The complex illustrated is very easily oxidised (+0.24V vs. standard calomel electrode in acetonitrile to [Ni(III)(macrocycle) (CN₃CN)]⁺, with the predicted esr and electronic spectra. More surprisingly, it will react with dioxygen to form an intensely brown, neutral species [Ni(macrocycle²⁻)(O₂⁻)]. Further study of the dioxygen complex established that it was the intermediate in the Ni(II) (macrocycle²⁻)catalysed oxidation of benzene to phenol.
Another method found to lower the redox potential is to substitute acetate groups for the amine protons. The macrocycle 1,4,7-triazacyclononane-N,N',N''-triacetate (Figure 2.348), for example, forms the very stable octahedral nickel (II) complex 

**Figure 2.348**

TACNTA

\[ \text{(1,4,7-triazacyclononane-N,N',N''-triacetate).} \]
H$_3$O[Ni(TACNTA)] on recrystallisation from dilute nitric acid. On standing, dilute nitric acid solutions of the blue nickel (II) complex turn pink as the neutral nickel (III) complex forms. This is deposited as pink crystals, which have been characterised by X-ray crystallography.

Figure 2.349. ORTEP drawing of [Ni(TACNTA)] viewed down the threefold axis (from reference 166)
Section 2.35. Phosphorus and Arsenic Donors

Introduction

Although the first nickel (III)-phosphine complex was made by Jensen in 1936, and Nyholm described a nickel (IV) complex of \( \text{C}_6\text{H}_4(\text{AsMe}_2)_2 \) in 1951, in general the co-ordination chemistry of nickel (III) and (IV) with these donors is in a poor state of development. Apart from detailed examination of the \([\text{Ni}(\text{C}_6\text{H}_4(\text{EMe}_2)_2X_2]^+ \) (\( X = \text{Cl}, \text{Br} \)) complexes by e.s.r. and X-ray crystallographic techniques in order to determine the distribution of the unpaired electron over the ligands, no intensive study of nickel (III)-heavy Group Vb donor complexes had been undertaken, and the work which does exist is largely as 'postscripts' to papers describing nickel (II) complexes, or five-co-ordination.

2.35 (i) Monodentate Ligands

Jensen noted that treatment of the red \([\text{Ni}(\text{PR}_3)_2X_2]\) (\( R = \text{Et}, \text{Pr}^\text{I}, \text{Bu}^\text{I} \), \( X = \text{Cl}, \text{Br} \)) with \( X_2 \) or \( \text{NO}_2 \) in solution caused a colour change to dark blue or dark green. Later, he isolated \([\text{Ni}(\text{PET}_3)_2\text{Br}_3]\) and determined the magnetic moment, and dipole moment in pentane, concluding that the complex was probably a trigonal bipyramid with equatorial halides. The material was unstable; although the lattice parameters were determined, a full crystal structure analysis could not be undertaken owing to decomposition. Similar ligands (\( \text{PR}_3; R = \text{Me}, \text{Pr}^\text{I}, \text{Bu}^\text{I} \)) gave complexes which could not be obtained pure, and chlorine was found to decompose the corresponding chlorides. These could, however, be made in an impure form by NOCl oxidation of the Ni (II) complexes. Spectroscopic data on all these materials is lacking.
Stalick and Ibers found that \([\text{Ni}(\text{PhPMe}_2)_2\text{Br}_3]\) was somewhat more tractable, partly owing to its lower solubility. A monomer in \(\text{CHCl}_3\), it was also a non-electrolyte in nitromethane. Recrystallisation from benzene-hexane afforded crystals suitable for crystal structure determination, albeit of a partly-reduced material of composition \([\text{Ni}(\text{PhPMe}_2)_2\text{Br}_3]\). \(\frac{1}{2}[\text{Ni}(\text{PhPMe}_2)_2\text{Br}_2].\text{C}_6\text{H}_6\).

The structure consists of well-separated nickel (II) and (III) units. The trans-square planar nickel (II) units have normal Ni-Br and Ni-P bond lengths and angles, and will not be considered further. The nickel (III) unit is trigonal-bipyramidal, with axial phosphines, as earlier suggested for \([\text{Ni}(\text{PET}_3)_2\text{Br}_3]\). (Figure 2.351). The Ni atom is essentially coplanar with the bromines and the P-Ni-P linkage is almost linear. Interestingly, there is distortion in the equatorial plane. As can be seen in Figure 2.351, one Ni-Br bond is significantly longer (ca 15σ) than the average of the others, and the angle opposite this bond is opened out from the expected 120° to 133°. The Ni-P bond lengths are not significantly different from those found in the four co-ordinate nickel (II) low spin complexes, but they are longer by ca.06Å than similar bonds in low spin five co-ordinate complexes. This was thought to be due to the increase in radius on going from a d⁸ spin-paired to a d⁷ odd-electron complex, more than compensating for the increase in oxidation state. Unexpectedly, no e.s.r. signal could be resolved either for the pure nickel (III) or the partially-reduced compound, even at low temperature, due to ill-understood relaxation effects.

The lack of e.s.r. spectra for the \([\text{Ni}(\text{L})_2\text{X}_3]\) complexes is a serious omission as far as attempts to assign the electron distribution in the complex are concerned. Although the X-ray data on the \([\text{Ni}(\text{PhPMe}_2)_2\text{Br}_3]\) unit, particularly the Ni-P bond lengths, and the lack of an e.s.r. signal even at -196°C
appear to militate against a nickel (II)-stabilised cation radical description, nevertheless esr data on $[\text{Ni}(\text{P(alkyl}L_3)_2X_3]_2$ complexes is necessary as Drago and Baucom have suggested that the ligand radical description could be truer, given the fact that phosphorus is a soft donor (that is, it is capable of good metal orbital-ligand mixing).
2.35. (ii) Complexes of Formula \( \text{Ni}(L-L)\text{Br}_3 \) (\( L-L = \) bidentate ligand; \( X = \text{Cl,Br} \))

A few poorly-characterised complexes of formula \( \text{Ni}(L-L)\text{Br}_3 \) (\( L-L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2, \text{cis-Ph}_2\text{PCHCHPPh}_2 \)) have been made by Br oxidation of the Ni(II) cis-planar complexes and reported at the end of a paper on nickel (II) complexes, or as a note. The spectroscopic data obtained did not allow unequivocal assignment of stereochemistry, owing to the low symmetry of the possible isomers. Also the e.s.r. spectra were puzzling; the expected \( g \)-tensor anisotropy was not resolved even at low temperatures. On the basis of apparent coupling to one \( \text{Br} \), with further, superimposed, coupling to two \( \text{P} \) donors in solution e.s.r spectra, a tentative suggestion of \( C_{2v} \) symmetry for the \( \text{cis-Ph}_2\text{PCHCHPPh}_2 \) complex was made.

Apparently similar complexes with alkyl-substituted bidentate ligands are even more obscure. Polymeric octahedral structures were assumed, on the tenuous grounds of poor solubility, for \( \text{Ni}\{\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)\}_2\text{Br}_3 \), \( \text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)\text{Br}_3 \), and \( \text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMMe}_2)\text{Br}_3 \), but the only physical data obtained were analyses and magnetic moments (ca 2.00 BM). No spectroscopic data was reported. As suggested by the heading, no corresponding chlorides have been prepared. The product of prolonged reaction between \( \text{Cl}_2 \) and \( [\text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)\text{Cl}_2] \) in \( \text{CCl}_4 \) suspension is reported to be \( \text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)\text{Cl}_4 \), but the observed magnetic moment (3.36 BM) is inconsistent with a Ni(IV) formulation.

2.35 (iii) Complexes of formula \( [\text{Ni}(L-L)\text{X}_2]^+ \)

In his pioneering studies in unusual oxidation states, Nyholm found that on refluxing ethanol solutions of \( \text{Ni}\{\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)\}_2\text{Cl}_2 \) in a stream of air in the presence of HCl, brown crystals of
composition Ni(L-L)\(_2\)Cl\(_2\) precipitated. The corresponding bromide and thiocyanate could be made by metathesis. On the basis of their magnetic and physico-chemical properties, Nyholm suggested a trans-pseudooctahedral Ni(III) formulation, later confirmed by an X-ray crystallographic study. Crystals of [Ni(C\(_6\)H\(_4\)(AsMe\(_2\))\(_2\)]\(_2\)Cl\(_2\)]Cl, space group P2\(_1\)/C, were examined. Figure 2.352 shows a picture of the monocation and a table of important bond distances. In particular the Ni-As distances in the Ni(III) complex are somewhat longer than in Ni(C\(_6\)H\(_4\)(AsMe\(_2\))\(_2\)]\(_2\)I\(_2\) (2.34 - 2.37 Å, vs. 2.28 - 2.30 Å).

<table>
<thead>
<tr>
<th>Bond</th>
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</tr>
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<tr>
<td>Ni-As(_1)</td>
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</tr>
<tr>
<td>Ni-As(_2)</td>
<td>2.34</td>
</tr>
<tr>
<td>Ni-Cl(_1)</td>
<td>2.43</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(_1)-Ni-As(_2)</td>
<td>86.2</td>
</tr>
<tr>
<td>As(_1)-Ni-Cl(_1)</td>
<td>92.9</td>
</tr>
<tr>
<td>As(_2)-Ni-Cl(_4)</td>
<td>92.0</td>
</tr>
</tbody>
</table>

Figure 2.352. Structure of [Ni(C\(_6\)H\(_4\)(AsMe\(_2\))\(_2\)]\(_2\)Cl\(_2\)]Cl. Important bond distances and angles are given in the accompanying table. From reference 176.
Interpretation of the e.s.r. spectra of 
\[ \text{[Ni} \{ \sigma-C_6H_4(EMe_2) \}_2Cl_2 \}^+ \ (E = P, As) \] has been a subject of controversy. Initially, on the basis of preliminary results \( (E = As) \) it was suggested that the unpaired electron occupied a molecular orbital composed largely of As \( \sigma \)-character, signifying that the complex was best described as that of \( \text{Ni}^{\text{II}} \) with a cation radical, \[ \sigma-C_6H_4(\text{AsMe}_2)_2 \]. Later this interpretation was challenged, as it was observed that hyperfine coupling to the axial halide co-ligands, as well as to As, occurred, inconsistent with the extreme cation-radical description. It was suggested, in fact, that only ca. 3% of the total spin density was localised on the As atoms, irrespective of the axial ligand.

A detailed study, using dilute single crystals of \( \text{Ni}^{\text{III}} \) in the analogous diamagnetic, near-isomorphic, Co(III) complex, was undertaken. With low concentrations of \( \text{Ni}^{\text{III}} \) sites, an axial spectrum, consistent with a \( d^7(d_z^2) \) ground state, was observed.

Recently, the development of convenient syntheses of \( \sigma-C_6H_4(PMe_2)_2 \) made the synthesis and study of complexes of this ligand, and comparison with those of \( \sigma-C_6H_4(\text{AsMe}_2)_2 \), a feasible undertaking. In particular, \[ \text{[Ni} \{ \sigma-C_6H_4(PMe_2)_2 \}_2X_2 \text{ClO}_4 \ (X = \text{Cl, Br}) \] were synthesised. Analytical and spectroscopic examination indicated that they are very similar to the corresponding complexes of \( \sigma-C_6H_4(\text{AsMe}_2)_2 \).

E.s.r. examination of these complexes has revealed a similar ground state as for the diarsine complex, \( \sigma-C_6H_4(\text{AsMe}_2)_2 \), although these authors assigned a far greater delocalisation of spin density onto the ligand frame than did Manoharan and Rogers.

In summary, for this system, detailed e.s.r. measurements have led to three different bonding models being suggested, viz. \( \text{Ni}^{\text{II}}\)-
cation radical complex, Ni(III) [low spin d^7(d^2)_1] complex with very small covalency, and Ni(III) complex with a large degree of covalency.

Little other data has been published which might help to resolve the question. Nakamoto assigned the vibrations in the i.r. spectrum of [Ni{O-C_6H_4(AsMe_2)_2}_2X_2]^n+ (X = Cl, Br, n = 0, 1, 2) due principally to v_{Ni-X}. The large increase in v_{Ni-X} upon oxidation from Ni(II) to Ni(III) and Ni(III) to Ni(IV) (e.g. for X = Cl; Ni(II) - not observed down to 100 cm^{-1}; Ni(III) - 240 cm^{-1}; Ni(IV) - 420 cm^{-1}) suggests consecutive removal of (antibonding) electrons from the d_x^2 orbital on successive oxidations (d^8 \rightarrow d^7 \rightarrow d^6). Significantly, vibrations tentatively assigned as principally in character did not alter greatly on oxidation. This evidence, then, suggests a predominantly metal-based oxidation.

The question as to the exact description of the electron density distribution in these complexes must remain open to discussion, as the answer obtained seems to depend on the technique used.

The formation of [Ni(L-L)_2X_2]^n+ (X = Cl, Br; n = 1, 2) is not restricted entirely to o-phenylene-based chelates. The ligand cis-1,2-bis(dimethylarsino)ethene (cis-edas) stabilises Ni(III) in [Ni(cis-edas)_2Cl_2]PF_6. This was made by air oxidation of the Ni(II) complex in ethanol-HCl followed by metathesis with NaPF_6; it was very similar to the O-C_6H_4(AsMe_2)_2-containing analogue. However, attempted metathesis with LiBr in ethanol led to reduction and the Ni(III) bromo-complex was also inaccessible by air oxidation in the presence of HBr. Free halogen attacked the ligand double bond.
So far, the successful synthesis of cisMe₂PCHCHPMe₂ has eluded organophosphorus chemists, but the saturated analogue Me₂PCH₂CH₂PMe₂, commonly known as dmpe, has been available for twenty years. Booth and Chatt reported the synthesis, by air oxidation of [Ni(dmpe)₂Br₂] in ethanol-HBr, of [Ni(dmpe)₂Br₂]Br. An attempt to oxidise this further with Br₂ in ethanol, resulted only in the precipitation of [Ni(dmpe)₂Br₂]Br₃. No Ni(III) chloro-complex was reported.

No bis-ligand Ni(III) complex (ligand = aryl-substituted diphosphine) has been reported, although it was briefly mentioned that [Ni(cis-Ph₂PCHCHPPh₂)₂Br]BPH₄ appeared to be oxidised by bromine, but the product decomposed in a few hours. No analytical or spectral data were reported.

2.35 (iv) Multidentate Ligands

Nickel (III) complexes with multidentate ligands are rare. The initial report that As(CH₂CH₂CH₂AsMe₂)₃ gave exclusively nickel (III) complexes was later shown to be erroneous (page 39). However, the square pyramidal [Ni(MeAs(CH₂CH₂CH₂AsMe₂)₂)Br₂] was shown to be oxidised to a black, paramagnetic complex, which was easily reduced back to the nickel (II) complex and which could not be obtained pure. This was formulated [Ni(ligand)Br₃]. The more rigid ligand ttas (Figure 2.353) stabilised nickel (III) more.

Figure 2.353. "ttas"
effectively. A complex \([\text{Ni(ttas)Br}_3]\), made by bromine oxidation of the \(\text{Ni(II)}\) analogue, was obtained as red crystals, soluble in organic solvents with slow decomposition to \(\text{Ni(II)}\). It was a non-electrolyte in nitromethane. Its infra red spectrum closely resembled that of \text{mer-[Rh(ttas)Br}_3\text{]} and the two complexes were isomorphous - hence its configuration too is \text{mer}.

In an attempt to isolate \(\pi\)-olefin complexes of \(\text{Ni(II)}\), Booth et al. reacted the complex \([\text{Ni}_2(\text{bdpa})_3(H_2O)](\text{ClO}_4)_4\) (Figure 2.354) with tetracyanoethylene and tetracyanoquinodimethane (tcne and tcnq respectively). With tcnq in excess, under anaerobic conditions, a complex was obtained whose electronic spectrum, magnetic moment and e.s.r. spectrum suggested \(\text{Ni(III)}\), and whose structure was proposed to be as in Figure 2.354. Here, the tcnq acts as both a ligand and a one-electron oxidant. The infra red spectrum also strongly suggested the presence of tcnq.

Figure 2.354

\[
\begin{align*}
\text{Me}_2\text{As} & \quad \text{As} & \quad \text{AsMe}_2 \\
\text{As} & \quad \text{Ph} & \quad \text{As}
\end{align*}
\]

(Above) \text{bdpa}

(Left) \([\text{Ni}_2(\text{bdpa})_2(\text{tcnq})_2]^+\)
The formation of nickel (IV) complexes of phosphines and arsines is restricted to the rigid bidentates, with methyl substituents, viz. $\sigma$-$C_6H_4(AsMe_2)_2$, $\sigma$-$C_6H_4(PMe_2)_2$ and $\text{cis-Me}_2\text{AsCHCHAsMe}_2$. No Ni(IV) complexes of $\text{MePCH}_2\text{CH}_2\text{PMe}_2$ were reported, although no mention was made of attempted HNO$_3$ oxidations.

Nyholm first noted that potentiometric ceric sulphate titrations of $[\text{Ni}(\sigma$-$C_6H_4(AsMe_2)_2)_2\text{Cl}]\text{Cl}$ could be continued after one equivalent of oxidant had been consumed, to yield a deep green material. Later, this was isolated by oxidation of the nickel (III) complex in concentrated HNO$_3$ followed by precipitation with HClO$_4$, as $[\text{Ni}(\sigma$-$C_6H_4(AsMe_2)_2)_2\text{Cl}_2][\text{ClO}_4]_2$, a deep blue material. The corresponding bromide could also be made in this way, as deep green crystals. The complexes were carefully analysed, especially for N; none was found, ruling out the possibility that they were nitrosyls. Both were found to have $\mu_{\text{eff}} \leq 0.7$ BM. This could be due to partial decomposition to nickel (III) or temperature-independent paramagnetism. The infra red spectra of both complexes have been recorded ($\nu_{\text{Ni-Cl}} = 421.5$, $\nu_{\text{Ni-Br}} = 312.5$ cm$^{-1}$).

The corresponding diphosphine similarly yields deep purple $[\text{Ni}(\sigma$-$C_6H_4(PMe_2)_2)_2\text{Cl}_2][\text{ClO}_4]_2$. Preliminary spectroscopic data was obtained, but the corresponding bromide was not synthesised.

The instability of $\text{cis-Me}_2\text{AsCHCHAsMe}_2$ complexes of Ni(II) relative to their $\sigma$-$C_6H_4(AsMe_2)_2$ counterparts has been noted. With Ni(IV) the difference is more marked. Although $[\text{Ni}(\text{cis-Me}_2\text{AsCHCHAsMe}_2)_2\text{Cl}_2][\text{PF}_6]_2$ could be isolated as dark blue crystals from nitric acid solution, by addition of NH$_4$PF$_6$, the solid decomposed, apparently directly to nickel (II), on drying.

Finally, it has been reported that (C$_6$F$_5$)$_2\text{TLBr}$ is capable of acting as an inorganic oxidant, and on reaction with
Ni\{\sigma-C_6H_4(AsMe_2)_2\}Br_2 \text{ yields } [Ni\{\sigma-C_6H_4(AsMe_2)_2\}Cl_2\}Br_2].

However, in view of the instability of $[Ni\{\sigma-C_6H_4(AsMe_2)_2\}Cl_2]Cl_2$ (the chloride ion apparently catalysing decomposition by reduction) the nature of the perfluorophenyl adduct is open to further examination.

### 2.36 $\sigma$-Bonded Organometallic Ligands

Recently nickel (III) has been shown to be stabilised by a most unusual donor set, namely $N_2C^\cdot X_2$ ($X = Cl^-$, Br$^-$, I$^-$), in the complexes $[Ni(C_6H_3(CH_2NMe_2)_2]Cl_2\}$. These are made by $X_2$ (or CuCl$_2$) oxidation of the square planar $[Ni(C_6H_3(CH_2NMe_2)_2]Cl_2\}$ and are square pyramidal. The iodide has been examined by X-ray crystallography, and is the only well-characterised Ni (III) iodide in the literature (see Chapter 4, page 192). The molecule is illustrated in Figure 2.36 (i). Significant bond lengths are in Table 2.36 (ii).

**Figure 2.36 (i) Structure of $[Ni(C_6H_3(CH_2NMe_2)_2]Cl_2\}$ from reference 183.**

**Table 2.36 (ii)**

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-I1, 2.613 (1)</td>
<td>Ni-I2, 2.627 (1)</td>
</tr>
</tbody>
</table>
Table 2.36 (ii) Significant bond lengths and angles

in [NiC₆H₃(CH₂NMe₂)₂]₂I₂, reference 183.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angles (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Il</td>
<td>2.613(4)</td>
<td></td>
</tr>
<tr>
<td>Ni-Il₂</td>
<td>2.627(4)</td>
<td></td>
</tr>
<tr>
<td>I₁-NiC₁</td>
<td>1.898(5)</td>
<td>I₁-NiC₁ = 88.2(2)</td>
</tr>
<tr>
<td>Ni-Ni₁</td>
<td>2.050(4)</td>
<td>Ni-Ni-N₂ = 152.0(2)</td>
</tr>
<tr>
<td>Ni-Ni₂</td>
<td>2.038(4)</td>
<td>C₁-Ni-I₂ = 168.8(2).</td>
</tr>
</tbody>
</table>

The esr spectra were complicated, but no $^{14}$N coupling was observed. For X = Cl, the expected four-line ($^{35}/^{37}$Cl; I = 3/2) pattern was observed in the $g_{∥}$ region, consistent with coupling to the single apical Cl. This, and the lack of any coupling to the phenyl ring protons, indicated a $(d_2^2)^1$ ground state, with the odd electron localised on the metal. Since dimerisation would theoretically give a stable 18 electron species, it was proposed that the steric bulk of the -NMe₂ group prevented this. Clearly, the co-ordination of this ligand confers unusual properties on the nickel centre. Recently the first stable nickel (II)-formato complex, with this ligand, was isolated, and this, too, can be oxidised to Ni(III).
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   and following paper.


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CHAPTER 3: NICKEL(III) COMPLEXES OF PHOSPHORUS,
ARSENIC, ANTIMONY AND SULPHUR NEUTRAL DONOR
LIGANDS
CHAPTER 3

SECTION 3.1. Ni(III) Complexes of Monodentate Ligands

Introduction

Previous literature concerning the compounds examined here has been reviewed (Chapter 2, page 82). No previous attempt to characterise a series of complexes of Ni(III) with monodentate phosphines by spectroscopic means has been made. This is probably because the synthesis of analytically satisfactory samples of \([\text{Ni(PR)}_3_2 \text{X}_3]\) \((R = \text{Me, Bu}^n, X = \text{Br, Cl}; R = \text{Me, Et, Pr}^n, \text{Bu}^n, X = \text{Cl})\) has not been achieved\(^1\), and the samples which have been made are extremely difficult to handle. They are very soluble (with decomposition) in all organic solvents, and decompose in the solid state in a few hours at room temperature.\(^1,2\)

The oxidation of other nickel (II) complexes of monodentate ligands (arsines,\(^3\) stibines,\(^4\) phosphites,\(^5\) amines\(^6\)) has not been reported. In some instances, higher co-ordination numbers are more readily achieved in Ni(II) complexes with these ligands (for example, Ni (Me,As)\(^3\) )\(^3\) ) and it was of interest to determine whether these complexes could be oxidised and if the product of oxidation was significantly different in properties to the corresponding phosphine complex.

Results and Discussion

(i) \([\text{Ni(PR)}_3_2 \text{X}_3]\)

A number of nickel (II)-monodentate phoshine complexes \([\text{Ni(PR)}_3_2 \text{X}_3]\) \((X = \text{Cl, Br}; R_3 = \text{Me}, \text{Et}, \text{Bu}^n, \text{Cy}, \text{Me}_2 \text{Ph}, \text{Et}_2 \text{Ph}, \text{MePh}_2, \text{Ph}_3, X = \text{I}; R = \text{Et}_3)\) were prepared (see Chapter 7, page 293) in order
that optimum conditions for oxidation to analytically pure Ni(III) materials could be established. For the bromides, Ni(III) samples were best obtained by adding a small excess of Br₂ to a dry CH₂Cl₂ solution of the Ni (II) complex at -20°C, then pumping off the solvent in vacuo. Higher-boiling solvents such as benzene, used by Jensen, required pumping either at higher temperatures or for longer times, during which significant decomposition of the Ni(III) complex apparently ensued. An even lower boiling solvent, CFCl₃, was tried, but the advantage of its lower boiling point (21°C) was offset by the greater volume needed to dissolve the Ni(II) complexes.

Similarly, several methods were tried for preparing [Ni(PR₃)₂Cl₃]. Jensen used a large excess of neat NOCl, condensed onto the Ni (II) complex at -80°C and subsequently removed in vacuo at room temperature. Analytically pure samples were eventually obtained by treating CH₂Cl₂ solutions of the Ni (II) complexes at -78°C (acetone slush bath) with a small excess of pure NOCl, then pumping off the solvent, eventually warming to ca 10°C. (See Figure 3.11 for a diagram of the apparatus).

The complexes of PMe₃ were generally less soluble than their longer-chain analogues, and it was possible to isolate pure samples of [Ni(PMe₃)₂Br₃] by precipitation from CH₂Cl₂ solution with pentane, followed by filtration under nitrogen.

Once isolated, most of the complexes may be stored under nitrogen at -20°C for a few days. However, they all decompose at room temperature in 5-24 hours. The chlorides decomposed significantly more quickly than the bromides. Indeed [Ni(PhPET₂)₂Cl₃] decomposed to a sticky oil within 4 hours of preparation even if stored at -20°C.

The bromides were obtained as intensely dark green or dark red-green, dichroic waxy crystals. The PMe₃ complex was
Figure 3.11.

A diagram of the apparatus used to synthesise \([\text{Ni}(L)_2\text{Cl}_2]\) complexes.

A. to vacuum/\(N_2\) double manifold line
B. standard vacuum tap
C. solid \(\text{NOCl}\) pre-purified by distillation in \textit{vacuo}
D. \([\text{Ni}(L)_2\text{Cl}_2]\) in \(\text{CH}_2\text{Cl}_2\) solution, frozen to glass and evacuated.

Taps \(B_1\) and \(B_3\) are then closed, tap \(B_2\) opened and \(C\) is allowed to warm up so that \(\text{NOCl}\) condenses in \(D\). Tap \(B_2\) is closed and \(D\) allowed to warm until the glass of \(\text{CH}_2\text{Cl}_2\) melts and the colour changes from red to purple-blue. Tap \(B_3\) is opened and the \(\text{CH}_2\text{Cl}_2\) removed in \textit{vacuo} as rapidly as feasible, while \(C\) is again frozen down.
a dark purple colour. (Table 3.12 gives physical and analytical data obtained for all the complexes). The chlorides were, similarly, blue-green dichroic crystals, except for the PMe$_3$ complex which was purple. Careful comparison of the i.r. spectrum of the Ni(III) complexes with those of their Ni(II) analogues confirmed that, for freshly prepared samples, no phosphine oxide or nitrosyl impurities were present in the Ni(III) materials. However, on exposure to the atmosphere, CH$_2$Cl$_2$ solutions of the Ni(III) complexes change colour at varying rates from dark green ($X = \text{Br}$) or blue-green ($X = \text{Cl}$) to a light blue colour characteristic of Ni(II) phosphine oxide complexes. This change was monitored by electronic spectroscopy for Ni(PET$_3$)$_2X_3$ ($X = \text{Cl, Br}$). The moderately intense bands at 16,900 and 24,800 ($X = \text{Cl}$) and 16,300, 21,600 cm$^{-1}$ ($X = \text{Br}$) (Table 3.13) were replaced by much weaker bands at ca 17,000 cm$^{-1}$, characteristic of the tetrahedral Ni(II) phosphine oxide complexes. This process is particularly fast for the PMe$_3$ complexes. Previous workers have noticed that even [Ni(PMe$_2$)$_2X_2$] ($X = \text{Cl, Br}$) are air-sensitive in solution, being oxidised to unspecified products. Also, the Co (II) complexes [Co(PMe$_2$)$_2X_2$] ($X = \text{Br, Cl, I}$) are air-sensitive, giving [Co(O = PMe$_3$)(PMe$_3$)$_2X_2$], and the reactivity of other Co (II)/Phosphine systems with dioxygen has been the subject of intense investigation. All attempts at recrystallisation of the complexes failed, owing to their extreme solubility in organic solvents. Although they could be precipitated from pentane solution at low temperatures, significant decomposition occurred, presumably owing to the susceptibility of the solvent to halogenation.

Unlike the complexes of bidentate aryl phosphines and arsines (L-L), [Ni(L-L)X$_3$], which revert cleanly to [Ni(L-L)X$_2$] on heating in vacuo or on thermogravimetric analysis (see page 132), the [Ni(PR$_3$)$_2X_3$] decomposed under similar conditions to a mixture of phosphonium salts, phosphine oxides and [Ni(PR$_3$)$_2X_2$]. In particular for [Ni(PET$_3$)$_2$ Br$_3$] the product of heating in vacuo (80°C final temp. 0.5 mmHg) was a foul-smelling oil, and [Ni(PET$_3$)$_2$Br$_2$],
<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour (a)</th>
<th>$C_b$ (b)</th>
<th>$I_%$</th>
<th>$\nu_{\text{eff}}$ (d)</th>
<th>IR (cm$^{-1}$) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(PMe}_3\text{)}_2\text{Cl}_3]$</td>
<td>purple-red</td>
<td>23.2 (22.7)</td>
<td>5.6 (5.7)</td>
<td>1.84</td>
<td>328</td>
</tr>
<tr>
<td>$[\text{Ni(PMe}_3\text{)}_2\text{Br}_3]$</td>
<td>purple-black</td>
<td>15.5 (16.0)</td>
<td>3.6 (4.0)</td>
<td>2.20</td>
<td>262</td>
</tr>
<tr>
<td>$[\text{Ni(PEt}_3\text{)}_2\text{Cl}_3]$</td>
<td>turquoise</td>
<td>36.4 (35.9)</td>
<td>7.6 (7.5)</td>
<td>1.95</td>
<td>294</td>
</tr>
<tr>
<td>$[\text{Ni(PEt}_3\text{)}_2\text{Br}_3]$</td>
<td>dark green</td>
<td>26.5 (26.9)</td>
<td>5.6 (5.6)</td>
<td>1.72(e)</td>
<td>226</td>
</tr>
<tr>
<td>$[\text{Ni(p}^6\text{Bu}_3\text{)}_2\text{Cl}_3]$</td>
<td>dark blue</td>
<td>44.3 (44.5)</td>
<td>8.3 (8.7)</td>
<td>2.16</td>
<td>317</td>
</tr>
<tr>
<td>$[\text{Ni(p}^6\text{Bu}_3\text{)}_2\text{Br}_3]$</td>
<td>dark green</td>
<td>41.5 (41.0)</td>
<td>8.0 (7.7)</td>
<td>1.88</td>
<td>228</td>
</tr>
<tr>
<td>$[\text{Ni(PPhMe}_2\text{)}_2\text{Cl}_3]$</td>
<td>blue-purple</td>
<td>44.1 (43.9)</td>
<td>5.0 (5.1)</td>
<td>2.15</td>
<td>308</td>
</tr>
<tr>
<td>$[\text{Ni(PPhMe}_2\text{)}_2\text{Br}_3]$</td>
<td>red-black</td>
<td>33.6 (33.4)</td>
<td>4.0 (3.8)</td>
<td>2.17(e)</td>
<td>247</td>
</tr>
<tr>
<td>$[\text{Ni(PPhEt}_2\text{)}_2\text{Cl}_3]$</td>
<td>blue-green</td>
<td>48.9 (48.3)</td>
<td>6.2 (6.1)</td>
<td>1.70</td>
<td>310</td>
</tr>
<tr>
<td>$[\text{Ni(PPhEt}_2\text{)}_2\text{Br}_3]$</td>
<td>dark green</td>
<td>37.7 (38.1)</td>
<td>4.5 (4.8)</td>
<td>1.70</td>
<td>224</td>
</tr>
<tr>
<td>$[\text{Ni(Ph}_2\text{PMe}_2\text{)}_2\text{Cl}_3]$</td>
<td>blue-green</td>
<td>55.5 (55.2)</td>
<td>4.7 (4.6)</td>
<td>dec</td>
<td>317</td>
</tr>
<tr>
<td>$[\text{Ni(Ph}_2\text{PMe}_2\text{)}_2\text{Br}_3]$</td>
<td>dark green</td>
<td>44.6 (44.7)</td>
<td>3.8 (3.7)</td>
<td>1.87</td>
<td>245</td>
</tr>
</tbody>
</table>

(a) Ni(III) complexes are dichroic. (c) $\nu_{\text{Ni-X}}$. The IR spectra showed no evidence for $\nu_{\text{P=O}}$ when freshly prepared samples were used.
(b) found (calc).
(d) Measured on Ni(III) species generated by $X_2$ oxidation in situ in CHCl$_3$, by the Evans nmr method. Units BM.
(e) Lit values$^3,4$ (Gony measurements).
Table 3.13. Electronic spectra of $[\text{Ni}(\text{PR}_2)_2X_3]$. 

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{max}}$ (diffuse reflectance)$^a$</th>
<th>$E_{\text{max}}$ (c$_{\text{mol}}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^5$ cm$^{-1}$</td>
<td>$10^5$ cm$^{-1}$ (dm$^3$ cm$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PMe}_3)_2\text{Cl}_3]$</td>
<td>16.6(sh), 18.1, 18.9(sh), 26.0</td>
<td>18.5(6105), 25.9(5940), 37.9(8030)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PMe}_3)_2\text{Br}_3]$</td>
<td>13.6(sh), 16.8(br), 18.1, 24.2</td>
<td>18.1(6700), 21.7(3865), 25.5(4650), 32.5(13,160)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PET}_3)_2\text{Cl}_3]$</td>
<td>13.6(sh), 14.6(sh), 16.6, 18.3, 24.5, 27.6(sh), 28.9</td>
<td>16.9(1590), 24.8 (1455), 27.3(5315), 37.0(6950)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PET}_3)_2\text{Br}_3]$</td>
<td>16.0(br), 18.2, 23.8, 26.3</td>
<td>16.3(3610), 21.6(11,520)(sh), 22.7(12,370), 33.6(40,500)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PBU}_3)_2\text{Cl}_3]$</td>
<td>16.2(sh), 16.9, 17.7(sh), 24.6, 33.1</td>
<td>16.9(-), 24.4 (-), 27.2 (-).</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PBU}_3)_2\text{Br}_3]$</td>
<td>13.1(sh), 14.3, 15.0, 24.2(sh), 26.0, 27.8</td>
<td>16.2(6690), 21.6(2625)(sh), 23.0(3020)(sh), 25.0(3100), 32.9(7150)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PPhMe}_2)_2\text{Cl}_3]$</td>
<td>14.7(sh), 15.1(sh), 16.2, 17.5(sh), 23.5, 35.1</td>
<td>17.4(3387), 24.9(3380), 27.3(8805),</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PPhMe}_2)_2\text{Br}_3]$</td>
<td>13.8(sh), 15.9(sh), 16.7, 18.2(sh), 20.6, 24.8</td>
<td>16.8(2674), 21.3(1140)(sh), 24.8(2100)(sh), 26.2(2250), 30.1(1310)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PPhEt}_2)_2\text{Cl}_3]$</td>
<td>13.8(sh), 14.5, 15.5(sh), 16.6(sh), 24.2</td>
<td>16.6(-), 24.0(-)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{PPhEt}_2)_2\text{Br}_3]$</td>
<td>13.8(sh), 15.1, 16.6(sh), 17.4(sh), 20.9, 25.8, 35.7(sh)</td>
<td>16.1(6360), 20.8(3150), 26.0(6560), 30.1(6430)</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Ph}_2\text{PMe})_2\text{Cl}_3]$</td>
<td>15.5(br), 16.8(sh), 20.9, 24.2</td>
<td>Decomposes too quickly</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Ph}_2\text{PMe})_2\text{Br}_3]$</td>
<td>13.9(sh), 15.9, 17.0, 20.0, 30.1</td>
<td>16.4(7070), 20.5 (3225), 24.5(7940), 29.8(6950)</td>
</tr>
<tr>
<td>&quot;$[\text{Ni}(\text{Et}_3\text{As})_2\text{Br}_3]&quot;$</td>
<td>-</td>
<td>14.7, 21.4, 23.8, 33.8</td>
</tr>
</tbody>
</table>

(a) Nujol mull spectra 12-35000 cm$^{-1}$.
(b) $e_{\text{mol}}$ values are approximate. Species generated in situ by $X_2$ oxidation of $\text{NiL}_2X_2$ in $\text{CH}_2\text{Cl}_2$.

Solutions decompose at varying rates.
in near-equal proportions. The oil had $v_{\text{P-H}}$ at 2305 cm$^{-1}$ and a strong band due to $v_{\text{P=O}}$ at 1190 cm$^{-1}$ in its infra red spectrum. A colourless gas which gave white fumes with ammonia, therefore presumably HBr, was condensed in the pump trap.

Attempts were made to react $[\text{Ni(PEt}_3)_2\text{X}_3]$ with X$^-$ in CH$_2$Cl$_2$. Previous work on complexes of Pd(IV) had established that the anions R$_4$N $[\text{Pd(L)X}_5]$ (L = monodentate donor) were considerably more stable than neutral $[\text{Pd(L)}_2\text{X}_4]$, indicating the preference of Pd(IV) for binding the anionic halides. However, the esr spectrum of a 1:1 mole ratio of Ph$_3$Me$^+$Br$^-$ and $[\text{Ni(PEt}_3)_2\text{Br}_3]$ in CH$_2$Cl$_2$ showed no significant changes from that of the Ni (III) complex alone, indicating that formation of $[\text{Ni(PEt}_3)_2\text{Br}_4]^- \text{Br}_3$ had not occurred. At room temperature, the electronic spectra of $[\text{Ni(PEt}_3)_2\text{X}_3]$ showed no variation with increasing concentration of X$^-$, although solution decomposition appeared to be faster in the presence of X$^-$. Similar results were obtained with complexes of the less-bulky PMe$_3$. Other attempts to achieve higher co-ordination numbers by addition of excess PMe$_3$ to a solution of $[\text{Ni(PMe}_3)_2\text{Br}_3]$ also led to decomposition of the complex. No reaction appeared to occur with pyridine. Attempts to synthesise anions directly by reaction of Bu$_4$N$[\text{Ni(PPh}_3)\text{Br}_3]$ with Br$_2$ also failed. Similar Ni(II) anions with the stronger donor trialkylphosphines could not be made.

Apart from an illustration of the electronic spectrum of $[\text{Ni(PPr}_3)_2\text{Cl}_3]$ generated in situ in pentane, spectroscopic data in the literature is confined to $[\text{Ni(PhPMe}_2)_2\text{Br}_3]$. As this has been the subject of a crystal structure determination, a comparison of spectroscopic data on other $[\text{Ni(PR}_3)_2\text{X}_3]$ with that obtained for $[\text{Ni(PhPMe}_2)_2\text{Br}_3]$ should determine whether the complexes are isostructural.

Electronic spectroscopic data is summarised in Table 3. and Figure 3. shows the spectra of $[\text{Ni(PEt}_3)_2\text{Cl}_n](n=2,3)$. 

-111-
Figure 3.14. A comparison of the electronic spectra of $[\text{Ni(PEt}_3)_2\text{ Cl}_3]$ (——) and $[\text{Ni(PEt}_3)_2\text{ Cl}_2]$ (--------) in $\text{CH}_2\text{Cl}_2$. 

(x10)
The spectra are essentially similar for solid and solution samples, confirming the conclusions from earlier molecular weight and conductivity studies that the complexes maintain their integrity in solution.

Two main bands are observed in the visible region at ca 16-18,000 and ca 20-25,000 \( \text{cm}^{-1} \), with high \( (\varepsilon = \text{ca} \ 5000 \ \text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}) \) extinction coefficients (although these are approximate owing to decomposition in solution). The spectra are all similar including that of \([\text{Ni(PhPMe}_2]_2\text{Br}_3]\). As this molecule is known to be a distorted trigonal bipyramid with axial phosphines (see page 81), similar structures are proposed for all the complexes, in agreement with Jensen's suggestion on the basis of a dipole moment study on \([\text{Ni(PPh}_3]_2\text{Br}_3]\) in pentane. For \( D_3h \) symmetry, a low-spin \( d^7 \) ion is expected to have the \((d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2})^3(d_{z^2})^0 \) ground state. The distortion of the NiBr\(_3\) plane in \([\text{Ni(PhPMe}_2]_2\text{Br}_3]\) suggests that the expected Jahn-Teller distortion of the \((d_{xy}, d_{x^2-y^2})^3 \) levels does occur, although steric factors may be important also. Taking this into account, the ground state \((e'')^4(e_a')^2(e_b')_1(a_1)_0\) results. An angular overlap, one-electron scheme has been devised for trigonal bipyramidal complexes of the isoelectronic Co(II), and the predicted electronic transitions are \((e'')^4(e_a')_2(e_b')_1(a_1)_0 \rightarrow (e'')^4(e_a')_1(e_b')^2, \rightarrow (e'')_4(e_a')_2(a_1)_1, \rightarrow (e'')^3(e_a')_2(e_b')_2\). The two observed bands may therefore be due to transitions to the \((e'')^4(e_a')_2(a_1)_1\)

* All the Ni (III) complexes decomposed at varying rates in solution. The electronic spectra were recorded on freshly-made solutions in dry solvents and in some cases, repetitive scans were performed to monitor decomposition. Decomposition was fastest for the chlorides, \([\text{Ni(PhPPh}_2]_2\text{Cl}_3]\) and \([\text{Ni(PPh}_2]_2\text{Cl}_3]\) being particularly quick (half-life ca 2 minutes at room temperature).
and \((e'')^3 (e_a')^2 (e_b')^2\) states respectively, with the third and lowest energy transition too far into the infra-red to be identified. The molar extinction coefficients are very high for d-d bands, but this is observed for other five-co-ordinate phosphine complexes also, and 'tailing' from the relatively low-energy ligand - metal charge transfer bands at > 26,000 cm\(^{-1}\) is also likely to be partly responsible.

One fairly broad band in the far infra-red spectra of the complexes is attributed to \(\nu_{Ni-X}\), at ca 300-330 cm\(^{-1}\) (\(X = Cl\)) and 220-260 cm\(^{-1}\) (\(X = Br\)) (Table 3.12). In \(D_{3h}\) symmetry, one band (E) is predicted and the broadening may be due to distortion, with consequent lowering of the degeneracy. Figure 3.15 shows the far infra-red spectrum of a typical Ni (III) complex and its Ni (II) precursor.

![Figure 3.15](image)

**Figure 3.15.** The far i.r. spectra of Ni (PhPMe\(_2\))\(_2\) Cl\(_3\) (broken line) and Ni(PhPMe\(_2\))\(_2\) Cl\(_2\) (solid line) showing lowering of \(\nu_{Ni-X}\) on oxidation.
Page 115 is missing from this Thesis
The lowering of $\nu_{\text{Ni-X}}$ on oxidation from Ni(II) to Ni(III) is also observed for [Ni(L-L)X$_3$] (page 129) and is probably a consequence of the higher co-ordination number and the presence of the anti-bonding electron in the Ni-X bonding orbitals in the Ni(III) complex.

All the other Ni(III)-phosphine complexes which have been synthesised have a (d$^8$) ground state (see Chapter 3.2, page 154). Their esr spectra are readily observed in solution and the solid phase at room temperature, under a variety of conditions, and the lines are comparatively sharp for metal complexes. Meek reported that the esr spectrum of [Ni(PhPMe$_2$)$_2$Br$_3$] could not be resolved under all conditions tried (room temperature, -196°C; solid, solution in CH$_2$Cl$_2$). This was confirmed in the course of this study. It is unfortunate that the only complex for which there is X-ray structural information is also the only one for which an esr spectrum could not be obtained. Attempts to obtain single crystals of another Ni(III) complex were not made. Comparison of the X-ray powder photographs of [Ni(PhPMe$_2$)$_2$Br$_3$] and [Ni(PhPMe$_2$)$_2$Cl$_3$] (for which an esr signal was obtained) indicated that they were isostructural, although the lines were rather weak. Although at room temperature all the complexes are either e.s.r.-silent, or give signals too broad to be interpretable, at -196°C the signals are resolvable. Optimum conditions for achieving the best resolution were determined by trial and error. The best spectra were obtained at -196°C, by generating the Ni(III) complex in situ in CH$_2$Cl$_2$/CCl$_4$ solution (1:5) with Br$_2$ or Cl$_2$, then rapidly freezing in liquid nitrogen.

Even under optimum conditions, the esr signals are broad (Table 3.16). For D$_3h$ symmetry, two g-values would be anticipated ($g_{\|}$ and $g_{\perp}$) and for a (d$^8$, d$^{x^2-y^2}$) ground state, the order $g_{\|} > g_{\perp} > 2.000$ is predicted. With distortion, this becomes $g_{zz} > g_{xx} = g_{yy} > 2.000$, regardless of whether the unpaired electron occupies the d$_{xy}$ or d$_{x^2-y^2}$ orbital. As illustrated in Table 3.16 and Figure 3.17 the spectra obtained conform to this.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions (a)</th>
<th>$g_{zz}$</th>
<th>$g_{yy}$</th>
<th>$g_{xx}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(PMe$_3$)$_2$Cl$_3$</td>
<td>P</td>
<td>1.9(2400)</td>
<td></td>
<td></td>
<td>Very broad signal, poorly resolved.</td>
</tr>
<tr>
<td>Ni(PMe$_3$)$_2$Br$_3$</td>
<td>P</td>
<td>2.4</td>
<td>1.9</td>
<td></td>
<td>Broad signal. g-values approximate</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>2.3</td>
<td>1.9</td>
<td></td>
<td>Broad signal, g-values approximate</td>
</tr>
<tr>
<td></td>
<td>Gi</td>
<td>2.35</td>
<td>1.97(350)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(PPET$_3$)$_2$Cl$_3$</td>
<td>P</td>
<td>2.37</td>
<td>ca 1.90</td>
<td>ca 1.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>2.39</td>
<td>2.17</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Ni(PPET$_3$)$_2$Br$_3$</td>
<td>P</td>
<td>2.51</td>
<td>2.08(70)</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>2.26(200)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ni(PnBu$_3$)$_2$Cl$_3$</td>
<td>P</td>
<td>ca 2.40</td>
<td>ca 1.89</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Ga</td>
<td>2.63</td>
<td>2.18(400)</td>
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</tr>
<tr>
<td>Ni(PnBu$_3$)$_2$Br$_3$</td>
<td>P</td>
<td>2.53</td>
<td>2.07</td>
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</tr>
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<td></td>
<td>Ga</td>
<td>2.41</td>
<td>2.14(216)</td>
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<tr>
<td>Ni(PhPET$_2$)$_2$Cl$_3$</td>
<td>P</td>
<td>2.50</td>
<td>2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>2.68</td>
<td>2.21</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>Ni(PhPET$_2$)$_2$Br$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>No signal resolved</td>
</tr>
<tr>
<td>Ni{6-C$_6$H$_4$(PMe$_2$)(OMe)}$_2$Br$_3$</td>
<td>Ga</td>
<td>2.18(230)</td>
<td></td>
<td></td>
<td>No -OMe co-ordination (P ).</td>
</tr>
<tr>
<td>Ni(PhPET$_2$)$_2$Br$_3$</td>
<td>Ga</td>
<td>ca 2.5</td>
<td>ca 2.1</td>
<td>ca 1.95</td>
<td></td>
</tr>
<tr>
<td>Ni(PhPET$_2$)$_2$Br$_3$</td>
<td>P</td>
<td>2.54</td>
<td>2.08(190)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continued overleaf/...
Table 3.16 continued...

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<thead>
<tr>
<th>Complex</th>
<th>Conditions</th>
<th>$g_{zz}$</th>
<th>$g_{yy}$</th>
<th>$g_{xx}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(PhPEt$_2$)$_2$Br$_3$</td>
<td>Ga</td>
<td>ca 2.20(240)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(Ph$_2$PMe)$_2$Cl$_3$</td>
<td>Ga</td>
<td>ca 2.00(720)</td>
<td></td>
<td></td>
<td>Very broad</td>
</tr>
<tr>
<td>Ni(Ph$_2$PMe)$_2$Br$_3$</td>
<td>Ga</td>
<td>ca 2.17(290)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTES:
(a) $P$ = Polycrystalline powder, $G$ = CCl$_4$ glass. Gi = CH$_2$Cl$_2$/CCl$_4$ glass, Ga = Generated in situ.
(b) Where two $g$ values are resolved, these are attributed to $g_{zz}$ and $g_{xx}$, $g_{yy}$. Where 3 $g$-values are resolved, $g_{xx}$ and $g_{yy}$ are assigned arbitrarily (see text, page 124). Figures in parentheses are linewidths, derivative peak-to-peak, in Gauss.
(c) Some evidence of hyperfine coupling in $g_{zz}$ region - 3 lines, (2 $^{31}$P) $A_{iso} = ca$ 120G. (See Figure 3/17).
(d) Traces of hyperfine coupling discernable in $g_{xx}$, $g_{yy}$ region. 6 lines, $A_{iso} = ca$ 110G. ($^{35/37}$Cl).
(e) See Figure 3/17. Some hyperfine coupling in $g_{xx}$, $g_{yy}$ region. 10 lines, $A_{iso} = 57G$. ($^{79/81}$Br).
Figure 3.17. ESR spectrum of (A) Ni (P Bu\textsuperscript{n})\textsubscript{2} Br\textsubscript{3} in the g\textsubscript{1} region (g\textsubscript{xx} / g\textsubscript{yy} region) showing evidence for hyperfine coupling to \textsuperscript{79/81}Br. Inset is the same features, at higher gain.

(B) Ni (PEt\textsubscript{3})\textsubscript{2} Cl\textsubscript{3} showing evidence for coupling to \textsuperscript{31}P in the g\textsubscript{11} (g\textsubscript{zz}) region.
pattern, except where poor resolution leads to broad signals. Occasionally only two g-values (\(g_{zz}'\), and a broader signal where there is evidence that \(g_{xx}', g_{yy}'\) overlap) are observed. Of necessity, given the fact that data was obtained on amorphous powders or glasses, \(g_{xx}'\) and \(g_{yy}'\) are arbitrarily assigned, where two signals are sufficiently resolved to be distinguishable.

As low-spin \(d^7\) complexes are unusual in the 3d series, stable examples being restricted to Co(II), few comparisons can be made with other systems. E.s.r. has been used to distinguish the distorted trigonal bipyramidal and square pyramidal forms of \([\text{Co(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2 X']^+ (X = \text{Cl, Br, NCS, NO}_3)\), since from theoretical considerations, the ordering \(g_{zz}' = 2.0, g_{xx}' > g_{yy}' = 2.0\) is predicted for pseudo square pyramidal stereochemistry and \(g_{zz} > g_{xx}, g_{yy} > 2.0\) for trigonal bipyramidal stereochemistry. Data on Co (II) - monodentate phosphine complexes \((P_{\text{donor set}})\) is consistent with a distorted trigonal-bipyramidal symmetry, with equatorial halides.

For \(D_{3h}\) symmetry, with distortion due to the Jahn-Teller effect, the expected values of \(g\) are given by

\[
g_{xx} \simeq g_{yy} = 2.0023 + \frac{2\xi}{E_{yz}E_{xz} - E_{xy}}
\]

\[
g_{zz} = 2.0023 + \frac{8\xi}{E_{x^2-y^2} - E_{xy}}
\]

where the z-axis is the threefold axis. The symbol \(\xi\) represents the one-electron spin-orbit coupling constant. For Ni(III), this is \(715 \text{ cm}^{-1}\). However, since attempts to identify the transition \((e^{'})^2 (e_1^{'})^2 (e_2^{'})^1 + (e^{'})^4 (e_1^{'})^1 (e_2^{'})^2\) in the near-infra red spectrum of selected examples of the Ni (III) complexes failed it is not possible to compare observed and calculated g-values.

A weak feature at ca. \(10,300 \text{ cm}^{-1}\) may be due to this transition in
\[ \text{[Ni(PhPMe\textsubscript{2})\textsubscript{2}Cl\textsubscript{2}]} \]. If this is the case, the calculations yield \( g_{zz} = 2.56 \), \( g_{xx}, g_{yy} = 2.10 \). The observed \( g_{zz} \) value for this complex was 2.50 (polycrystalline powder), and 2.68 (CCl\textsubscript{4} glass), with \( g_{xx}, g_{yy} \) 2.08 (polycrystalline powder). Although the esr spectra can distinguish pseudo trigonal bipyramidal from pseudo-square pyramidal stereochemistries, an unequivocal point group assignment is not possible with the data obtained. Further support for the assignment of \( g_{11} \) and \( g_{1} \) for the Ni (III) complexes is lent by the observation of some hyperfine interactions with the ligand nuclei. Specifically, for \([\text{Ni(P}_{\text{Et}}\text{3})\text{2Cl}3]\), three-line pattern in the \( g_{11} \) region, due to coupling to two phosphorus nuclei (\( ^{31}\text{P}, \text{100\%}, I = \frac{3}{2} \)) may be seen, while in the spectra of \([\text{Ni(PhPMe}\text{2})\text{2Cl}3]\) and \([\text{Ni(PBu}\text{3})\text{2Br}3]\) evidence for interaction with the halide nuclei (\( ^{35/37}\text{Cl}, I = \frac{3}{2}, \text{79/81}\text{Br}; I = \frac{3}{2} \)) in the region assigned to \( g_{1} \) is evident. (Figure 3.17). Interestingly, when the complex \([\text{Ni}\{\text{o-C}6\text{H}4(\text{PMe}\text{2})(\text{OMe})\}_2\text{Br}2]\) was oxidised \textit{in situ} in an esr tube, an esr spectrum of \([\text{Ni}\{\text{o-C}6\text{H}4(\text{PMe}\text{2})(\text{OMe})\}_2\text{Br}3]\) was observed. It is known that in the Ni(II) complex, the ligand is co-ordinated only through P, making this the exact analogue of \([\text{Ni(PhPMe}\text{2})2\text{Br}2]\). Given the lack of reactivity of \([\text{Ni(PR}3\text{)}2\text{X}3]\) with other donors (\( \text{X}^-, \text{PMe}3, \text{pyridine}) and the electronic spectrum of \([\text{Ni}\{\text{o-C}6\text{H}4(\text{PMe}\text{2})(\text{OMe})\}_2\text{Br}3]\) (analogous to other \([\text{Ni(PR}3\text{)}2\text{X}3]\), it is highly unlikely that the -OMe groups co-ordinate on oxidation. The Ni(III) complex is therefore closely related to \([\text{Ni(PhPMe}\text{2})2\text{Br}3]\) for which no esr signal could be resolved, indicating the sensitivity of esr signals to small changes in the ligand. Further, a conventional, although broad, signal was resolved for \([\text{Ni(PhPMe}\text{2})2\text{Cl}3]\).

\(\text{(ii) Other Donors}\)

To study the susceptibility of other monodentate ligand-nickel (II) systems to oxidation the interaction of anhydrous
nickel (II) halides with various ligands (thioethers, phosphine oxides, phosphine sulphides, amines, arsines, phosphites) in rigorously dry conditions was first attempted. Nickel (II) salts are reported not to react with monodentate thioethers. On refluxing a CH₂Cl₂ suspension of anhydrous NiBr₂ with Me₂S for several days a yellow solid analysing approximately for NiBr₂ · Me₂S was obtained, but this readily decomposed and was not examined further. Phosphine oxide complexes [Ni(Ph₃P=O)₂Br₂]¹⁰ and [Ni(Pr₃P=O)₂Br₂] were readily obtained, the latter, however, only as a blue oil. Neither reacted with bromine and both decomposed with stronger oxidants such as HNO₃. In contrast, Ph₃P=S did not react with NiBr₂ under any conditions tried. Dimethyl amine yielded a green solid, Ni(Me₂NH)₂Br, but this was unaffected by anhydrous Br₂/CCl₄, as monitored by e.s.r. and visual appearance. The familiar octahedral [Ni(NH₃)₆]Br₂ was also unchanged on treatment with bromine.

More success, however, accompanied the attempted oxidations of the complexes [Ni{P(OR)₃}₂X₂], themselves made as sticky red-brown oils by the method of Jensen. These complexes show electronic spectra characteristic of trans-square planar Ni(II)-phosphine species, and so they have analogous geometry. They are even more soluble in organic solvents than their phosphine analogues, and all attempts to obtain solids failed. On treatment with bromine or NOCl, intensely green oils were observed, which decomposed in 2 minutes. These (Table 3.18) could be observed by e.s.r., when generated in CCl₄ in situ, followed by rapid freezing. Although only broad, featureless spectra were seen, (Table 3.18, Figure 3.19), these complexes are apparently similar to the phosphine analogues.

The only reported complex of Ni(II) with a monodentate arsine is [Ni(AsMe₃)₃]³⁺. Interaction of AsEt₃ with NiBr₂ or NiCl₂ yielded dark green, and dark red complexes [Ni(AsEt₃)₂]X₂]
Table 3.18. E.P.R. of Transient \([\text{Ni}(L)_2 X_3]\) Species

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions</th>
<th>(g)-values, line widths</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}(\text{PCy}_3)_2\text{Cl}_3])</td>
<td>(\text{CH}_2\text{Cl}_2) glass, (-196^\circ\text{C})</td>
<td>(g = \text{ca} 2.1) (750\text{G})(^{(c)})</td>
</tr>
<tr>
<td>([\text{Ni}(\text{P}(\text{OEt})_3)_2\text{Cl}_3])</td>
<td>(\text{CCl}_4) glass, (-196^\circ\text{C})</td>
<td>(g = 2.06) (750\text{G})</td>
</tr>
<tr>
<td>([\text{Ni}(\text{P}(\text{OME})_3)_2\text{Cl}_3])</td>
<td>(\text{CH}_2\text{Cl}_2/\text{CCl}_4) glass, (-196^\circ\text{C})</td>
<td>(g = 2.0) (1000\text{G})</td>
</tr>
<tr>
<td>([\text{Ni}(\text{P}(\text{OME})_3)_2\text{Br}_3])</td>
<td>(\text{CCl}_4) glass, (-196^\circ\text{C})</td>
<td>(g = 2.0) (1700\text{G})</td>
</tr>
<tr>
<td>([\text{Ni}(\text{AsEt}_3)_2\text{Cl}_3])</td>
<td>(\text{CH}_2\text{Cl}_2) glass, (-196^\circ\text{C})</td>
<td>(g_{zz} = 2.52, g_{xx} = 2.12) (500),(^{(c)}) (g_{yy} = 1.98)</td>
</tr>
<tr>
<td>([\text{Ni}(\text{AsEt}_3)_2\text{Br}_3])</td>
<td>(\text{CH}_2\text{Cl}_2) glass, (-196^\circ\text{C})</td>
<td>(g_{</td>
</tr>
<tr>
<td>([\text{Ni}(\text{PPh}_3)_2\text{Cl}_3])</td>
<td>(\text{CH}_2\text{Cl}_2) glass, (-196^\circ\text{C})</td>
<td>(g_1, g_2, g_3 = 2.56,1.97,1.93) (^{(c)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) All generated in situ and frozen immediately.

\(^{(b)}\) Values quoted to 1 decimal place approximate, owing to broad lines (deriv. peak-to-peak, in parentheses).

\(^{(c)}\) See Figure 3.19.
Figure 3.19 Esr spectra of Ni(AsEt₃)₂ Br₃ (A) and Ni(PPh₃)₂ Cl₃ (B) generated in situ and frozen to -196°C in CH₂Cl₂ glass.

--- = A

--- = B
(X = Br, Cl respectively), although the chloride could not be obtained pure. Although no pure Ni(III) complex could be obtained in the solid state by NOX or X$_2$ oxidation under any conditions, esr evidence suggests Ni (III) formation (Table 3.18, Figure 3.19), and a dry CH$_2$Cl$_2$ solution of the Ni (III) bromo-complex, generated in situ, was stable enough to enable the electronic spectrum to be obtained (Table 3.13). This is similar to those of the Ni (III)-phosphine complexes, suggesting that the arsine complex is similar, but markedly more unstable.

As Ni(II)-monodentate stibine complexes are unstable in solution except in the presence of excess ligand, this precluded attempts to study the oxidation of such systems.

It had previously been reported that [Ni(PPh$_3$)$_2$X$_2$] and [Ni(PCy$_2$)$_2$X$_2$] were not oxidised by X$_2$ or NOX. In the course of this work it was found that [Ni(PCy$_2$)$_2$Cl$_2$] reacted with Cl$_2$ in CH$_2$Cl$_2$ forming a blue solution which rapidly decomposed, with decolourisation. All attempts to obtain a solid material failed. Nitrosyl halides did not react with [Ni(PCy$_3$)$_2$X$_2$] and Br$_2$ failed to oxidise [Ni(PCy$_3$)$_2$Br$_2$]. When [Ni(PCy$_3$)$_2$Cl$_2$] was oxidised by Cl$_2$ in situ in an esr tube, in CH$_2$Cl$_2$/CCl$_4$, a broad signal could be detected on freezing the solution, indicative of Ni(III).

The tetrahedral complexes [Ni(PPh$_3$)$_2$X$_2$] (X = Cl, Br) failed to give Ni(III) complexes. Chlorine and nitrosyl chloride caused decomposition of CH$_2$Cl$_2$ solutions of [Ni(PPh$_3$)$_2$Cl$_2$]. Bromine did not react at all with [Ni(PPh$_3$)$_2$Br$_2$] in CCl$_4$ suspension, even on standing for several days and appeared not to react significantly in solution. However, it has been noted that when a saturated solution of [Ni(Ph$_3$P)$_2$Cl$_2$] is cooled to -78°C, red crystals (of the trans planar isomer) appear, which on standing revert to the dark blue-green tetrahedral form in ca 5 hours.
The trans-square planar isomer reacted at -85°C with a small amount of NOCl, to give a dark green substance, analysing poorly for \([\text{Ni(PPh}_3^2\text{Cl}_2]\). Some nitrosyl impurity was present, reflected in detection of N in the analysis and the presence of \(v_{\text{NO}}\) at 1855 cm\(^{-1}\) in the i.r. spectrum. Both the solid sample and a CH\(_2\)Cl\(_2\) glass prepared in situ, displayed quite sharp e.s.r. signals at -196°C, with all 3 g-values well-resolved. (Figure 3.19). The magnitude of \(g_{zz}\) (2.71) suggests that the bulk material is probably isostructural with the alkyl phosphine analogues.

Conclusions

The stability of the \([\text{Ni(ER}_2^2\text{X}_2]\) depend upon the donor atom (E), substituents (R) and halide (X) in a well-defined progression. Firstly the phosphine complexes are much more stable than the arsine complexes, which must be attributed to their greater ability to bind to 'hard' metal centres. Among the phosphine complexes, the stability order is \(\text{PMe}_3 > \text{PET}_3 > \text{PMe}_2\text{Ph} > \text{PBu}_3 > \text{PET}_2\text{Ph} > \text{Ph}_2\text{PMe} > \text{PPh}_3, \text{PCy}_3\). The order roughly parallels the \(\sigma\)-donor capacity of the ligands with the exception of \(\text{PCy}_3\), which is a strong \(\sigma\)-donor but does not give isolable \(\text{Ni(III)}\) compounds. The series is also approximately in order of increasing size. The cone angles as defined by Tolman increase from 118° (\(\text{PMe}_3\)) to 145° (\(\text{PPh}_3\)) and the instability of the \(\text{PCy}_3\) complexes is probably a result of steric effects (cone angle 170°). It has been suggested that even in the \(\text{Ni(II)}\) complexes of this ligand, the ligand field is smaller than expected due to steric hindrance elongating the \(\text{Ni-P}\) bond. A higher co-ordination number may enhance this effect.

The instability of the phosphite complexes must be due to their weaker \(\sigma\)-donor properties (-OR groups are electron-withdrawing) rather than

\[*\text{ (Found: C = 61.3, H = 4.4, N = 0.5\%. Calc. for } C_{36}H_{30}\text{Cl}_3\text{NiP}_2: C = 62.7, H = 4.4, N = 0\%)\]
steric factors, as phosphites have smaller cone angles than the corresponding phosphines.

In general, the bromides are more stable, as solids and in solution, than are the chlorides, and this is possibly due to the weaker binding of the soft PR₃ groups to the harder NiCl₃ acceptor. That this rule is broken by [Ni(PR₃)₂Cl₃] (R = Ph, Cy), (chlorides only can be isolated), is presumably due again to steric factors, which may become paramount with the bulkier ligands.
SECTION 3.2. \([\text{Ni}(L-L)X_2]\) (L-L = bidentate ligand; \(X = \text{Cl,Br}\))

Results

The complexes \([\text{Ni}(L-L)X_2]\) were prepared by halogen or NOCl oxidation of the corresponding square planar Ni(II) complexes. While a very comprehensive series of such Ni(II) complexes has been synthesised over the past twenty five years, few of the Ni(III) complexes are known, and they have been subjected only to cursory examination (see Chapter 2, page 82). This study was performed to examine the range of Ni(II) complexes for which oxidation was possible, and to explore the factors dictating the stability of the products.

To this end, a wide variety of Ni(II) complexes \([\text{Ni}(L-L)X_2]\) were synthesised (for references and methods, see Chapter 7, page 300) and oxidation by a number of techniques was attempted. First, those complexes obtained as analytically satisfactory solids will be considered.

The complexes \([\text{Ni}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{FPh}_2)\text{Br}_3]\) (\(n = 2,3\)) and \([\text{Ni cis-Ph}_2\text{PCHCPh}_2\text{Br}_3]\) had been prepared previously, by bromine oxidation in benzene suspension. This method was found to give impure products when tried for other ligands. In particular, varying degrees of oxidation occurred, as assessed by magnetic moment determinations (Gouy method), and the products were often partially solvated, making analytical confirmation of the degree of oxidation difficult.

Treatment of finely-ground suspensions of the Ni(II) bromo-complexes in dry CCl_4 with a slight excess of a solution of Br_2
(2% by volume) in the same solvent, for ca one hour, was generally found to be the best method. This yielded unsolvated complexes [Ni(L-L)Br₃] with satisfactory analyses and magnetic moments (Gouy method) (Table 3.21) for the following ligands; Ph₂P(CH₂)ₙPPh₂ (n = 2,3), cis-Ph₂PCHCHPPPh₂, o-C₆H₄(AsPh₂)₂, Me₂PCH₂CH₂PMe₂ and o-C₆H₄(PPh₂)₂SMe. Particular care was necessary in the synthesis of the last three-named complexes as they were very prone to decomposition, or (Me₂PCH₂CH₂PMe₂) moisture-catalysed rearrangement, so the oxidations were carried out in Schlenk glassware under dry nitrogen.

Oxidation in suspension proved to be unsatisfactory for [Ni(L-L)Br₂]; L-L = o-C₆H₄(AsPh₂)(PPh₂) and o-C₆H₄(PPh₂)₂. These complexes were only partially oxidised, as observed from their colour. All the complexes (X = Br) darkened from red-orange to dark brown or black on oxidation in suspension, but the above examples were nearly unchanged. Treatment of a dry CH₂Cl₂ solution of these materials with excess bromine, followed by rapid removal of the solvent in vacuo and/or precipitation with diethyl ether was necessary to effect complete oxidation.

Prior to this work, no complexes of the type [Ni(L-L)Cl₃] had been reported. The oxidation of [Ni(L-L)Cl₂] (L-L = Ph₂P(CH₂)ₙPPh₂; n = 2,3; cis-Ph₂PCHCHPPPh₂, 28 Me₂PCH₂CH₂PMe₂) with a small excess of Cl₂ in CCl₄ yielded the corresponding [Ni(L-L)Cl₃] satisfactorily, but difficulty was again experienced in preparing pure [Ni(o-C₆H₄(PPh₂)₂)Cl₃] by this route. Chlorine oxidation in CH₂Cl₂ solution caused extensive decomposition of this, and other, complexes, with formation of phosphine oxides. However, NOCl could be employed as a mild oxidant in the same manner as for the monodentate phosphine complexes, (Chapter 3.1, page 105). Treatment of [Ni(o-C₆H₄(PPh₂)₂)Cl₂] with NOCl in CH₂Cl₂ at room temperature resulted in a colour change from light yellow to dark
olive green; on concentration of the solution and precipitation with diethyl ether or pentane, a green solid of composition [Ni(L-L)Cl$_3$] was obtained. This method gave satisfactory products for the other complexes also, with the exception of [Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)Cl$_2$], for which it was not attempted.

Some limitations on the range of Ni(III) complexes which could be prepared from Ni(II) complexes are imposed by Ni(II) chemistry. In particular, [Ni(L-L)Cl$_2$] (L-L = phenyl-substituted bidentate arsine ligand) cannot be obtained. Also, the series of ligands o-C$_6$H$_4$(EMe$_2$)$_2$ (E = P, As, Sb) form only Ni(L-L)$_2$X$_2$ with nickel(II) salts in organic solvents. However, the dark red-purple [Ni{o-C$_6$H$_4$(AsMe$_2$)$_2$}X$_3$] (X = Br, Cl) were obtained by halogen oxidation of the nickel (0) complex [Ni(CO)$_2$(o-C$_6$H$_4$(AsMe$_2$)$_2$)] under moisture-free conditions.

Physical and analytical data for the complexes obtained as pure solids are in Table 3.21. All the complexes are more deeply-coloured than the Ni(II) materials. Although they decomposed in solution at varying rates, conductivity measurements on representative examples (10$^{-3}$ M solutions in 1,2-C$_2$H$_4$Cl$_2$) confirmed that the complexes were non-electrolytes. That they maintain their stereochemistry in solution is supported by the similarity of their diffuse reflectance and solution electronic spectra (Table 3.23, Figure 3.23 i). Stability varied, as estimated by shelf life and half life in solution, but most of the complexes could be kept, sealed in ampoules, at -20°C for several weeks. Eventually, decomposition to the Ni (II) starting materials, and other products, largely P(V) or As(V) materials, appeared to occur. When left open to the atmosphere, a sample of [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Cl$_3$] reverted cleanly to [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Cl$_2$] (checked by comparison of its analytical and spectroscopic properties with those of a genuine sample) over ten days. Similar observations have been made for [Ni(cis-Ph$_2$PCHCHPPh$_2$)Br$_3$]. Heating in vacuo
### Table 3.21. Analytical and Physical Data \((\text{Ni(L-L)}\text{X}_3)\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>(C^\circ(a))</th>
<th>(H%)</th>
<th>(X%)</th>
<th>(\mu_{\text{eff}}\text{BM}^{(b)})</th>
<th>(v(\text{NiX})\text{ cm}^{-1}^{(c)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Ni(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{Cl}_3]</td>
<td>olive green</td>
<td>55.1(55.4)</td>
<td>4.4(4.5)</td>
<td>18.3(18.9)</td>
<td>2.10</td>
<td>325,308</td>
</tr>
<tr>
<td>[\text{Ni(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{Br}_3]</td>
<td>dark brown</td>
<td>44.4(44.8)</td>
<td>3.3(3.5)</td>
<td>-</td>
<td>1.98</td>
<td>284,269,215w</td>
</tr>
<tr>
<td>[\text{Ni(Ph}_2\text{P(CH}_2)_3\text{PPh}_2\text{Cl}_3]</td>
<td>olive green</td>
<td>56.5(56.2)</td>
<td>4.5(4.5)</td>
<td>18.5(18.4)</td>
<td>2.01</td>
<td>338,310,286</td>
</tr>
<tr>
<td>[\text{Ni(Ph}_2\text{P(CH}_2)_3\text{PPh}_2\text{Br}_3]</td>
<td>brown-black</td>
<td>45.8(45.6)</td>
<td>3.3(3.8)</td>
<td>-</td>
<td>1.81</td>
<td>276,265,220w</td>
</tr>
<tr>
<td>[\text{Ni(Ph}_2\text{PCHCHPPh}_2\text{Cl}_3]</td>
<td>olive green</td>
<td>55.8(55.6)</td>
<td>4.0(4.0)</td>
<td>18.8(19.0)</td>
<td>1.80</td>
<td>334,315</td>
</tr>
<tr>
<td>[\text{Ni(Ph}_2\text{PCHCHPPh}_2\text{Br}_3]</td>
<td>dark brown</td>
<td>45.2(44.9)</td>
<td>3.2(3.2)</td>
<td>-</td>
<td>2.00</td>
<td>276,265,210w</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(PPh}_2)_2\text{Cl}_3]</td>
<td>dark-green</td>
<td>59.3(58.9)</td>
<td>4.2(4.0)</td>
<td>-</td>
<td>2.02(c)</td>
<td>346,311,297(w)</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(PPh}_2)_2\text{Br}_3]</td>
<td>dark-brown</td>
<td>48.2(48.4)</td>
<td>3.2(3.2)</td>
<td>31.9(32.2)</td>
<td>-</td>
<td>293,267,211(w)</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(AsPh}_2)_2\text{Br}_3]</td>
<td>black</td>
<td>42.2(41.8)</td>
<td>3.5(3.6)</td>
<td>25.2(26.4)</td>
<td>1.72</td>
<td>282,252,197(w)</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(PPh}_2)_2\text{SMe}_3\text{Br}_3]</td>
<td>black</td>
<td>38.0(37.6)</td>
<td>2.9(2.8)</td>
<td>38.5(39.6)</td>
<td>-</td>
<td>307,232</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(PPh}_2)_2\text{(AsPh}_2)_2\text{Br}_3]</td>
<td>black</td>
<td>45.4(45.7)</td>
<td>3.2(3.1)</td>
<td>31.8(30.4)</td>
<td>1.75</td>
<td>261,248,212(w)</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(AsMe}_2)_2\text{Cl}_3]</td>
<td>dark brown</td>
<td>26.4(26.6)</td>
<td>3.5(3.6)</td>
<td>25.2(26.4)</td>
<td>2.3</td>
<td>340,329</td>
</tr>
<tr>
<td>[\text{Ni(O-C}_6\text{H}_4\text{(AsMe}_2)_2\text{Br}_3]</td>
<td>brown-black</td>
<td>19.8(20.55)</td>
<td>2.7(2.8)</td>
<td>43.0(41.1)</td>
<td>2.4</td>
<td>298,267</td>
</tr>
<tr>
<td>[\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_3]</td>
<td>red-brown</td>
<td>23.1(22.9)</td>
<td>5.2(5.2)</td>
<td>-</td>
<td>-</td>
<td>320,295(?)</td>
</tr>
<tr>
<td>[\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Br}_3]</td>
<td>green-black</td>
<td>15.8(16.1)</td>
<td>3.8(3.6)</td>
<td>-</td>
<td>2.1</td>
<td>304(w), 258</td>
</tr>
</tbody>
</table>
Also resulted in reversion to the Ni(II) complex, for \([\text{Ni}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{Br}_2]\) and \([\text{Ni} \text{C}_6\text{H}_4(\text{AsPh}_2)_2\text{Br}_3]\), again checked analytically and spectroscopically. More precise information was obtained by thermo-gravimetric analysis (Table 3.22) on selected examples, which showed a clean loss of halogen.

**Table 3.22 Thermogravimetric Analysis Data**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Weight Loss (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_3])</td>
<td>10.6</td>
<td>170</td>
</tr>
<tr>
<td>([\text{Ni}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{Br}_3])</td>
<td>10.3</td>
<td>170</td>
</tr>
<tr>
<td>([\text{Ni}(\text{Ph}_2\text{PCHCHPPh}_2)\text{Br}_3])</td>
<td>10.7</td>
<td>170</td>
</tr>
<tr>
<td>([\text{Ni}\text{C}_6\text{H}_4(\text{PPh}_2)_3\text{Cl}_3])</td>
<td>6.2</td>
<td>280</td>
</tr>
<tr>
<td>([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_3])</td>
<td>6.0</td>
<td>150</td>
</tr>
</tbody>
</table>

*Calc. for \([\text{Ni}(\text{L-L})\text{X}_2]\) → \([\text{Ni}(\text{L-L})\text{X}_2]\)+\(\frac{1}{2}\text{X}_2\).*

*Temperature at which decomposition is complete, +10°C. At > 360°C, large weight loss due to loss of the diphosphine occurs. Experiments performed under dynamic argon atmosphere.*

Spectroscopically, all the complexes appear closely related, and the similar pattern of Ni-X stretching vibrations in
their infra red spectra and the close similarity of their electronic spectra are particularly notable. A similar structure is therefore proposed for all the aryl-diphosphine and -diarsine complexes. However, the determination of the precise co-ordination geometry about nickel is not possible purely on spectroscopic evidence.

As Van Hecke and Horrocks pointed out, for any nickel (III) complex $\text{[Ni(L-L)X_3]}$, one would anticipate four spin-allowed d-d transitions in the electronic spectrum. Similarly, three infra-red active nickel-halogen stretching vibrations would be anticipated for either $C_2(2A' + A'')$ or $C_2(2A_1 + B_1)$ local symmetry.

Three or four bands were observed for the complexes in the visible region (Table 3.23) the main absorption being at $\text{ca 20,000 cm}^{-1}$, with weaker bands, sometimes shoulders, at $\text{ca 15,000 and ca 9,000 cm}^{-1}$ (Figure 3.23 i). The latter was often only observed in the diffuse reflectance spectrum, being of low intensity. The extinction coefficients in CH$_2$Cl$_2$ solution are somewhat high; this has already been noted for the $\text{[Ni(PR_2)_2X_2]}$ complexes (Chapter 3.1, page 114) and the explanation is presumably similar. As the complexes decompose at varying rates in solution, these values should be treated as approximate. Three bands in the far infra red spectra of the complexes were usually observable, although often they were quite weak, and the presence of ligand bending modes in the same region made assignment of bands difficult. Values for $\nu_{\text{Ni-X}}$ in Table 3.21 are given for bands which could be assigned with reasonable certainty. The presence of two bands of similar, and one of lower, energy where three bands could be identified, is notable, as is the fact that in general, the energies are lower than for $\nu_{\text{Ni-X}}$ of the corresponding Ni (II) complexes. In Figure 3.25, the far infra red spectra of $\text{[Ni[\alpha-C_6H_4(PPh_2)_2]Cl_n]}$ ($n = 2, 3$) are compared.

Rather more interesting from the point of view of prediction of the structure of the complexes were their esr spectra.
Table 3.23. Electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_{\max} \times 10^{3}$ cm$^{-1}$ (c~mol$^{-1}$ dm$^{3}$ mol$^{-1}$ cm$^{-1}$)</th>
<th>Note(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Cl$_3$]</td>
<td>$dr$ (a) 8.9 (br), 15.5, 22.0, 31.3</td>
<td></td>
</tr>
<tr>
<td>[Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$]</td>
<td>$dr$ 7.9, 14.5 (br), 19.5, 25.0</td>
<td></td>
</tr>
<tr>
<td>[Ni(Ph$_2$P(CH$_2$)$_3$PPh$_2$)Cl$_3$]</td>
<td>$dr$ 9.2 (sh), 14.3, 21.3, 29.1</td>
<td></td>
</tr>
<tr>
<td>[Ni(Ph$_2$P(CH$_2$)$_3$PPh$_2$)Br$_3$]</td>
<td>$dr$ 13.1, 20.2 (sh)</td>
<td></td>
</tr>
<tr>
<td>[Ni(Ph$_2$PCHClPPh$_2$)Cl$_3$]</td>
<td>$dr$ 15.1, 22.0, 25.0</td>
<td></td>
</tr>
<tr>
<td>[Ni(Ph$_2$PCHClPPh$_2$)Br$_3$]</td>
<td>$dr$ 8.3, 13.5, 20.0, 25.5</td>
<td></td>
</tr>
<tr>
<td>[Ni(o-C$_6$H$_4$(PPh$_2$)$_2$)Cl$_3$]</td>
<td>$dr$ 14.4, 20.0 (sh), 21.8 (sh), 25.2, 29.4</td>
<td></td>
</tr>
<tr>
<td>[Ni(o-C$_6$H$_4$(PPh$_2$)$_2$)Br$_3$]</td>
<td>$dr$ (c) 13.7 (br), 18.3, 23.9, 25.1, 28.6</td>
<td></td>
</tr>
<tr>
<td>[Ni(o-C$_6$H$_4$(PPh$_2$)$_2$)Br$_3$]</td>
<td>$dr$ (c) 14.20 (br), 21.88 (sh), 25.97 (sh), 28.33 (sh)</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.23 (CONTINUED)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{max}} \times 10^3 \text{ cm}^{-1}$</th>
<th>$\epsilon_{\text{mol}} \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni}(o-C_6H_4(AsPh_2)_2)Br_3]$</td>
<td>dr</td>
<td>12.8, 17.6, 25.3</td>
</tr>
<tr>
<td>$[\text{Ni}(o-C_6H_4(PPPh_2)SMe)Br_3]$</td>
<td>dr</td>
<td>12.1, 18.2, 29.3</td>
</tr>
<tr>
<td>$[\text{Ni}(o-C_6H_4(PPPh_2)(AsPh_2))Br_3]$</td>
<td>dr</td>
<td>13.45, 18.25, 20.5, 24.4</td>
</tr>
<tr>
<td>$[\text{Ni}(o-C_6H_4(AsMe_2)_2)Cl_3]$</td>
<td>dr</td>
<td>8.0, 11.8, 17.0, 18.2, 25.4</td>
</tr>
<tr>
<td>$[\text{Ni}(o-C_6H_4(AsMe_2)_2)Br_3]$</td>
<td>$\epsilon^{(c)}$</td>
<td>9.7, 12.0, 15.4, 20.0, 24.1, 28.4</td>
</tr>
<tr>
<td>$[\text{Ni}(Me_2PCH_2CH_2PMe_2)Cl_3]$</td>
<td>dr</td>
<td>- , 14.4, 15.6, 18.6, 23.15, 25.5, 28.4</td>
</tr>
<tr>
<td>$[\text{Ni}(Me_2PCH_2CH_2PMe_2)Br_3]$</td>
<td>dr</td>
<td>- , 16.4, 16.95, 22.4, 24.5</td>
</tr>
</tbody>
</table>

(a) diffuse reflectance, diluted with BaSO$_4$.
(b) decomposes rapidly in solution.
(c) See Figure 3.2, page .
1. The similarity of the diffuse reflectance spectra of
\([\text{Ni}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)\text{Br}_3]\)
(A) and \([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2)\text{Br}_3]\) (B) is evidence of structural similarity.

2. A comparison of the solution spectra \((\text{CH}_2\text{Cl}_2)\) of \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_3]\)
(solid line) and \([\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2]\) (broken line). The
lower energy absorbances, and higher extinction coefficients
of the Ni(III) complex are evident. The Ni(III) complex was
generated by addition of Cl\(_2\) to the Ni(II) complex. Chlorine
is transparent in this region.
The far infra-red spectra of [Ni(o-C₆H₄(PPh₂)₂)Cl₂] (solid line) and [Ni(o-C₆H₄(PPh₂)₂)₂Cl] (broken line). Peaks marked 'a' are assigned to $\nu_{\text{Ni-Cl}}$. 

Figure 3.25. (I.R. Spectrum)
Broad, isotropic signals were observed previously at room temperature for \([\text{Ni}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{Ph}_2)\text{Br}_3] (n = 2, 3)\) as polycrystalline powders, and for \([\text{Ni}(\text{cis-Ph}_2\text{PCHCHPPPh}_2)\text{Br}_3]\). In \(\text{CH}_2\text{Cl}_2\) solution, \([\text{Ni}(\text{cis-Ph}_2\text{PCHCHPPPh}_2)\text{Br}_3]\) was reported to exhibit a four-line pattern due to hyperfine coupling to one \(\text{Br}\) atom \((^{79/81}\text{Br}; I = 3/2)\), with evidence for further splitting of each line into a 1:2:1 triplet \((2x^1\text{P}; I = \frac{3}{2})\). On this basis it was proposed that a \(C_{2v}\) structure with the bidentate ligand in the equatorial plane was most likely with, presumably, a \((d_{2}^2)^1\) ground state (Figure 3.24).

![Figure 3.24. Structure proposed for \([\text{Ni}(\text{cis-Ph}_2\text{PCHCHPPPh}_2)\text{Br}_3]\) on the basis of coupling to atoms marked* in the esr spectrum](image)

However, it is evident that this pattern can also be rationalised as due to a pseudo-square pyramidal stereochemistry and a \((d_{z^2})^1\) ground state, where the weak coupling to \(\text{P}\) is due to some orbital mixing, which might be expected in such a complicated, low symmetry, molecule.

Generally, the \([\text{Ni}(\text{L-L})\text{Br}_3]\) gave spectra similar to those observed previously in the literature, viz isotropic,
broad lines as polycrystalline powders, and four lines due to coupling to one bromine atom as CH$_2$Cl$_2$ solutions. However, additional features were sometimes observed. In CH$_2$Cl$_2$ solution, for [Ni o-C$_6$H$_4$(AsPh)$_2$(PPh$_2$)$_2$Br$_3$] it is just possible to discern three g-values (Table 3.27). It is clear that the observation of fine structure and anisotropy is dependent upon the particular ligand, and probably upon other factors such as concentration, and the amount of distortion in the molecule. It is also halogen dependent; under all conditions tried, only a single, broad isotropic line was seen for all the [Ni(L-L)Cl$_3$] complexes. (Figure 3.26; Table 3.27). No hyperfine coupling was observed for [Ni(L-L)X$_3$] (L-L = Me$_2$PCH$_2$CH$_2$PMe$_2$, o-C$_6$H$_4$(AsMe$_2$)$_2$) either, although in solution, the diarsine complexes gave spectra characteristic of [Ni(L-L)$_2$X$_2$]$^+$, probably owing to the general tendency of this and similar ligands to give octahedral 2:1 complexes in solution.

The inadequacy of spectroscopic data in establishing the stereochemistry about nickel led to attempts to grow crystals suitable for X-ray crystallography. Many attempts were made to obtain crystals of [Ni(L-L)Cl$_3$] (L-L = Ph$_2$PCH$_2$CH$_2$PPh$_2$, o-C$_6$H$_4$(PPh$_2$)$_2$) by either slow concentration of CH$_2$Cl$_2$ solutions, or pentane vapour diffusion into CH$_2$Cl$_2$ solutions at -20°C. The Ni(III) solutions were generated by NOCl oxidation of the Ni(II) complex. Unfortunately these failed to yield suitable materials, so recourse was made to the bromides. Random attempts to grow crystals by crystallisation from CH$_2$Cl$_2$ or CHCl$_3$ in the presence of excess Br$_2$ led either to precipitation of powders or decomposition. By careful control of conditions, using carefully measured concentrations of [Ni(L-L)Br$_2$] and Br$_2$ in CH$_2$Cl$_2$/toluene mixtures, suitable crystals of [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$],C$_6$H$_5$Me were eventually obtained.
Figure 3.26. See overleaf/...
Figure 3.26. Representative e.s.r. spectra of Ni(L-L)X$_3$ complexes

(A) [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$] in CH$_2$Cl$_2$ solution, room temperature, an isotropic line, $g_{av} = 2.10$, showing coupling to one Br nucleus (4 lines; $A_{iso} = 65$ G).

(B) [Ni(α-C$_6$H$_4$(AsPh$_2$)$_2$)Br$_3$] as a solid (broken line), showing evidence of anisotropy, and as a solution in CH$_2$Cl$_2$ in the presence of excess Br$_2$ (solid line).

(C) Spectra of [Ni(α-C$_6$H$_4$(PPh$_2$)(SMe))X$_3$] in CH$_2$Cl$_2$ solution. X = Br (solid line), shows coupling to one Br nucleus; X = Cl (broken line) showing 2 g-values. The chloride decomposed rapidly, and was generated in situ and scanned immediately; $t_{1/2} < 10$s.

(D) Spectrum of [Ni(α-C$_6$H$_4$(PPh$_2$)$_2$)Cl$_3$] in CH$_2$Cl$_2$ - a typical spectrum obtained for [Ni(L-L)X$_3$], consisting of one isotropic signal.
<table>
<thead>
<tr>
<th>Compound</th>
<th>g Values, linewidths and comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Ph₂PCH₂CH₂PPh₂)Cl₃]</td>
<td>(a): ( g = 2.21 ) (200) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g = 2.20 ) (200) (isotropic)</td>
</tr>
<tr>
<td>[Ni(Ph₂PCH₂CH₂PPh₂)Br₃]</td>
<td>(a): ( g = 1.95 ) (700) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g_{av} = 2.10 ) (quartet; ( A_{iso} = 65G ))</td>
</tr>
<tr>
<td>[Ni(Ph₂P(CH₂)₃PPh₂)Cl₃]</td>
<td>(a): ( g = 2.13 ) (400) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g = 2.09 ) (110) (isotropic)</td>
</tr>
<tr>
<td>[Ni(Ph₂P(CH₂)₃PPh₂)Br₃]</td>
<td>(a): ( g = 2.15 ) (260) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g_{av} = 2.105 ) (quartet, ( A_{iso} = 60G )); ( g = 2.015 ) (90)</td>
</tr>
<tr>
<td>[Ni(Ph₂PCH₃PPh₂)Cl₃]</td>
<td>(a): ( g = 2.21 ) (200) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g = 2.16 ) (85) (isotropic)</td>
</tr>
<tr>
<td>[Ni(Ph₂PCH₃PPh₂)Br₃]</td>
<td>(c): ( g = 2.09 ) (280) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g_{av} = 2.15 ) (quartet, ( A_{iso} = 65G ))</td>
</tr>
<tr>
<td>[Ni(o-C₆H₄(PPh₂)(SMe))Br₃]</td>
<td>(a): ( g = 2.11 ) (300) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g_{av} = 2.12 ) (some ill-defined fine structure)</td>
</tr>
<tr>
<td>[Ni(o-C₆H₄(AsPh₂))Br₃]</td>
<td>(a): ( g = 2.14 ) (100) (isotropic)</td>
</tr>
<tr>
<td>[Ni(o-C₆H₄(AsPh₂))Br₃]</td>
<td>(a): ( g = 2.00 ) (250) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g_{av} = 2.21 ) (quartet; ( A_{iso} = 53G ), split further into partly-resolved triplets, ( A_{iso} = 6G )); ( g_{av} = 2.00 ) (partly resolved into 2 lines)</td>
</tr>
<tr>
<td>[Ni(o-C₆H₄(PPh₂)₂)Cl₃]</td>
<td>(a): ( g = 2.25 ) (95); ( g = 2.073 ) (broad)</td>
</tr>
<tr>
<td></td>
<td>(b): ( g = 2.197 ) (43) (isotropic)</td>
</tr>
</tbody>
</table>

/continued.......

Table 3.27 continued /....

<table>
<thead>
<tr>
<th>Compound</th>
<th>g Values, linewidths and comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(PPh(_2))(_3)Br(_3)]</td>
<td>(a): (g_{av} = 2.17(120)) (anisotropic; 2 lines partly resolved).</td>
</tr>
<tr>
<td></td>
<td>(b): (g_{av} = 2.18) (quartet; (A_{iso} = 60)G)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(AsMe(_2))(_2)Cl(_3)]</td>
<td>(a): (g = 2.10) (110) (isotropic).</td>
</tr>
<tr>
<td></td>
<td>In CHCl(_3), gives spectrum characteristic of [Ni(L-L)(_2)Cl(_2)](^+) (33).</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(AsMe(_2))(_2)Br(_3)]</td>
<td>(a): (g = 2.12) (250) (isotropic).</td>
</tr>
<tr>
<td></td>
<td>In CH(_2)Cl(_2) or CH(_3)CN, gives spectrum characteristic of [Ni(L-L)(_2)Br(_2)](^+) (33).</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Me(_2)PCH(_2)CH(_2)PMe(_2))Cl(_3)]</td>
<td>(a): (g = 2.18) (100) (isotropic).</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Me(_2)PCH(_2)CH(_2)PMe(_2))Br(_3)]</td>
<td>(a): (g = 2.16) (150) (isotropic).</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(PPh(_2))(SMe)(_3)]</td>
<td>(d): (g = 2.12) (50). (g = 2.04) (anisotropic spectrum).</td>
</tr>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(PPh(_2))(SeMe)(_3)]</td>
<td>(e): (g = 2.17) (45) (isotropic)</td>
</tr>
<tr>
<td>[Ni(_{\text{o}})-C(_6)H(_4)(PPh(_2))(GeMe)(_3)]</td>
<td>(e): (g = 2.17) (145) (isotropic)</td>
</tr>
<tr>
<td></td>
<td>(f): (g_{av} = 2.15); 4 lines; (A_{iso} = 43)G.</td>
</tr>
<tr>
<td>[Ni(Ph(_2)PCH(_2)PPh(_2))Br(_3)]</td>
<td>(d): (g = 2.00) (isotropic)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>continued/...</td>
</tr>
</tbody>
</table>
Table 3.27 continued/....

<table>
<thead>
<tr>
<th>Compound</th>
<th>g-Values, linewidths and comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(cisPh₂AsCHCHAsPh₂)Br₃]</td>
<td>(d): g = 2.01 (200) (isotropic)</td>
</tr>
<tr>
<td>[Ni(Ph₂PCH₂CH₂AsPh₂)Br₃]</td>
<td>(d): g = 2.01 (210) (slight anisotropy).</td>
</tr>
</tbody>
</table>

+ Figures in parentheses are linewidths (derivative peak-to-peak) in Gauss. Conditions used:

(a) powdered solid, room temperature.
(b) CH₂Cl₂, room temperature
(c) powdered solid, -196°C.
(d) CH₂Cl₂, glass (-196°C). Generated in situ, by addition of X₂ to Ni (II) solution, rapidly frozen.
(e) Generated by addition of X₂ in CCl₄ to solid Ni (II) precursor, frozen to -196°C and run immediately.
(f) Generated in CH₂Cl₂ in situ; run at room temperature. t¹/₂ ca 45s.
Structure of $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_2].\text{C}_6\text{H}_5\text{Me}]$

Crystals were grown by the following procedure. To a saturated solution of $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_2]$ in dry $\text{CH}_2\text{Cl}_2$ (10 cm$^3$) was added a 2-fold molar excess of $\text{Br}_2$ in the same solvent (1 cm$^3$) with stirring. Toluene was then slowly added (2:1 toluene: $\text{CH}_2\text{Cl}_2$ by volume) and the mixture slowly cooled to $-20^\circ\text{C}$. The black, moisture-sensitive reflective needles developed over 48-60h.

Suitable examples were sealed in Lindemann capillaries in the presence of a small amount of $\text{Br}_2$ vapour. A crystal was mounted along its needle axis and Weissenberg and oscillation photographs were taken. These revealed a monoclinic system (systematic absences $h,0,l\ (n+1=2n+1)$ and $0,k,0\ (k=2n+1)$; mirror plane; space group $P2_1/a$), and preliminary cell dimensions. Unit cell volume was calculated as 3309 Å$^3$. Since density measurements (flotation in $\text{CH}_2\text{I}_2/\text{BrCH}_2\text{CH}_2\text{Br}$) gave $d_{\text{obs}} = 1.61$ g cm$^{-3}$, $Z$ was calculated to be 4 ($d_{\text{calc}} = 1.583$ g cm$^{-3}$). At this stage, chemical analysis of the crystals suggested the presence of a molecule of toluene per Ni(III) atom. Found C = 50.7, H = 4.2%. Calc. for $C_{33-32}\text{Br}_3\text{NiP}_2$; C = 50.2, H = 4.1%.

Summary of Data

$[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_2].\text{C}_6\text{H}_5\text{Me}]$. 1/1 $C_{33}H_{32} = C_{33}H_{32}\text{Br}_3\text{NiP}_2$,

$M = 789.01$. Monoclinic; $a = 15.567(3)$, $b = 14.627(2)$, $c = 15.151(3)$ Å.

$\beta = 113.38(2)^\circ$, $U = 3166.60$ Å$^3$, $D_{\text{obs}} = 1.61(2)$ g cm$^{-3}$, $D_{\text{calc}} = 1.654$ g cm$^{-3}$;

$Z = 4$, $F(0,0,0) = 1572$, $\mu(\text{Mo} - \text{K}a) = 44.22$ cm$^{-1}$, $\langle \text{Mo}-\text{K}a \rangle = 0.7107$ Å,

space group $P2_1/a$.

Solution of the Structure

Intensity data were recorded on an Enraf-Nonius CAD-4
diffractometer at room temperature on a crystal of dimensions 0.25 x 0.10 x 0.15 mm, sealed in a lithium borate glass tube in the presence of a small amount of bromine vapour to suppress reversible reduction. Graphite-monochromated Mo-Kα radiation was employed. Twenty five accurately-centred reflections were used to obtain precise cell dimensions (above) and three check reflections monitored on a time basis showed no evidence for decomposition during the experiment. After averaging multiple measurements (R = 0.008) there remained 3386 out of 3883 reflections originally recorded. Eliminating reflections with F < 3 σ (F) (1803) left 1583 unique reflections used in the refinement. No absorption correction was applied to the initial data. The normalised structure factors (E) strongly supported a centro-symmetric space group, in accord with the systematic absences.

The structure was solved by a combination of direct methods and Patterson techniques. The SHELX centro-symmetric direct methods programme gave two possible solutions, both with high figures of merit (2.62, 2.50) and both with E-maps with pseudo-symmetry showing two overlapping images of the heavy atom (Ni,Br) skeleton. Only the second solution was consistent with the Patterson map however, and a series of structure factor calculations and electron density syntheses readily located the P and C atoms. The toluene molecule was located from a difference electron density synthesis, together with evidence for some of its H-atoms. H atoms were added to the model in geometrically calculated positions (d_C-H = 1.08 Å) with a common temperature factor (0.1 Å^2). Least squares refinement with all atoms isotropic gave R = 0.096. A large temperature factor for the toluene methyl group was found, and investigated. There was no evidence for disorder or partial occupancy of the toluene and removal of the methyl group led to its

* X-Ray data collection by Dr. M. B. Hursthouse, using the SERC/QMC CAD-4 diffractometer service.
re-appearance in difference electron density syntheses.

Since no empirical psi-scan measurements were available and the crystal faces were not well-defined, the empirical method of Walker and Stuart was applied after isotropic refinement. The heavy atoms and the toluene methyl C-atom were allowed anisotropic thermal motion and least-squares refinement converged to $R = 0.0562$ ($R' = 0.0505$) (136 parameters, anisotropic (Ni, Br, P and C(5), i.e. toluene Me carbon) and isotropic (remaining C,H) atoms; rigid phenyl groups ($d_{C-C} = 1.395 \text{ Å}$); empirical weights ($W = 1/\sigma^2(F) + 0.0003F^2$)). The ratio reflections/parameters is 11.6 and a final difference electron density synthesis showed all features in the range 0.65 to -0.57 e Å$^3$. Final atomic co-ordinates are given in Table 3.28.

Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX (Br, P, C, H) and reference 36. All calculations were performed on an ICL 2970 computer using the programs SHELX, DIFABS, PLUTO and XANADU.

Discussion of the Structure of $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}_2].1/1\text{C}_7\text{H}_6$

The discrete molecule is illustrated in Figure 3.29, and the packing diagram in Figure 3.210. Selected bond lengths and angles are given in Table 3.211.

The complex has approximate $C_8$ symmetry, being a distorted square pyramid with an apical bromine. The basal plane is distorted by the chelating diphosphine; the P-M-P angle is 82.6(2)$^\circ$. This is similar to that found in the isoelectronic square pyramidal isomer of $[\text{Co(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}]\text{[SnCl}_3]^{39}$ (82.7, 81.7$^\circ$), but smaller than those in $[\text{Ni}^{\text{II}}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Br}(\eta^3\text{-C}_3\text{H}_4\text{Me})]$ (88.8$^\circ$) or $[\text{Pd(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2]$ (85.8$^\circ$). This is probably a consequence of the higher co-ordination number of the Ni(III) and Co(II) complexes. The Br-Ni-Br angle in the basal plane is 95.3$^\circ$, while those involving the apical and basal bromines are 101 and 105$^\circ$. 
Table 3.28.

Final atomic co-ordinates ($\times 10^4$) for [Ni(Ph$_2$PCH$_3$CH$_3$PPh$_2$)Br$_3$]C$_6$H$_5$Me with estimated standard deviations in parentheses

<table>
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<th>Atom</th>
<th>$X/a$</th>
<th>$Y/b$</th>
<th>$Z/c$</th>
<th>Atom</th>
<th>$X/a$</th>
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<td>3 284(1)</td>
<td>1 183(1)</td>
<td>C(31)</td>
<td>4 100(7)</td>
<td>4 612(7)</td>
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<td>3 855(1)</td>
<td>1 287(1)</td>
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<td>2 215(11)</td>
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<td>2 540(7)</td>
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<td>6 941(14)</td>
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<td>C(48)</td>
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<td>7 694(14)</td>
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<td>1 002(6)</td>
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</table>

Carbon atoms of the phenyl groups are labelled C(ij) where i (1—5) indicates the ring and j (1—6) the carbon atoms within each ring.
Figure 3.29. Discrete Molecule of $[\text{Ni(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{)}\text{Br}_3]$, showing the atom numbering scheme, plotted using the PLUTO program, reference 37.
Figure 3.210. A packing diagram for [Ni(Ph₂PCH₂CH₂PPh₂)Br₃].C₅H₈ showing Ni, Br, P and C atoms of the ligand backbone and the toluene solvate arrangement. The view is along the a direction and the atom numbering is as in Figure 3.29.
Table 32M. Selected bond lengths (Å) and angles (°) for [Ni(Ph₂PCH₂CH₂PPh₂)Br₅]·C₇H₈

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<tr>
<th>Bond/Angle</th>
<th>Distance/Value</th>
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<tr>
<td>C-C(aromatic)</td>
<td>1.595(fixed)</td>
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<tr>
<td>P(1)...P(2)</td>
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<td>C(31)-P(2)-C(41)</td>
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</table>

CONTINUED....
P(1)-C(1)-C(2)  112(1)  C(5)-C(51)-C(52)  113(2)
P(2)-C(2)-C(1)  112(1)  C(5)-C(51)-C(56)  127(2)
P(1)-C(1)-C(2)-P(2)  -15.0
The Ni atom lies ca 0.34 Å above the P₂Br₂ plane and the methylene carbons of the ligand backbone are above the plane, in a conformation similar to that found for [Co(Ph₂PCH₂CH₂PPh₂)₂Cl]⁺. The internal dimensions of the diphosphine are unexceptional.

It is notable that the basal Ni-Br bond lengths differ by ca 6σ(2.346(3) and 2.363(3) Å, but the bond to the apical Br is 20σ longer than the average of the basal Ni-Br bonds. These bond lengths may be compared with those in the trigonal bipyramidal [Ni(PhPMe₂)₂Br₃] (2.349(2), 2.339(2), 2.375(2) Å). In this case one bond is longer (ca 15σ) than the average of the other two, attributable to the Jahn-Teller distortion due to the non-symmetrical electron distribution ((dx²-y²)² (dyz)² (dxz)² (dyz)² (dxy)¹ (dz²)⁰) in the equatorial plane.

However in [Ni(Ph₂PCH₂CH₂PPh₂)Br₃] the elongation of the axial Ni-Br bond is probably due to the occupation of the σ-anti bonding dz² orbital by one electron in the d⁷ configuration.

This elongation has been noted before, for example in [NiIII{(O-C₆H₄(AsMe₂)₂)₂Cl₂}ClO₄] and is generally typical of d⁷ and d⁸ low spin complexes with apical halides.

The molecule [Ni{C₆H₃(CH₂NMe₂)₂-0,0'}I₂] (see Chapter 2, page 89) has similar stereochemistry, with the Ni atom displaced by the same distance, 0.34 Å, from the basal (C,N,N,I) plane, while esr and MO calculations indicate a (dz²)¹ configuration for this complex also.

General Discussion of [Ni(L-L)X₃] Complexes

The solution of the structure of [Ni(Ph₂PCH₂CH₂PPh₂)Br₃]. C₇H₈ sheds some light on the properties of the other complexes and upon the results of attempted oxidations which failed to yield stable Ni(III) complexes. In particular it is probable that the observation
of two similar frequencies for $\nu_{\text{Ni-X}}$ involves the basal $\text{NiX}_2$ unit and the one at lower frequency may be due to the long axial Ni-X bond.

The coupling to one halogen in the esr spectra of the $[\text{Ni(L-L)}\text{Br}_3]$ complexes is presumably due to the axial bromine, although the expected anisotropy is not resolved, and the g-value is ca 2.1-2.2 (Table 3.27). In $[\text{Ni}[\text{C}_{6}H_{3}(\text{CH}_2\text{NMMe}_2)_2]_2\text{Cl}_2]$ all g-values are resolved, as would be predicted, with coupling to the axial chlorine only in the $g_{zz}$ region ($A = 28G$).

Many examples of complexes $[\text{Ni}(L-L)X_2]$ were subjected to oxidation experiments with less success. In particular, the only aryl diarsine ligand capable of giving a Ni(III) complex in the solid state was $\circlearrowleft\text{C}_{6}H_{4}(\text{AsPh}_2)_2$. Careful Br$_2$/CCl$_4$ oxidation of the purple Ni(II) complex under dry conditions gave the unstable, black Ni(III) complex, but similar reactions with $[\text{Ni}(L-L)\text{Br}_2]$ ($L-L = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2, \text{cis-Ph}_2\text{AsCHCHAsPh}_2$) failed to yield solid products $[\text{Ni}(L-L)\text{Br}_3]$. Instead, partial decomposition occurred, and treatment of the Ni(II) materials with excess Br$_2$ gave yellow NiBr$_2$ and organo-arsenic (V) derivatives, identified by $^1$H n.m.r. spectroscopy. In the case of cis Ph$_2$AsCHCHAsPh$_2$, a transient darkening of the Ni(II) complex before obvious decomposition occurred was noted, and esr spectroscopy (Table 3.27) of a solution of the Ni(II) complex treated with Br$_2$ and rapidly frozen to -196°C showed evidence of Ni(III) formation. It is interesting that an ordering of stability with the rigidity of the ligand backbone is evident here; the rigidity of the $\circlearrowleft\text{C}_{6}H_{4}$ group has been implicated previously in the unusual donor properties of $\circlearrowleft\text{C}_{6}H_{4}(\text{EMe}_2)_2$ ($E = \text{P,As}$). This effect is again underlined by the successful isolation of $[\text{Ni}[\circlearrowleft\text{C}_{6}H_{4}(\text{AsPh}_2)(\text{PPPh}_2)]\text{Br}_3]$; $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2)\text{Br}_2]$ decomposed on treatment with Br$_2$. Particularly interesting was the isolation of the black, extremely unstable ($t_{1/2} = 5$ hours as a solid, -20°C) complex $[\text{Ni}[\circlearrowleft\text{C}_{6}H_{4}(\text{PPh}_2)(\text{SMe})]\text{Br}_3]$. This is the first reported example of Ni(III) co-ordinated to a thioether donor. Nickel (II) complexes of RSCH$_2$CH$_2$SR ($R = \text{Me, -CH(CH}_3)_2$)
decomposed on treatment with Br₂, and it was found that even
[Ni(o-C₆H₄(SMe)₂)₂Br₂], which shares the advantage of the rigid
o-C₆H₄ group was decomposed by Br₂. Unfortunately [Ni(o-C₆H₄(PPh₂)
(SMe)₂)Cl₃] could not be made; with NOCl, the Ni(II) complex
gave an uncharacterised nitrosyl complex (v(NO) = 1830 cm⁻¹) and Cl₂
caused decomposition. However, esr evidence was obtained for transient
Ni(III) formation with Cl₂, by a similar procedure to that employed
for "[Ni(cis Ph₂AsCHCHAsPh₂)Br₃]" (Table 3.27). In situ oxidation
of octahedral [Ni(o-C₆H₄(PPh₂XSeMe)₂)₂Br₂] with excess halogen also
gave products with esr spectra characteristic of [Ni(L-L)X₃], in
particular, the bromide showed the expected four-line coupling to
one Br (Figure 3.26, Table 3.27). No solid products could be
isolated, however, probably due to difficulties in separating the
Ni(III) complex from the oxidised ligand, in the reaction
[Ni(o-C₆H₄(PPh₂XSeMe)₂)₂Br₂] + Br₂ ➝ [Ni(o-C₆H₄(PPh₂XSeMe)₃)Br₃]
+ oxidised ligand.

The advantages of the rigid o-C₆H₄ backbone and
phosphorus donor atom also apply for o-C₆H₄(PPh₂Xs₄Ph₂),
but the complex [Ni(o-C₆H₄(PPh₂Xs₄Ph₂)Br₂], itself a mixture of
planar and halide-bridged octahedral forms, was merely decomposed
by Br₂ and no esr evidence for transient Ni(III) species could be
found.

For the diphosphine ligands with saturated carbon
backbones, behaviour on attempted oxidation depended notably on
chain length. The complexes [Ni(Ph₂PCH₂PPh₂)X₂] (X = Cl,Br),
where a strained four-membered M-P-C-P ring is present, were
decomposed by halogens. The chloride gave a green nitrosyl on
treatment with NOCl (v(NO) = 1837 cm⁻¹). Again, esr evidence
(Table 3.27) for a transient Ni(III) bromo-complex was obtained.

No discernable difference existed between [Ni(Ph₂(CH₄)ₐ]
PPh₂)X₃] (n = 2,3) in terms of stability although it might have been
anticipated that the five-membered ring present in complexes of \( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \) would be significantly more stable than the six-membered ring in \( \text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2 \) complexes. Attempts to oxidise \([\text{Ni(Ph}_2\text{P(CH}_2)_4\text{PPh}_2]X_2\] and \([\text{Ni(trans-Ph}_2\text{PCHCHPPh}_2)\text{Br}_2\] \( (X = \text{Cl, Br}) \) failed; these complexes are high-spin pseudo tetrahedral polymers, and were apparently unchanged even on prolonged exposure to halogens.

The nature of the complexes \([\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2]\text{Br}_3\] and \([\text{Ni}^\text{0-C}\text{H}(\text{AsMe}_2)_2\text{Br}_3\] was of particular interest as previous authors have assumed octahedral polymeric (halogen-bridged) structures. However, the spectroscopic evidence would indicate five-co-ordination, as the far i.r. and electronic spectra are quite similar to those found for the aryl-diphosphines and -diarsines. The solids gave isotropic esr signals (Table 3.27) but in CHCl\(_3\) or CH\(_3\)CN solution, \([\text{Ni}^\text{0-C}\text{H}_4(\text{AsMe}_2)_2\text{X}_3\] gave the complex hyperfine splitting pattern previously observed for \([\text{Ni}^\text{0-C}\text{H}_4(\text{AsMe}_2)_2\text{X}_2]^\text{+}\), indicating a rearrangement in solution. The mechanism by which this occurs is far from clear; it might be expected that dissociation of the free ligand, for example, would lead to decomposition, as it is strongly reducing. The tendency of the Ni(II) complexes \([\text{Ni}^\text{0-C}\text{H}_4(\text{AsMe}_2)_2\text{X}_2\] \( (X = \text{Cl, Br}) \), made by treatment of the Ni (0) dicarbonyl with HX, to revert to NiX\(_2\) + Ni(L-L)\(_2\)X\(_2\) in solution, has been noted previously. In fact, few \(1:1\) metal:ligand complexes of \( \text{0-C}\text{H}_4(\text{AsMe}_2)_2\) are known. The solution instability restricted physical and spectroscopic measurements to the solid state.

Treatment of the corresponding diphosphine - Ni(0) complex \([\text{Ni}^\text{0-C}\text{H}_4(\text{PMe}_2)_2]\text{(CO)}_2\] with \( \text{X}_2 \) in CH\(_2\)Cl\(_2\), even under rigorously dry conditions, failed to yield a solid Ni (III) complex. For \( X = \text{Br} \), a green oil was obtained which defied all attempts to solidify it by stirring with various solvents. This contained much phosphine oxide, but esr evidence suggested the presence of some Ni(III) complex. It was not, however, possible to exclude
the possibility that this was simply some \([\text{Ni}(L-L)_2 \text{Br}_2]^+\) produced by rearrangement. For \(X = \text{Cl}\), an extremely moisture-sensitive light blue powder was produced, which was largely a \(\text{Ni}(\text{II})\) -phosphine oxide complex. Significantly, when similar reactions were carried out using \([\text{Ni}^0(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)(\text{CO})_2]\), bromine gave a mixture of the required \(\text{Ni}(\text{III})\) complex and phosphine oxide, and chlorine again gave a pale blue phosphine oxide complex. It is possible that even if all moisture and oxygen is excluded from these reactions, the generation of \(\text{COX}_2\) could cause decomposition. Also, the reaction probably proceeds via \(\text{Ni}(\text{II})\) and, perhaps, \(\text{Ni}(\text{I})\) intermediates, and these will be labile, enabling facile ligand dissociation and oxidation.

It is difficult to compare the effectiveness of the methyl- and aryl-substituted bidentates in stabilising \(\text{Ni}(\text{III})\) in these complexes because of the different decomposition routes favoured by the complexes.

This study has established that a wide range of complexes of the formula \([\text{Ni}(L-L)X_3]\) can be made \((L-L = \text{bidentate phosphine or arsine})\), and the stability of the complexes depends on donor atoms, halide and ligand structure in well-defined ways (in order of stability, \(\text{Br} > \text{Cl}^*; \text{PPh}_2 > \text{AsPh}_2 > \text{SMe}, (\text{SeMe} > \text{SbPh}_2); \text{cis-vinyl} > \text{alkyl}\)). These trends may be rationalised in a straightforward manner. As the ligands are only moderate \(\sigma\)-donors (except \(\text{cis-}C_6\text{H}_4(\text{AsMe}_2)_2\) and \(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\)) towards 3d metal ions, the symbiotic effect could explain the greater stability of the bromides. That is, the fairly 'soft' ligands would

* Although tga data showed little difference between the stability of the chlorides and bromides to heat, the shelf-life of complexes and the half life in solution in the absence of excess halogen, used as criteria for stability in this study, were notably longer for the bromides.
bind preferentially to the 'softer' NiBr\(_3\) unit. The ordering of donor groups is approximately the same as the ordering of their \(\sigma\)-donor abilities. This parallels the observations made for [Ni(ER\(_2\))\(_2\)X\(_2\)] (Chapter 3.1, page 126) and [Ni(L-L)\(_2\)X\(_2\)]\(^+\) (Chapter 3.3, page 181), and the same explanation applies.

The rigidity of the ligand backbone is important as, particularly for a relatively labile system such as Ni (III) (low-spin d\(^7\)), for stability, any tendency to ligand dissociation should be suppressed as much as possible. If dissociation is possible, the resulting free E (III) (E = P, As, Sb) group is a very good reducing agent.

It has previously been observed that for Pd (IV) complexes of neutral ligands, stability follows the ordering


and this has been rationalised in terms of the preference of the high oxidation state metal centre to bind anionic halide ions.

Investigation was therefore made into the reaction of [Ni(L-L)X\(_2\)] complexes with X\(_-\).

The ESR spectrum of [Ni(Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\))Br\(_3\)] in CH\(_2\)Cl\(_2\) was unaffected by the presence of varying concentrations of Bu\(_4\)NBr. In particular, the four-line coupling to one bromine remained. Oxidations of [Ni(L-L)Br\(_2\)] \((L-L = \text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2, \text{cis-Ph}_2\text{PCHCHPPh}_2; n = 2, 3) in the presence of Bu\(_4\)NBr gave only [Ni(L-L)Br\(_3\)]. Attempts to react [Ni(Me\(_2\)PCH\(_2\)CH\(_2\)PMe\(_2\))Br\(_3\)] with Bu\(_4\)NBr also failed (the presence of the excess halide ion merely appeared to catalyse decomposition), ruling out the synthesis of the anion with the potentially less sterically-demanding methyl-substituted ligand.

The lack of reaction with Br\(^-\) could be due to the fact that the small, d\(^7\) Ni (III) ion is unable to accommodate
additional negatively charged, ($\sigma + \pi$)-donor, halide ions. It should be noted that in the case of the Pd (IV) compounds, the co-ordination number is not increased on proceeding from the dication to the anion, but neutral ligands are progressively displaced.
Section 3.3 Octahedral Ni(III) Complexes

3.3a. Synthesis

Octahedral Ni(III) complexes isolated during this study were restricted to the cations [Ni(L-L)X2]2+ (L-L = alkyl-substituted bidentate ligand; X = Cl,Br) exemplified by the well-known complexes of o-C6H4(AsMe2)2 and o-C6H4(PMe2)2, and the neutral [Ni(L-L-L)X3] (L-L-L = tridentate phosphine or arsine). Only two examples of the latter, both with X = Br, had been made before, and were incompletely characterised. 53,54 (Chapter 2, page 86).

The complexes [Ni{o-C6H4(AsMe2)2}2X2]Y (X = Cl,Br; Y = ClO4,C1,Br) were made conveniently by methods described in the literature (X = Cl; reflux of the Ni(II) complex in aqueous HCl-ethanol, in air. 31 X = Br; Ni(II) complex + Br2 in ethanol31), for comparison with similar complexes. The phosphine analogues were best prepared by treatment of [Ni{o-C6H4(PMe2)2}2Cl]ClO4* with a slight excess of Cl2 in CH3CN-EtOH solution, and by treatment of [Ni{o-C6H4(PMe2)2}2Br]ClO4 with Br2/CCl4. Attempts to prepare [Ni{o-C6H4(PMe2)2}2Br2]ClO4 by metathesis of the chloro complex with LiBr in methanol32 always led to partial reduction (reduced magnetic moments and poor analyses), although this method proved adequate for the synthesis of [Ni{o-C6H4(AsMe2)2}2Br2]Br31.

The ligand o-C6H4(AsMe2)(PMe2) has more recently been prepared. Its Ni(II) complexes are, as expected, closely related to those of o-C6H4(EMe2)2 (E = P or As)62. The corresponding Ni(III) complexes, synthesised as for those of o-C6H4(PMe2)2, are also close analogues of [Ni{o-C6H4(EMe2)2}2X2]Y (E = P or As; X = Cl,Br; Y = Cl,Br,ClO4).

* For preparations of the nickel(II) complexes, see Chapter 7, page 306.
The complexes \([\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMMe}_2)_2\text{Br}_2]\) \(Y\) \((Y = \text{Br}, \text{Br}_3)\) have been synthesised before, but characterised only analytically. Their synthesis was repeated, and additionally, \([\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMMe}_2)_2\text{Cl}_2]\) \(\text{BF}_4\) was isolated by \(\text{Cl}_2\) oxidation\(^*\) of \([\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMMe}_2)_2\text{Cl}_2]\) in \(\text{CH}_3\text{CN}-2\text{-propanol}\) in the presence of \(\text{LiBF}_4\).

In view of the failure to prepare \([\text{Ni(o-C}_6\text{H}_4\text{(PPh}_2)(\text{SbF}_h_2))\text{Br}_3]\) the attempts at oxidation of \([\text{Ni(o-C}_6\text{H}_4\text{(PMe}_2)(\text{SbMe}_2))_2\text{X}_2\text{Y}^{**}\) \((X = \text{Cl}, \text{Br}; Y = \text{Cl}, \text{Br}, \text{ClO}_4)\) were viewed with considerable interest. In fact, \(\text{Cl}_2\) decomposed the salt \([\text{Ni(o-C}_6\text{H}_4\text{(PMe}_2)(\text{SbMe}_2))_2\text{Cl}]\text{ClO}_4\) and other methods tried, including \(\text{NOCl}\) oxidation and treatment with \(\text{FeCl}_3\) in ethanol, resulted in nitrosyl formation and partial decomposition respectively. However, \(\text{Br}_2\) oxidation of the corresponding bromide in \(\text{CH}_3\text{CN}\) gave a red crystalline solid whose analyses, bulk magnetic and spectroscopic properties indicated a genuine \(\text{Ni(III)}\) complex, \([\text{Ni(o-C}_6\text{H}_4\text{(PMe}_2)(\text{SbMe}_2))_2\text{Br}_2]\) \(\text{ClO}_4\) - the first example of a \(\text{Ni(III)}\)-stibine bond. In spite of this, all attempts at the oxidation of \([\text{Ni(o-C}_6\text{H}_4\text{(SbMe}_2))_2\text{X}]\text{X}^{**}\) and of \([\text{Ni(Me}_2\text{Sb(CH}_2)_2\text{SbMe}_2)_2\text{X}]\text{Y}^{**}\) failed, yielding anhydrous \(\text{NiX}_2\) and organoantimony (V) derivatives, identified by 'H nmr spectroscopy.

Recently, the perfluoroaryl-backbone ligand \(\text{o-C}_6\text{F}_4\text{(PMe}_2)\) has been synthesised, and its complexes with \(\text{Ni(II)}, \text{Pd(II)}, \text{Pd(IV)}\) and \(\text{Fe(II)}, \text{Fe(III)}\) have been investigated. The \(\text{Ni(III)}\) complexes \([\text{Ni(o-C}_6\text{F}_4\text{(PMe}_2)_2\text{X}_2]\text{ClO}_4\) \((X = \text{Cl}, \text{Br})\) were also synthesised as part of this study, by halogen oxidation of

\(^*\) Excess \(\text{Cl}_2\) causes oxidation to \(\text{Ni(IV)}\) (Chapter 5, page 34).

\(^**\) The \(\text{Ni(II)}\) complexes of \(\text{o-C}_6\text{H}_4\text{(PMe}_2)(\text{SbMe}_2)\) had not themselves been described in the literature until this study. Details of their preparation and properties are included in Chapter 7, page 306.
In view of the preparation of $[\text{Ni}(o-C_6H_4(PPh_2)(SMe)_2)]Br_3$ (Chapter 3.2, page 128), the attempted oxidation of the new octahedral Ni(II) complexes $[\text{Ni}(o-C_6H_4(PMe_2)(SMe)_2)]X_2$ ($X = Cl, Br$) (see Chapter 7, page 306 for details of their preparation and spectroscopic properties) was also viewed with some interest. However, rather surprisingly these complexes decomposed partially on attempted oxidation ($X_2/CCl_4, X_2/CH_3CN, X_2/CH_2Cl_2$). Investigation of these reactions by e.s.r. spectroscopy was unsuccessful in determining the reaction products with excess halogen, as only broad lines with no hyperfine coupling were observed. These could be due either to Ni(III) complexes with a $\sigma^3\sigma^1\sigma^1$ donor set ($\sigma^3\sigma^1\sigma^1$ with one ligand dissociated and oxidized).

The neutral, octahedral Ni(III) complexes of the tridentate ligands MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$ and PhP(CH$_2$CH$_2$PPh$_2$)$_2$ were prepared in rigorously moisture-free conditions by $X_2/CCl_4$ (PhP(CH$_2$CH$_2$PPh$_2$)$_2$) or $X_2/CH_2Cl_2$ solution (MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$) oxidation of the corresponding five-co-ordinate Ni(II) complexes.$^{55,54}$ The Ni(II) complex, $[\text{Ni(MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$}Cl_2]$ has never been obtained analytically pure.$^{54}$ Unsurprisingly, a solid Ni(III) complex could not be obtained. Chlorine oxidation of the impure Ni(II) complex in CH$_2$Cl$_2$ yielded a bright red, air-sensitive, oil which was not solidified on trituration with any solvent. (Oxidation in CCl$_4$ suspension resulted in only partial oxidation of chloride and bromide, necessitating solution oxidations with this ligand). The complex $[\text{Ni(MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$}Br_3]$ was obtained pure for the first time, as a purple-red solid.

All the neutral complexes decomposed rapidly in solution, even in dried solvents, restricting measurements to the
solid state, although esr spectra could be recorded for the triarsine complexes in the presence of excess halogen by scanning rapidly.

3.3b. Physical Data and Electronic Spectroscopy

Physical and analytical data for the octahedral complexes are in Table 3.31. The cations \([\text{Ni}(L-L)_{2}X_{2}]^{+}\) have conductivities in CH\textsubscript{3}NO\textsubscript{2} typical of 1:1 electrolytes, and all exhibit one halogen-dependent band in the far-infra red spectra, consistent with the trans-configuration as found for \([\text{Ni}(\sigma-\text{C}_6\text{H}_4(\text{AsMe}_2)\text{}_2)_{2}X_{2}]Cl\) by X-ray crystallography\textsuperscript{42}. It is clear from the infra red and electronic spectral data (Table 3.32) that the cations are all close analogues of \([\text{Ni}(\sigma-\text{C}_6\text{H}_4(\text{AsMe}_2)\text{}_2)_{2}X_{2}]^{+}\). In particular, the far infra red spectra show the presence of a single Ni-X stretch (\(\nu_{\text{Ni-X}}\)) at relatively low frequency (ca 240 cm\(^{-1}\); \(X = \text{Cl}\). ca 190 cm\(^{-1}\); \(X = \text{Br}\)). In the case of some of the bromides, assignment of this band was difficult as it occurred at the limits (ca 175 cm\(^{-1}\)) of instrumental capacity. The unusually low frequency of \(\nu_{\text{Ni-X}}\) in these complexes is a consequence of the occupation of the \(d_{z^2}\) orbital by a single \(\sigma\)-antibonding, electron in the low-spin \(d^{7}\) configuration. The electronic spectra (Table 3.32) contain a single, weak absorption at 12,000-15,000 cm\(^{-1}\) which (in D\textsubscript{2h} symmetry) is probably due to the nearly degenerate \(2^{2}A_g \rightarrow 2^{2}B_{2g}^{2}, 2^{2}B_{3g}\) transitions.\textsuperscript{50} The spectra in this region are closely similar to those of the isoelectronic Co(II) analogues, in particular \([\text{Co}(\sigma-\text{C}_6\text{H}_4(\text{AsMe}_2)\text{}_2)_{2}X_{2}]\) and \([\text{Co}(\sigma-\text{C}_6\text{H}_4(\text{PMe}_2)\text{}_2)_{2}X_{2}]\), but the charge transfer transitions at > 20,000 cm\(^{-1}\) in the Ni(III) complexes are at lower energies than those in the Co(II) analogues, as expected for the higher oxidation state.

Spectroscopic investigation of the complexes of multidentate ligands were necessarily restricted because of their instability in solution. However, comparison of their
TABLE 3.31

<table>
<thead>
<tr>
<th>Complex</th>
<th>Analysis (%)</th>
<th>Colour</th>
<th>C</th>
<th>H</th>
<th>X</th>
<th>$\mu_{\text{eff.}}/\mu_{\text{B.M.}}$</th>
<th>$\Lambda^a/\text{ohm}^{-1}$ cm$^2$ mol$^{-1}$</th>
<th>$\nu$(NiX)$^d$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$_2$][BF$_4$]</td>
<td>Light green</td>
<td>28.2</td>
<td>6.3</td>
<td>14.1</td>
<td>2.01$^c$</td>
<td>96$^f$</td>
<td>248</td>
<td></td>
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<tr>
<td>[Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Br$_2$]Br</td>
<td>Dark brown</td>
<td>24.0</td>
<td>5.2</td>
<td>39.4</td>
<td>1.90</td>
<td>70$^f$</td>
<td>176</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$_2$][ClO$_4$]</td>
<td>Light green</td>
<td>38.3</td>
<td>5.3</td>
<td>—</td>
<td>1.86$^c$</td>
<td>—</td>
<td>263</td>
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<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$Br$_2$][ClO$_4$]</td>
<td>Orange-brown</td>
<td>33.8</td>
<td>4.4</td>
<td>—</td>
<td>2.10$^c$</td>
<td>—</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(AsMe$_2$)(PMe$_2$)$_2$Cl$_2$][ClO$_4$]</td>
<td>Green</td>
<td>34.2</td>
<td>4.5</td>
<td>—</td>
<td>2.07</td>
<td>91$^f$</td>
<td>248</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(AsMe$_2$)(PMe$_2$)$_2$Br$_2$][ClO$_4$]</td>
<td>Light brown</td>
<td>29.7</td>
<td>4.1</td>
<td>—</td>
<td>1.90$^c$</td>
<td>80$^f$</td>
<td>189</td>
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<tr>
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<td>Red</td>
<td>26.5</td>
<td>3.6</td>
<td>—</td>
<td>1.99$^c$</td>
<td>100$^f$</td>
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<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$_2$][ClO$_4$]</td>
<td>Light green</td>
<td>31.4</td>
<td>3.3</td>
<td>—</td>
<td>2.10$^c$</td>
<td>—</td>
<td>235</td>
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<tr>
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<td>Red brown</td>
<td>28.2</td>
<td>2.8</td>
<td>—</td>
<td>1.95$^c$</td>
<td>—</td>
<td>183$^d$</td>
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<td>58.7</td>
<td>4.7</td>
<td>—</td>
<td>—</td>
<td>decomp.</td>
<td>323, 303, 250</td>
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<td>48.6</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
<td>decomp.</td>
<td>250, 224, 198</td>
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<tr>
<td>[Ni(MeAs(CH$_2$CH$_2$AsMe)$_2$)_2Br$_3$]</td>
<td>Red-purple</td>
<td>19.1</td>
<td>4.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>250, 244 (sh), 196</td>
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</table>

$^a$ Calculated values in parentheses. $^b$ ± 0.05 B.M.: Gouy method except where indicated otherwise. $^c$ 10$^{-3}$ mol dm$^{-3}$ in 1,2-dichloroethane. $^d$ Nujol mulls. $^e$ Evans method in CH$_3$CN or CH$_2$Cl$_2$. $^f$ 10$^{-3}$ mol dm$^{-3}$ in nitromethane. 1:1 Electrolytes have $\Lambda = 70-120$ ohm$^{-1}$ cm$^2$ mol$^{-1}$. 
<table>
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<tr>
<th>Compound</th>
<th>$E_{\text{max}}^3 \text{cm}^{-1}$ ($\text{mol}^{-1}\cdot \text{dm}^3\cdot \text{mol}^{-1}\cdot \text{cm}^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$_2$BF$_4$]</td>
<td>CH$_2$Cl$_2$ 15.15(103), 28.6(6300)</td>
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<tr>
<td>[Ni(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Br$_2$]Br</td>
<td>dr$^a$ 14.2(br), 17.1(ω), 21.0, 26.9</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$<em>2$]Br$</em>{104}$</td>
<td>CH$_2$Cl$_2$ 14.58(53), 22.4(750), 28.74(4020)</td>
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<tr>
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<td>CH$_2$Br$_2$ 14.8(60), 28.4(8000), 30.7(8930)</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$Br$<em>2$)]Br$</em>{104}$</td>
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<tr>
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<tr>
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<td>CH$_3$CN 13.27(22), 24.00(2260), 26.20(5540)</td>
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<td>[Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$Br$<em>2$]Br$</em>{104}$</td>
<td>CH$_3$CN 12.80(41), 24.20(7750), 29.1sh(8400)</td>
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<tr>
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<td>CH$_2$Cl$_2$ 12.92(93), 19,23(400)sh, 23.90(3300), 27.80(3070)</td>
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<tr>
<td>[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)(SbMe$_2$)$<em>2$]Br$</em>{104}$</td>
<td>dr$^a$ 12.5, 19.2sh, 22.7, 26.6</td>
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<tr>
<td><a href="ClO$_4$">Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)</a></td>
<td>CH$_3$CN 14.53(130), 27.78(14,500)</td>
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<tr>
<td><a href="ClO$_4$">Ni(o-C$_6$F$_4$(PMe$_2$)$_2$)</a></td>
<td>dr$^a$ 14.8(br), 25.0, 30.3</td>
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<td>[Ni(o-C$_6$F$_4$(PMe$_2$)$<em>2$)]Br$</em>{104}$</td>
<td>CH$_3$CN 14.28(42), 21.20(800), 27.3(4750)</td>
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<tr>
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<td>dr$^a$ 14.5, 20.75, 25.0, 30.5</td>
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<tr>
<td>[Ni(PhP(CH$_2$CH$_2$PPh$_2$)$_2$Cl$_3$)</td>
<td>dr$^a$ 14.8sh, 16.4, 22.6, 27.0(br)</td>
<td></td>
</tr>
<tr>
<td>[Ni(PhP(CH$_2$CH$_2$PPh$_2$)$_2$Br$_3$)</td>
<td>dr$^a$ 15.2, 19.0, 22.8, 30.85</td>
<td></td>
</tr>
<tr>
<td>[Ni(MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$)]Br$_3$</td>
<td>dr$^a$ 14.8sh, 16.7, 19.45, 22.2sh, 27.0</td>
<td></td>
</tr>
<tr>
<td>[Ni(MeAs(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$)]Br$_3$</td>
<td>CH$_2$Cl$_2$ 18.55(1440), 23.58sh, 28.09(4820)</td>
<td></td>
</tr>
</tbody>
</table>

(a) diffuse reflectance diluted with BaSO$_4$
diffuse reflectance spectra, and the solution spectrum of
\([\text{Ni\{AsMe(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_2\text{Br}_3}]\) obtained by in situ oxidation,
with other Ni(III) spectra and spectra of the starting materials,
indicate that oxidation at the metal centre has occurred.

Although the far infra red spectra of the Ni(III)
complexes were very complex, owing to the presence of strong
ligand modes in this region, tentative assignments of three
vibrations to \(v_{\text{Ni-X}}\) supported the mer-configuration for the
complexes. (Table 3.31).

3.3c. ESR Spectroscopy

The esr spectra of all the cations are similar in
form to those found for \([\text{Ni\{o-C}_6\text{H}_4\text{(AsMe}_2\}_2\text{X}_2}]^+\) and
\([\text{Ni\{o-C}_6\text{H}_4\text{(PMe}_2\}_2\text{X}_2}]^+\). Previous authors \(^{33,50,57}\) have noted
that the signals observed for these, and similar Co(II) complexes,
are very sensitive to rather esoteric parameters, such as solvent
polarity and viscosity, counter ion (solution spectra), crystal
system and state of subdivision (spectra of solid materials).
This was noted also in the current investigation. When
\([\text{Ni\{o-C}_6\text{H}_4\text{(PMe}_2\}_2\text{Cl}_2}]\text{ClO}_4\) was recrystallised from CH\(_3\)CN-
diethyl ether, the e.s.r. spectrum of the solid material at
room temperature showed five lines, whereas at the most, 3 g-values
would be expected for a solid material (Table 3.33, Figure 3.34).
This is probably due to partial resolution of hyperfine coupling
(unusual in a solid complex, but not unknown). In contrast,
\([\text{Ni\{o-C}_6\text{H}_4\text{(PMe}_2\}_2\text{Br}_2}]\text{ClO}_4\) exhibits one broad line under these
conditions (\(g = 2.107\), linewidth, derivative peak-to-peak,
90G; Table 3.33).

In solution in CH\(_3\)CN:CHCl\(_3\) mixtures (chosen to
achieve the optimum of complex solubility and machine cavity
characteristics), the diphosphine and diarsine complexes gave the complex hyperfine splittings similar to those previously reported in the literature $^{33,50}$, although significant differences in coupling constants and linewidths were observed.

The initial assignment of the Ni(II)-diarsine radical cation description to $[\text{Ni}(o-C_6H_4(\text{AsMe}_2)_2)_2\text{Cl}_2]\text{Cl}$ was the result of the observation of hyperfine coupling to four As atoms in the (isotropic) spectrum obtained in frozen ethanol at -196°C. However, Manoharan and Rogers, on recording the spectrum at room temperature in ethanol obtained 23 discernable lines (see Figure 3.34) and, using computer fitting, concluded that the 'additional' lines were due to coupling to $^{35/37}$Cl ($I = 3/2$) $^{57}$.

The spectrum of $[\text{Ni}(o-C_6H_4(\text{AsMe}_2)_2)_2\text{Cl}_2]\text{ClO}_4$ in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ at room temperature shows 13 lines, although these are clearly asymmetric (Figure 3.34).

Similar variations (with solvent, temperature and anion) of the spectra occur with $[\text{Ni}(o-C_6H_4(\text{AsMe}_2)_2)_2\text{Br}_2]^+$. In neat $\text{CH}_2\text{Cl}_2$ at room temperature, the perchlorate was found to exhibit distinct $g_{\text{II}}$ (13 lines; coupling to $4 \times ^{75}$As; $I = 3/2$) and $g_\perp$ regions (Table 3.33), whereas isotropic signals with coupling to both $^{75}$As and $^{79/81}$Br have been observed by other authors for the bromide salt $^{33}$.

For $[\text{Ni}(o-C_6H_4(\text{PMe}_2)_2)_2\text{Cl}_2]\text{ClO}_4$ a complex signal was observed for the polycrystalline powder (6 lines in an asymmetric arrangement; Table 3.33), in line with expectation given the exceedingly complex pattern observed for polycrystalline powders diluted by inclusion in diamagnetic Co(III) hosts $^{50}$. By contrast, a single, broad line is observed for the corresponding bromide. In solution, the patterns seen (9 lines for the chloride, 7 for the bromide) are similar to those previously
Table 3.33 E.S.R. data Co-ordinate Ni(III) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g$ Values, linewidths and comments</th>
</tr>
</thead>
</table>
| $[\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2]\text{BF}_4$ | (a): $g = 2.157$; $g = 2.116(35)$  
(b): $g_{av} = 2.117$ (9 lines; $A_{iso} = 15G$) |
| $[\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Br}_2]\text{Br}$ | (a): $g_{av} = 2.08$ (2 or 3 superimposed signals) (CH$_3$CN solution): $g_{av} = 2.095$ (7 lines, $A_{iso} = 57G$) |
| $[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PMe}_2)_2\text{Cl}_2\text{]}\text{ClO}_4$ | (a): $g = 2.12$ (complex pattern); $g = 2.03$. (CH$_3$CN solution): $g_{av} = 2.130$. $A_{iso} = 28G$ (9 lines) |
| $[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PMe}_2)_2\text{Br}_2\text{]}\text{ClO}_4$ | (a): $g = 2.107(90)$ (isotropic)  
(CH$_3$CN solution): extremely complex pattern |
| $[\text{Ni}(\text{o-C}_6\text{F}_4\text{(PMe}_2)_2\text{Cl}_2\text{]}\text{ClO}_4$ | (a): $g = 2.161$; $g = 2.110(12)$  
$g = 2.095$.  
(b): $g_{av} = 2.104$, 9 lines, $A_{iso} = 17G$; $g = 2.02(75)$. |
| $[\text{Ni}(\text{o-C}_6\text{F}_4\text{(PMe}_2)_2\text{Br}_2\text{]}\text{ClO}_4$ | (a): $g = 2.095(40)$; $g = 1.92$ (broad).  
(b): $g_{av} = 2.097$ (complex hyperfine pattern). $g = 2.00(75)$ (complex hyperfine pattern). |
| $[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PMe}_2\text{(AsMe}_2\text{)}_2\text{Cl}_2\text{]}\text{ClO}_4$ | (a): $g = 2.24$; $g = 2.16$; $g = 2.01$  
(b): complex pattern. |
| $[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PMe}_2\text{(AsMe}_2\text{)}_2\text{Br}_2\text{]}\text{ClO}_4$ | (a): $g = 2.08(95)$ (isotropic) |
\[ \text{Ni(C}_6\text{H}_4\text{PMe}_2\text{SbMe}_2)_2 \text{Br}_2\text{ClO}_4 \]

(a): \( g = 2.09(65); g = 2.00 \)

\[ \text{Ni(PhP(CH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_3} \]

(a): \( g = 2.193(180) \) (isotropic)

\[ \text{Ni(PhP(CH}_2\text{CH}_2\text{PPh}_2)_2\text{Br}_3} \]

(a): \( g = 2.181(135) \) (isotropic)

\[ \text{Ni(MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_2\text{Br}_3} \]

(a): \( g = 2.101(110) \) (isotropic)

(b): \( g_{av} = 2.077 \) (10 lines;
\( A_{iso} = 68G \))

+ Figures in parentheses are linewidths (derivative peak-to-peak) in Gauss. Conditions used:

(a) powdered solid, room temperature;
(b) \( \text{CH}_3\text{CN/solution, room temperature.} \)

\( \text{CH}_2\text{Cl}_2 \)
Figure 3.34. A comparison of ESR spectra obtained (A) at room temperature in CH$_3$CN (this work) and (B) in ethanol glass at -196°C (reference 57) for [Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$Cl$_2$]ClO$_4$, showing the dependence of resolution on solvent and temperature for this technique.
noted, perhaps because in this case, ClO$_4^-$ or PF$_6^-$ salts, and CH$_3$CN, were used in recording the literature spectra also.

Interestingly, the close analogues of the $\sigma$-$C_6H_4(PMe_2)_2$ complexes, those of Me$_2PCH_2CH_2PMe_2$ and $\sigma$-$C_6F_4(PMe_2)_2$, gave very similar spectra. (Table 3.33, Figure 3.35). Again, dependence on conditions was strong, and when it was found that $[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2]ClO_4$ gave only a broad, single-line signal in solution, the corresponding tetrafluoroborate salt was prepared. In 4:1 CH$_2Cl_2$/CH$_3$CN this gave a satisfactory, 9-line pattern analogous to those observed for the $\sigma$-$C_6H_4(PMe_2)_2$ and $\sigma$-$C_6F_4(PMe_2)_2$ complexes.

As would be anticipated, given the presence of three different ligand nuclei with nuclear spin I > 0, the Ni(III) complexes of the phosphine-arsine ligand, $\sigma$-$C_6H_4(PMe_2)(AsMe_2)$ gave even more complex solution spectra (Table 3.33) which were not readily interpretable.

The Ni(III)-stibine complex, $[Ni(\sigma-C_6H_4(PMe_2)(SbMe_2))_2Br_2]ClO_4$ gave a spectrum typical of D$_{2h}$ symmetry as a polycrystalline powder, but was insufficiently soluble in CH$_3$CN to enable a solution spectrum to be obtained. (Neat CH$_3$CN is not well-suited to esr measurements using the instrument available (Varian E4) as difficulties are experienced in tuning the cavity at high enough power levels to enable the observation of noise-free signals with this, and other, polar solvents). Attempts to observe a signal due to transient formation of Ni(III) material during the decomposition of $[Ni(\sigma-C_6H_4(SbMe_2)_2)_2Br]Br$ were rewarded; a broad, isotropic signal (g = 2.04, linewidth 100G) could be observed on treating the solid Ni(II) complex with Br$_2$ in CC1$_4$ in situ and running the spectrum immediately. This signal diminished so as to become unobservable in ca 4 minutes.
FIG. 3.35

FIELD (G)

3100  3200  3300

A

FIELD (G)

3100  3200  3300

B

continued overleaf/...
Figure 3.35. A Comparison of the solution e.s.r. spectra of the phosphine complexes:

(A) \([\text{Ni} \left\{ \text{a-C}_6\text{H}_4\text{(PMe}_2\text{)}_2 \right\}_2\text{Cl}_2\text{]}\text{ClO}_4\)

(B) \([\text{Ni} \left\{ \text{a-C}_6\text{F}_4\text{(PMe}_2\text{)}_2 \right\}_2\text{Cl}_2\text{]}\text{ClO}_4\)

(C) \([\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2\text{]}\text{BF}_4\)

all run at room temperature in \(\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2\) (1:3), showing the nine-line pattern common to these complexes. (B) also shows partial resolution of the \(g_{II}\) region (at ca. 3290G; \(g = \text{ca.} 2.002\)).
Figure 3.36. The e.s.r. spectra of (a) $[\text{Ni}\{\text{MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_2\text{Br}_2]\text{ in CH}_2\text{Cl}_2$ solution, room temperature, run in the presence of excess Br$_2$ and (b) $[\text{Ni}\{\text{PhP(CH}_2\text{CH}_2\text{PPh}_2\}_2\text{Br}_3]$ as a polycrystalline solid, also at room temperature.
The e.s.r. spectrum of \([\text{Ni} \{\text{MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_2\text{Br}_3]\)

in \(\text{CH}_2\text{Cl}_2\) in the presence of excess bromine shows an isotropic, 10-line pattern (Table 3.33, Figure 3.36) and since no coupling is observed for the chloride in the same conditions, it is probable that this is due to the three bromine atoms \((^{79/81}\text{Br}; I = 3/2; 2nI+1 = 10)\), although as has already been stated, the e.s.r spectra are strongly dependent on any perturbation in conditions or environment around the metal ion.

The e.s.r spectra of \([\text{Ni}(\text{TRIPHOS})X_3]\) (TRIPHOS = \(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(Ph)CH}_2\text{CH}_2\text{PPh}_2\)) as polycrystalline solids show a single, rather broad line at \(g = ca\ 2.1\), with varying degrees of anisotropy apparent at different temperatures, although no complete resolution of hyperfine coupling or of more than one 'g' value was possible. Evidently, for this tridentate, aryl-substituted (therefore bulky) phosphine, the stability of the octahedral configuration to dissociation of one P-donor is limited. Previous observations of the reluctance of either \([\text{Ni}(\text{PR}_3)_2X_3]\) or \([\text{Ni}(\text{bidentate})X_3]\) to co-ordinate additional donors are supported by the fact that when a solution of \([\text{Ni}(\text{TRIPHOS})\text{Br}_2]\) in \(\text{CH}_2\text{Cl}_2\) is treated with \(\text{Br}_2\) solution, in the e.s.r tube, a signal develops only after addition of several drops, and this shows the four-line pattern typical of \([\text{Ni}(\text{bidentate})\text{Br}_3]\) complexes. Evidently a process such as \([\text{Ni}(P-P-P)\text{Br}_2] \xrightarrow{\text{Br}_2} [\text{Ni}(P-P)\text{Br}_2] \xrightarrow{\text{Br}_2} [\text{Ni}(P-P)\text{Br}_3]\) is occurring although the 6-co-ordinate Ni(III) complex may be an intermediate.

3.3d. Cyclic Voltammetry

Cyclic voltammetry, in certain circumstances, is a most useful technique for probing the effects of alterations in the ligands in the redox potentials of metal complexes. (Chapter 1, page18). The most important proviso for successful
application of the technique to a particular system is that there should be no change in co-ordination number on electron transfer. This enables the electrochemical reversibility of the redox process to be assessed.

A number of examples of the Ni(II) complexes were investigated by cyclic voltammetry under different conditions, with interesting variations in the results. When the oxidation of the Ni(II) dihalides in CH$_3$CN using Bu$_4$NBF$_4$ as support electrolyte was tried, the oxidation wave corresponding to Ni(II) → Ni(III) + e$^-$ was irreversible. However, when the Ni(II) complexes were studied using Et$_4$NCl as support electrolyte, the oxidation became nearly reversible, judging from the usual electrochemical parameters used to assess this. (See Chapter 7, page 294). (Figure 3.37, Table 3.35). These results concurred with other work, where dependence of reversibility on halide ion concentration was also observed for [Ni(o-C$_6$H$_4$(EMe$_2$)$_2$)$_2$Cl$_2$]ClO$_4$ (E = P or As), and the dependence is doubtless due to the progression from Ni(II) (four, or five-co-ordinate in solution) to Ni(III) (6-co-ordinate in solution). Significantly, fully-reversible behaviour was observed for this couple with [Ni(o-C$_6$F$_4$(PMe$_2$)$_2$)$_2$][ClO$_4$]$_2$ using Et$_4$NCl as electrolyte. For this ligand, a genuine octahedral (4P + 2Cl) high-spin Ni(II) complex has been isolated$^{32}$ and in the presence of excess halide ion it is possible that a significant proportion of this species is present in solution, and as here there is no change in co-ordination number on oxidation, reversible behaviour is observed.

Although even in the presence of excess halide ion, fully reversible behaviour does not occur (with the above exception), it has been suggested that relative differences between the potentials for a given system are meaningful for "rough comparative purposes"$^{32}$. 

TABLE 3.37  
ELECTROCHEMICAL DATA

<table>
<thead>
<tr>
<th>Starting Complex</th>
<th>Ip(av)Ni&lt;sup&gt;II&lt;/sup&gt;/Ni&lt;sup&gt;III&lt;/sup&gt;&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni&lt;sub&gt;0&lt;/sub&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;_2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.29</td>
<td>e</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0&lt;/sub&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;_2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.36</td>
<td>e</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0&lt;/sub&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;_2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.35</td>
<td>f</td>
</tr>
<tr>
<td>[Ni&lt;sub&gt;0&lt;/sub&gt; - C&lt;sub&gt;6&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;_2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.41</td>
<td>e</td>
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<tr>
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<td>e</td>
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<td>0.21</td>
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<td>0.22</td>
<td>e</td>
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<tr>
<td>Ni&lt;sub&gt;0&lt;/sub&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;_2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.49</td>
<td>f</td>
</tr>
</tbody>
</table>

(a) Volts (± 0.01).  (b) 0.1M Et<sub>4</sub>NCl in CH<sub>3</sub>CN as supporting electrolyte.  
(c) 0.1M Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN as electrolyte.  (d) 0.1M Et<sub>4</sub>NClO<sub>4</sub> in CH<sub>3</sub>CN as electrolyte.  
(b) and (c) at carbon electrode, potentials versus standard calomel electrode (SCE).  (d) at Pt Electrode versus Ag/AgClO<sub>4</sub> - literature values converted to SCE by adding +0.46.  
(e) this work.  (f) Reference 32.
Figure 3.38. (See overleaf).
Figure 3.38. Cyclic Voltammetry performed on Ni(II) complex.

A. The first oxidation wave observed for Ni(Me₂PCH₂CH₂PMe₂)₂Cl₂ as a 0.002M solution in CH₃CN, with Bu₄NBF₄ (1M) as support electrolyte. Scan rate 100 mV s⁻¹; scale is relative to the standard calomel electrode.

B. Oxidation wave for (solid line) Ni(o-C₆H₄(PMe₂)₂)Cl₂, 0.002M in 1M Et₄NCl/CH₃CN; (broken line) [Ni(o-C₆F₄(PMe₂)₂)₂Cl₂] in the same conditions. Notable are the difference in electrochemical reversibility between A. and B. (due to the presence of Et₄NCl as electrolyte in B.) and the difference in the redox potential of the complexes of o-C₆H₄(PMe₂)₂ and o-C₆F₄(PMe₂)₂.
In general, for the ligands o-C\(_6\)H\(_4\)(EMe\(_2\))\(_2\) (E = P or As) and Me\(_2\)PCH\(_2\)CH\(_2\)PMe\(_2\) there was little difference in the redox potentials for the process Ni(II)→Ni(III)+e (Table 3.37, Figure 3.38). Contrary to what may be expected if o-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\) is a superior σ-donor to o-C\(_6\)H\(_4\)(AsMe\(_2\))\(_2\), as previous studies have shown\(^{34}\), the potentials observed were lower for the diarsine. However, the preference of the diphosphine for d\(^8\) metal centres has previously been noted\(^3\). Additionally, further oxidation to Ni(IV) was favoured significantly by the diphosphine (see Chapter 5, page247). The complex [Ni(Me\(_2\)PCH\(_2\)CH\(_2\)PMe\(_2\))\(_2\)]\(^{2+}\), in the presence of excess chloride ion, gave the lowest observed oxidation potential (Table 3.37) although it should be emphasised that the differences are almost comparable with overall experimental error\(^5\).

The perfluoroaryl diphosphine o-C\(_6\)F\(_4\)(PMe\(_2\))\(_2\), however, does seem to be significantly different. The redox potential for its Ni(II) chloro-complex is ca 110 mV higher than for that of o-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\). This illustrates the possibility that the incorporation of F into the ligand backbone may well influence the resulting complexes more significantly than changing the donor atom, at least for this system, and confirms the expectation that (at least electrochemically) o-C\(_6\)F\(_4\)(PMe\(_2\))\(_2\) is less able to promote oxidation of metal centres than o-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\).\(^{51}\) These differences become more pronounced on further oxidation to Ni(IV); this will be considered later (Chapter 5).

3.3e. Other Ligands : Discussion

It was hoped that, by using the ligand CH\(_3\)C(CH\(_2\)PPh\(_2\))\(_3\) which is sterically constrained to give fac isomers in 6-co-ordinate complexes, fac Ni(III) complexes could be made for spectroscopic
comparison with those of the above flexible, linear tridentate ligands. Unfortunately, controversy seems to surround the nature of the Ni(II) complexes of this ligand. While the original authors suggested that all three P atoms are co-ordinated in the Ni(II) halo-complexes, it has since been suggested that one P-donor is unco-ordinated (see Chapter 2.26, page 39).

Comparison of diffuse reflectance and solution electronic spectral data for the Ni(II) complexes of the tripodal ligand with those of known square planar and five co-ordinate complexes suggested that in the solid phase, all three P donors were co-ordinated (see Chapter 7, page 314) but in solution, the complexes were square planar, with one unco-ordinated P atom. However, attempts at oxidation in CCl₄ suspension with halogen gave products with poor, irreproducible C and H analyses, and bands in the i.r. spectra suggesting some phosphine oxide formation. The e.s.r. (in CH₂Cl₂ solution) of the product of such a reaction between [Ni(CH₃C(CH₂PPh₂)₃Br₂] and excess Br₂ gave the four-line pattern familiar from the studies of pseudo-square pyramidal [Ni(bidentate)Br₃] (Chapter 3.2, page 139).

Benner and Meek showed that the reported Ni(III) complexes of the tetradeionate arsine As(CH₂CH₂CH₂AsMe₂)₃ were trigonal-pyramidal Ni(II) compounds [Ni(L)X]X, and that attempts to oxidise these to Ni(III) produced diamagnetic materials with strong As = 0 vibrations in the i.r. spectra, indicating oxidation of the ligand, with detachment of some of the As donor atoms from Ni. The results of this study confirm these observations entirely. However, on treatment of the solid Ni(II) bromo-complex with Br₂/CCl₄ in situ in an e.s.r. tube, a broad, featureless signal at g = 2.13 developed. It was impossible from this information to determine the donor set of the presumed Ni(III) centre, (although the most likely one is As₂Br₃) since the brown solid produced in this way decomposed immediately in CH₂Cl₂, and attempts to obtain solid Ni(III) complexes of a similar bidentate
ligand (Me₃As(CH₂)₃AsMe₂) for possible comparison also failed.

Although the Ni(II) complexes of the tetraphosphines (Ph₂PCH₂CH₂P(Ph)CH₂P(CH₂CH₂PPh₂)₃) are known to have all the P-donors co-ordinated, attempts at oxidation resulted only in partial oxidation of the ligand. The only tetradentate ligand which showed any proclivity to support Ni(III) without the dissociation of neutral donor atoms was the methyl-substituted tetra-arsine FARS. (Figure 3.3).

![Figure 3.3. "FARS"](image)

This yielded five-co-ordinate Ni(II) halo-complexes [Ni(L)X]ClO₄ (see Chapter 7). On treatment with halogen in CH₃CN, transient light green (X = Cl) or brown (X = Br) colours characteristic of the Ni(III) octahedral cations [Ni(L-L)₂X₂]⁺ were seen, but these did not persist long enough to enable electronic spectra to be recorded (½t ca 5s). Unfortunately, in frozen CH₃CN, esr spectra of these solutions could not be resolved, probably owing to the problems previously outlined for this solvent (page 172). Therefore, the hyperfine coupling which might support the proposed Ni(III) octahedral cation structure for this intermediate could not be observed. Treatment of solid samples of the Ni(II) complex with X₂ in CCl₄ in situ produced materials with broad, isotropic esr signals centred at g = 2.1 - 2.2. It should be emphasised that all attempts to oxidise the Ni(II) complexes with stoichiometric quantities of
halogen, in solution or in suspension, resulted only in partially-decomposed Ni(II) products, even when the reactions were carried out in moisture-free conditions (Schlenk apparatus).

Attempts were also made to oxidise some examples of \([\text{Ni}(L-L)_2]^{2+}\) and \([\text{Ni}(L-L)_2X]^+\) \((L-L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{cis-Ph}_2\text{PCH_CH}_2\text{PPh}_2, \sigma-\text{C}_6\text{H}_4(\text{PPh}_2)_2)\). However, under all conditions tried, including the use of stoichiometric amounts of oxidant (halogen) in moisture-free conditions, no octahedral \([\text{Ni}(L-L)_2X_2]^+\) could be isolated for these ligands. The use of excess oxidant in solution led to the isolation of \(\text{Ni}(L-L)_X\) \((n = 2, 3)\) mixtures and organophosphorus (V) products (identified by \(^1\text{H n.m.r.)}\) in all cases, and this was confirmed by e.s.r. spectroscopy.

These results are in some respects similar to those obtained for Pt(IV) and Pd(IV) in earlier studies. In particular, the complex \([\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_2]\text{Cl}_2\) could be made by \(\text{Cl}_2/\text{CCl}_4\) oxidation of solid \(\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_2\), but in solution, \([\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2]\text{Cl}_2\) and oxidised ligand were obtained. Although Pt(IV) complexes of the tri- and tetra-dentate ligands used in this study could be made, they were notably less stable than the \([\text{Pt}(L-L)_2X_2]^{(\text{ClO}_4)_2}(L-L = \sigma-\text{C}_6\text{H}_4(\text{EMe}_2)(\text{E'Me}_2); \text{E}, \text{E'} = \text{P}, \text{As})\) \(^{61}\). In the case of Pd(IV), \([\text{Pd}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_2]\text{Cl}_2\) could not be made; \(\text{Pd}(L-L)\text{Cl}_4\) were isolated for \(L-L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2\), whilst only one (impure) complex of a multidentate ligand was obtained. The reasons for this behaviour are probably similar for Ni(III), Pd(IV) and Pt(IV).

For the formation of octahedral complexes of a metal in a high oxidation state with more than two neutral donor atoms the ligands will be required to have strong \(\sigma\)-donor ability and low steric requirements. The aryl-substituted bidentate ligands are only moderate \(\sigma\)-donors and the rigid phenyl substituents increase
their cone angles relative to those of methyl-substituted donors. It has been shown that in the square pyramidal \( \text{[Co(Ph}_{2}\text{PCH}_{2}\text{CH}_{2}\text{PPh}_{2})_{2}\text{Cl}]^{+} \), the 'sixth' co-ordination site is blocked by the \( \text{o-H} \) of the phenyl rings. As it has been established by other studies that higher oxidation states prefer to co-ordinate axial halide ions to assist in neutralising the charge at the metal ion, it might be anticipated that this steric hindrance would make the synthesis of an ion such as \( \text{[Ni(Ph}_{2}\text{PCH}_{2}\text{CH}_{2}\text{PPh}_{2})_{2}\text{X}_{2}]^{+} \) impossible. It is interesting that the tendency to achieve neutrality by co-ordination of sufficient halide ions is shared by \( \text{Ni(III)} \), \( \text{Pd(IV)} \) and \( \text{Pt(IV)} \). Only with the very strong \( \sigma \)-donor neutral ligands, which contribute significantly to ligand-field stabilisation energy as a result of their high position in the spectrochemical and nephelauxetic series, is this requirement relaxed.

The achievement of octahedral \( (E_{3}X_{3}) \) co-ordination with two tridentate ligands can be construed as an example of the operation of the 'chelate effect'. The treatment of \( \text{[Ni(L-L)X}_{3}] \) complexes with \( \text{PET}_{3} \) resulted only in accelerated decomposition, but in the case of the tridentates, the route to \( \text{Ni(III)} \) is the oxidation of a \( \text{Ni(II)} \) complex to which all three neutral donors are bound. The complexes are nevertheless of only marginal stability and, in solution in the presence of excess oxidant, show a tendency to decompose to five-co-ordinate \( \text{Ni(III)} \) species. Significantly, the alkyl-substituted triarsine complex decomposed in this manner at a far slower rate than the aryl-substituted triphosphine complex, presumably because of the larger steric requirements of the latter ligand and the greater reducing tendency of \( \text{P} \). Unfortunately a tridentate alkyl-substituted phosphine was not available for comparison.

That no tetradeionate ligand - \( \text{Ni(III)} \) complex could be obtained is not surprising given the factors promoting stability
discussed above. The advantages of the chelate effect in, for example, \((\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(Ph)CH}_2\text{PPh}_2\text{)}\) - Ni(II) complexes, must be outweighed by similar steric factors to those involved in \([\text{Ni(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{)}_2]\text{[CIO}_4\text{]}_2\).

The aims of this study, to investigate the factors promoting stability in Ni(III) complexes of Group Vb donor ligands, and the properties and stereochemistries of the Ni(III) complexes isolated, have largely been achieved. The isolation of the complexes \([\text{Ni}\{\text{C}_6\text{H}_3(CH,\text{NMe}_2)\text{CH}_2\text{O,0'}\}_2]\text{[X}_3\text{]}_2\) and the establishment of their geometry as very similar to that of the \([\text{Ni(L-L)X}_3]\) made during this study may be of some significance in future years if the chemistry of organometallic complexes of metals in higher oxidation states is developed further.
Chapter 3 References


51. S. J. Higgins and W. Levason. Submitted for publication.


59. D. Fletcher, personal communication.
CHAPTER 4

POLYIODIDE COMPLEXES OF Ni(II)
CHAPTER 4

POLYIODIDE COMPLEXES OF Ni(II)

4.1 Introduction

The relatively wide variety of nickel (III) complexes with bromide and chloride co-ligands (q.v.) suggested that attempts to synthesise nickel (III) iodo-complexes might be profitable.

While some platinum (II) iodo-complexes may be oxidised by diiodine to Pt(IV) (e.g. \([\text{Pt(PMe}_3]_2\text{I}_4]\)\(^1\), \([\text{Pt(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]\text{I}_4]\)\(^2\)) other ligands give Pt(II) polyiodides (e.g. \([\text{Pt(dimethylimidazole)}]_4(\text{I}_3)_2\)\(^3\). Palladium(II) complexes may give Pd(II) polyiodides (e.g. \([\text{Pd(NH}_3]_4\text{I}_8\), \([\text{Pd(cis-Ph}_2\text{PCH}_2\text{CHPPh}_2]\text{I}_4]\)\(^5\) or "partially oxidised" materials (e.g. \([\text{Pd(diphenylglyoximate)}]_2\text{I}_x\)\(^6\)) but, apart from the recently-reported \(\text{Cs}_2\text{PdI}_6\)\(^7\), no Pd(IV) iodo-complexes are known. As nickel displays the 'intermediate' Ni(III) oxidation state, this lends interest to reactions of nickel(II) iodo-complexes with diiodine; oxidation of Ni(II) to Ni(III) could be significantly easier than Pd(II) to Pd(IV).

4.2 Survey of the Literature

There are several reports in the literature of dark brown or black materials formed when nickel(II) iodo-complexes of Group Vb ligands are treated with diiodine. Nyholm in his pioneering studies found that the Ni(III) complex \([\text{Ni(o-C}_6\text{H}_4(\text{AsMe}_2)_2]\text{Cl}_2]\text{Cl}, when treated with aqueous KI, gave a black precipitate of composition \(\text{Ni(ligand)}_2\text{I}_3\)\(^8\). Its insolubility led Nyholm to suggest a polymeric nickel(IV) formulation as responsible for the observed (and unexpected) diamagnetism. Reaction of \([\text{Ni(o-C}_6\text{H}_4(\text{AsMe}_2)_2]}(\text{CO})_2\] with excess diiodine gave black \(\text{Ni(o-C}_6\text{H}_4(\text{AsMe}_2)_2}\text{I}_4\)\(^9\), also diamagnetic and postulated
as either a nickel(IV) complex, or a nickel(II) polyiodide. Treatment of \([\text{Ni\{bis\{o-dimethylarsinophenyl\}methyl arsine\}I}_2]\) with diiodine in benzene gave brown-black products of "indeterminate" composition, possibly a polyiodide.

The complex \(\text{[Ni}^{III}\{\text{As(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_3\text{I}_2]\), reportedly obtained by Barclay and Barnard\(^{10}\), was later shown to be trigonal bipyramidal \(\text{[Ni}^{II}\{\text{As(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_3\text{I}\).}\(^{11}\)

The diphosphine \(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\) is known to stabilise both nickel(III) and nickel(IV) complexes with chloride and nickel(III) with bromide co-ligands (q.v.) and the synthesis of brown \(\text{[Ni}^{III}\{\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\}_2\text{I}_2\text{I}\) by air oxidation of the corresponding nickel(II) complex in refluxing ethanolic HI has been briefly claimed. No spectral or magnetic data were reported, however. Recently, a (most unlikely) low-spin tetrahedral nickel(III) complex, \(\text{[Ni(Ph}_3\text{PO}^\text{Cl}_2 \text{I}_2]\), has been postulated as the product of the reaction of NOCl with \(\text{[Ni(Ph}_3\text{P})_2\text{I}_2]\).\(^{13}\)

The only well-characterised example of a nickel(III) iodo-complex to date appears to be \(\text{[Ni\{C}_6\text{H}_3\text{(CH}_2\text{NMe}_2\}_2\text{O}_2\}^\text{0}\text{O'}\text{I}_2]\), discussed in Chapter 2, which was the subject of an X-ray crystallographic and e.s.r. study.\(^{14}\)

All other products reportedly obtained by the treatment of nickel(II) complexes with diiodine can be divided into two categories, (a) "partially oxidised" complexes and (b) nickel(II) polyiodides. Well-documented examples of the former involve ligands with delocalised \(\pi\)-systems (for example, glyoximates, tetraazaannulenes, phthalocyanines and porphyrins), and are not therefore strictly relevant to these studies as it is probably the ligand that undergoes oxidation. This is borne out by the fact that substitution of Pd for Ni in the complexes hardly affects their physical properties.\(^{15}\) However, the structure
of the polyiodide units in these materials can be compared with those present in genuine nickel(II) polyiodides. This important and developing area of chemistry has recently been reviewed.\(^\text{15}\)

Structurally characterised nickel(II) polyiodides are rare. \([\text{Ni}(\text{NH}_3)_6]\text{I}_3\text{I}_2\) has been so characterised\(^\text{19}\), as part of a wider study of the bonding of polyiodide units and the effects of altering the charge and stereochemistry of the cation.\(^\text{16,17,18}\) This work has also been reviewed.\(^\text{19}\)

The complex \([\text{Ni}(\text{NH}_3)_6]\text{I}_3\text{I}_2\) is the first example of two forms of the \(\text{I}_3^-\) ion (linear and bent) in the same structure. The ions are separated by \(\gt 4.19\) \(\text{Å}\), a distance which suggests no significant interaction. A crystallographic study has been mentioned of \([\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]\text{I}_3\text{I}_2\)\(^\text{20}\), but few details were given. These are included in Table 4.21, together with some structural details of typical polyiodide ions.

The complex \([\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]\text{I}_3\text{I}_2\) was first synthesised by Nyholm et al.\(^\text{21}\) by successive treatment of nickel(II) acetate solution with ethylenediamine and \(\text{KI}_3\). Spectral and magnetic data suggested a tetragonal structure, with weak nickel(II)-\(\text{I}_3^-\) interaction responsible for the observed diamagnetism.

Attempts to oxidise methanol solutions of \(\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{I}_2\) or \([\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{I}_2\) with diiodine led to precipitation of the brick-red \([\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{I}_4\), \(\mu_{\text{eff}} = 3.13\) \(\text{BM}\), therefore presumably an octahedral nickel(II) polyiodide\(^\text{22}\), whilst treatment of \(\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{I}_2\) with excess diiodine in \(\text{CCl}_4\) again gave black, diamagnetic \([\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]\text{I}_3\text{I}_2\).
Somewhat better characterised were the black materials isolated upon treatment of nickel(II) complexes of dithioethers with diiodine. Nyholm found that, while attempts to oxidise $[\text{Ni(MeSCH}_2\text{CH}_2\text{SMe})_2X_2]$ ($X = \text{Cl}, \text{Br}$) with the appropriate halogen led to decomposition, diiodine ($X = \text{I}$) gave a black crystalline product of composition $\text{Ni(MeSCH}_2\text{CH}_2\text{SMe})_2\text{I}_4$. The magnetic moment (2.94 BM) indicated octahedrally co-ordinated nickel(II) and hence a polyiodide. Goodgame et al. found that under slightly different conditions, black $\text{Ni(MeSCH}_2\text{CH}_2\text{SMe})_2\text{I}_6$ was the product. The electronic spectrum in CHCl$_3$ solution showed the presence of $\text{I}_3^-$ (bands at $29$ and $33-35 \times 10^3 \text{ cm}^{-1}$). However, the broad, rather featureless diffuse reflectance spectrum, a common feature of polyiodide materials, prevented any reliable structural conclusion.

The foregoing examples indicate some of the difficulties involved in studying polyiodide materials. Bands due to $\text{I}_3^-$ or other polyiodide anions dominate the charge transfer region of the electronic spectrum and 'tail' into the visible region so obscuring any 'd-d' transitions. This hinders stereochemical assignment on the basis of the electronic spectrum, and is responsible for the dark colours observed for the complexes. Vibrations in the far infra-red of largely metal-iodide or iodine-iodine stretching character occur below $200 \text{ cm}^{-1}$, out of the range of most commercial spectrometers. Laser Raman measurements are also often difficult as the laser often causes decomposition of the dark-coloured materials.

This means that X-ray crystallography is invaluable in solving the problems of both the structure of the metal complex and of the polyiodide units. This has recently been achieved for two palladium(II) polyiodide complexes of 'soft' donor ligands, of relevance to this study.
Reaction of Pd(cis-Ph₂PCH₂CHPPh₂)I₂ with diiodine in a 1:4 mole ratio in dichloromethane gave crystals of composition Pd(ligand)I₄. Electronic spectra of this and similar materials with other bidentate ligands suggested a Pd(II) polyiodide rather than an octahedral Pd(IV) complex. X-ray crystallography revealed a cis planar Pd(II) centre, bridged by iodine molecules between co-ordinated iodide ions into infinite chains (Figure 4.22). The I⁻⁻⁻⁻I₂⁻⁻⁻⁻I⁻ interaction was, from the bond lengths, considered to be very weak. The I₂ unit showed little bond lengthening compared with the I-I distance in solid diiodine.*

The product of a similar reaction between [Pd{o-C₆H₄(SPh)₂}I₂] and diiodine was a material of composition Pd(ligand)I₃. Recrystallisation from 1,2-dichloroethane, however, gave black crystals which X-ray crystallography revealed to be [Pd(ligand)I₄]²⁻² with, again, cis-planar stereochemistry about Pd(II) and bridging diiodine molecules interacting even more weakly with the co-ordinated iodide ions. If these units are considered to be I₄⁻⁻ ions, they display the longest I⁻⁻⁻⁻I₂⁻⁻⁻⁻ bond yet found for that anion.²⁷ These two complexes are included in Table 4.21, and Figure 4.22 illustrates the individual molecule for Pd(cis-Ph₂PCH₂CHPPh₂)I₄ and the iodine packing arrangements in the crystals.

* The poly-centre bonding models used for polyiodide ions¹⁹ require that in, for example, I₄⁻⁻, as the I⁻⁻⁻⁻I₂ distance decreases (with increasing bond strength) so the I-I distance in the I₂ unit increases. Therefore, comparison of the I-I distance with that in free I₂, and of the I⁻⁻⁻⁻I₂ separation with the sum of the Van der Waals radii, provides an indication of the usefulness of the polyiodide description.
<table>
<thead>
<tr>
<th>Complex/Compound</th>
<th>Polyiodide Unit $(a)$</th>
<th>Crystal Packing of Iodines</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsI$_3$</td>
<td>$d_1=2.842(2)$, $d_2=3.038(2)$; $\alpha=178.00(6)^\circ$</td>
<td>Independent I$_3^-$ units</td>
<td>59</td>
</tr>
<tr>
<td>Ph$_4$AsI$_3$</td>
<td>$d_1,d_2=2.919(4)$; $\alpha=174.69(2)^\circ$</td>
<td>Isolated I$_3^-$ units</td>
<td>60</td>
</tr>
<tr>
<td>[Ni(NH$_3$)$_2$(I$_3$)$_2$</td>
<td>(i) $d_1,d_2=2.923(1)$; $\alpha=177.68(6)^\circ$</td>
<td>Two sets of independent I$_3^-$ units, with different symmetry</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>(ii)$d_1,d_2=2.917(1)$; $\alpha=177.68(6)^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$(I$_3$)$_2$</td>
<td>$d_1=2.78$, $d_2=3.38$; $\alpha=174^\circ$</td>
<td>&quot;I$_3^-$&quot; units more accurately described as I$^-$...I$_2$, with I$^-$ co-ordinated to Ni axially.</td>
<td>17</td>
</tr>
</tbody>
</table>

continued overleaf/...
<table>
<thead>
<tr>
<th>Complexes/Compound</th>
<th>Polyiodide Unit (a)</th>
<th>Crystal Packing of Iodines</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cd(NH$_3$)$_4$(I$_4$)]</td>
<td>$d_1=3.388(3), d_2=2.789(3)$, $\alpha=179.93(6)^\circ$</td>
<td>I$_4^-$ co-ordinated at both ends to metal centres in axial fashion, producing zig-zag chains.</td>
<td>17,16</td>
</tr>
<tr>
<td>[Cu(NH$_3$)$_4$(I$_4$)]</td>
<td>$d_1=3.344(3), d_2=2.808(3)$; $\alpha=179.9(1)^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pd(cis-Ph$_2$PCHCHPPh$_2$)(I$_4$)]</td>
<td>$d_1=3.527(1), d_2=2.745(1)$; $\alpha=174.9(1)^\circ$</td>
<td>I$_4^-$ co-ordinated at both ends to metal centres giving a cis-Pd(L-L)I$_2$ arrangement linked by I$_2$ molecules; (see Figure 4.22). Very weak I$^-$... I$_2$....I$^-$ links.</td>
<td>26,27</td>
</tr>
</tbody>
</table>
Figure 4.22. An ORTEP drawing of a single molecule of Pd\(\text{cis-Ph}_2\text{PCHCHPPh}_2\)I\(_4\), showing the linking of Pd(L-L)I\(_2\) units by I\(_2\). (Facing page) Packing diagrams for the same molecule, and the analogous Pd\(\text{o-C}_6\text{H}_4\text{(SPh)}_2\)I\(_4\). Iodine atoms shaded.
Figure 4.22 continued...

Unit Cell Packing Arrangement for Pd(cis-Ph,PCH=CHPh)_2I, Viewed Down the a Axis

Unit cell of Pd(o-C_6H_4(SPh)_2)I_4 showing the Pd, I and S atoms only, viewed from the positive y direction.
4.3 Results and Discussion

Selected examples of the reactions of a range of nickel(II) complexes with diiodine, mentioned in the literature, were repeated in an attempt to elucidate the nature of the products formed. New complexes were made by similar methods so that a series of related complexes, where possible, could be compared, and an X-ray crystallographic analysis was carried out, on the product of the reaction of [Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$I$_2$] with diiodine in dichloromethane.

4.3.1 Ni(L-L)$_2$I$_2$; L-L = bidentate ligand

The treatment of an aqueous solution of nickel(II) acetate with, successively, 1.9 mole equivalents of ethylenediamine and 2.0 equivalents of KI$_3$ solution (made by dissolving KI and I$_2$ in a 1:1 ratio in water) yielded a khaki-black precipitate of composition Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$I$_6$ (see Table 4.31). This exhibited broad, strong bands in the diffuse reflectance spectrum characteristic of the I$_3^-$ ion (Table 4.31) and showed no absorptions $<$ 17,700 cm$^{-1}$ in CH$_3$CN solution, consistent with an essentially planar nickel(II) cation. The complex was insoluble in CH$_2$Cl$_2$, ruling out attempts to determine whether the integrity of the I$_3^-$ ion is retained in this solvent. (The extent of the reaction I$_3^-$ $\rightarrow$ I$^-$ + I$_2$ cannot be determined in CH$_3$CN solution as I$_2$ is thought to be associated with the solvent and in that form gives a very similar spectrum to I$_3^-$$^{29}$).

Magnetic measurements on the solid indicated diamagnetism ($\mu_{\text{eff}} < 0.2$ BM) and no e.s.r. signal could be resolved either at room temperature or at $-196^\circ$C, effectively ruling out any nickel(III) formulation.
The other complexes \( \text{Ni(L-L)}_2\text{I}_6 \) were obtained by addition of excess diiodine in \( \text{CH}_2\text{Cl}_2 \) to solution of the Ni(II) iodide complexes, under standardised conditions, (five-fold molar excess of diiodine). These were chosen, and fixed, so that the effect of the ligands on the formation of particular polyiodide units could be examined; conceivably, varying the conditions, especially the mole ratio of reactants or the solvent mixture could alter the polyiodide favoured for a given ligand.

A material of analytical composition \( \text{Ni(MeSCH}_2\text{CH}_2\text{SMe)}_2\text{I}_6 \) was made as a matt black powder by treatment of \( \text{[Ni(MeSCH}_2\text{CH}_2\text{SMe)}_2\text{I)}_2 \) in \( \text{CH}_2\text{Cl}_2 \) solution with a five-fold molar excess of diiodine. No i.r. evidence for the presence of water could be found, ruling out the suggestion of Goodgame et al. on the basis of tentative assignments of d-d bands in the electronic spectrum, that the correct formulation could be \( \text{[Ni(MeSCH}_2\text{CH}_2\text{SMe)}_2\text{H}_2\text{O)}_2\text{I}_2 \). The selenoether analogue, \( \text{[Ni(MeSeCH}_2\text{CH}_2\text{SeMe)}_2\text{I}_2 \), also gave a hexaiodide under the same conditions. Both the polyiodides have weak absorptions in their diffuse reflectance spectra, at ca. 11,000 cm\(^{-1}\) and ca. 17,000 cm\(^{-1}\) and have magnetic moments corresponding to two unpaired electrons (Table 4.31), indicating pseudo-octahedral nickel(II) complex. Although the diffuse reflectance spectra are rather poorly defined, the presence of broad maxima at ca. 29,000 and 33-35,000 cm\(^{-1}\) (Table 4.31), corresponding to the allowed transitions (\( \pi \rightarrow \sigma^*_u \), \( \sigma_g \rightarrow \sigma^*_u \); \( D_5h \) symmetry) of the \( \text{I}_3^- \) group, are evidence for the \( \text{[Ni(ligand)}_2\text{(I}_3^\prime\text{)}_2 \) formulation. Diselenahexane complexes of the 3d metals are known to be somewhat less stable than the corresponding dithioether complexes, and this appears to be the case for nickel(II) also, as the diselenahexane complex smells strongly of the free ligand, is decomposed in moist air and in hydroxylic solvents, and has its low-energy electronic spectral band at lower energy than that for the dithiohexane complex (Table 4.31). For octahedral (high
Table 4.31 Analytical and Spectroscopic Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>Analyses</th>
<th>$\mu_{\text{eff}}$</th>
<th>Electronic Spectral Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>[$\text{Ni(MeSeCH}_2\text{CH}_2\text{SMe)}_2\text{I}_3\text{]}_2$</td>
<td>9.0(9.0)</td>
<td>1.7(1.9)</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.3, 11.9, 16.9(br), 24.8, 29.2, 33.1(sh), (c) 19.2(sh)(120); 27.9(28,200) 34.7(53,500)(d) decomposed</td>
</tr>
<tr>
<td>[$\text{Ni(MeSeCH}_2\text{CH}_2\text{SeMe)}_2\text{I}_3\text{]}_2$</td>
<td>8.0(7.7)</td>
<td>1.6(1.6)</td>
<td>60.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.0, 12.3(w), 17.1, 24.9(c)</td>
</tr>
<tr>
<td>[$\text{Ni(H}_2\text{NCH}_2\text{NH}_2\text{I}_3\text{]}_2$</td>
<td>5.3(5.1)</td>
<td>1.8(1.7)</td>
<td>diamagnetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.2(w), 24.9, 29.2, 34.5(c)</td>
</tr>
<tr>
<td>[$\text{Ni}(\alpha\text{-C}_6\text{H}_4\text{PMe}_2\text{)}_2\text{I}_3\text{]}_2$</td>
<td>19.7(19.75)</td>
<td>2.5(2.65)</td>
<td>61.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.2(br), 20.1(br), 23.9, 26.5, 27.9, 34.3(c)</td>
</tr>
</tbody>
</table>

Notes:
(a) $\mu_{\text{eff}}$ (B.M.)
(b) $\alpha$ (10$^{-3}$ mol dm$^{-3}$ MeNO$_2$)
(c) Decomposed
<table>
<thead>
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<tr>
<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
</tr>
<tr>
<td>(\text{PMe}_2)_2 \text{I}_3 ]</td>
</tr>
<tr>
<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
</tr>
<tr>
<td>(\text{PMe}_2)_2 \text{I}_3 ]</td>
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<tr>
<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
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</tbody>
</table>

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<th>ca0.3(b)</th>
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</thead>
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</tr>
<tr>
<td>(\text{PMe}_2)_2 \text{I}_3 ]</td>
<td>20.7(1350); 26.2(\text{sh}); 27.9(5600);</td>
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</tr>
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<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
<td>30.7(5600); 35.7(14,000)(\text{d})</td>
<td></td>
</tr>
<tr>
<td>(\text{PMe}_2)_2 \text{I}_3 ]</td>
<td>17.5(\text{sh}); 20.7(\text{sh}); 27.9; 34.7(\text{e})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
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<tr>
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<th>0.0</th>
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</thead>
<tbody>
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<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
<td>17.1, 24.9(\text{sh}) 29.9, 36.2(\text{c})</td>
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</tr>
<tr>
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<td>17.5(\text{sh}); 21.5(480); 30.9(1900)(\text{e})</td>
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</table>

<table>
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<th>0.0(b)</th>
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</thead>
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<tr>
<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
<td>16.9(\text{sh}); 23.3(\text{sh}); 27.8, 35.7(\text{c})</td>
<td></td>
</tr>
<tr>
<td>(\text{PMe}_2)_2 \text{I}_3 ]</td>
<td>Insoluble(\text{d})(\text{e})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
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<th>0.5</th>
</tr>
</thead>
<tbody>
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<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsPh}_2) } ]</td>
<td>18.5(\text{sh}); 26.7, 33.8(\text{c})</td>
<td></td>
</tr>
<tr>
<td>(\text{PPh}_2)_2 \text{I}_6 ]</td>
<td>Decomposes(\text{c}); Insoluble(\text{e})</td>
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</tr>
</tbody>
</table>

<table>
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<tr>
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<th>ca 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Ni} {\text{o-C}_6\text{H}_4(\text{AsMe}_2) } ]</td>
<td>26.5, 28.2(\text{sh}); 34.2(\text{c})</td>
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<tr>
<td>(\text{PPh}_2)_2 \text{I}_6 ]</td>
<td>Decomposes(\text{d})</td>
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<table>
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<th>ca 0.4</th>
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</thead>
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<tr>
<td>[ \text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2 ]</td>
<td>18.4, 27.2(\text{sh}); 28.7, 35.0(\text{c})</td>
<td></td>
</tr>
<tr>
<td>\text{PPh}_2)_6 ]</td>
<td>Decomposes(\text{d})</td>
<td></td>
</tr>
</tbody>
</table>

- Indicates decomposition or insolubility.
Notes for Table 4.31

(a) Measured by the Gouy method except (b) measured in CH$_3$CN by Evans method.

(c) Diffuse reflectance (d.r.) absorbance maxima ($\times 10^{-3}$ cm$^{-1}$)
recorded using BaSO$_4$ as reference and diluent.

(d) Solution maxima (in CH$_3$CN except (e) measured in CH$_2$Cl$_2$
solution; cm$^{-1} \times 10^{-3}$). Figures in parentheses are
$\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$).

(f) Nitrogen analyses.

(g) Units ohm$^{-1}$ cm$^2$ mol$^{-1}$.
spin) nickel(II), these bands are due to the $^3\Lambda_{2g} \rightarrow ^3\Pi_{2g}$ transition, which corresponds to $10Dq$; hence $10Dq$ is lower for the diselenohexane complex. An X-ray crystal structure determination would have been of interest for one of these complexes, which must contain co-ordinated $I_3^-$, as other complexes containing this ion in the literature have intriguing chain structures of $I_3^-$ ions, interlinked in various ways. However, their instability and lack of crystallinity precluded such investigations.

The reactions of $[Ni(L-L)_2I_2]$ (L-L = $C_6H_4(EMe_2)(E'Me_2)$, E, E' = P, As; E = P, E' = As) with diiodine under different conditions were examined with particular interest because of the well-known propensity of these ligands for stabilising Ni(III) and Ni(IV) complexes with bromide or chloride co-ligands ($q^V$). As the starting materials are only poorly soluble in CH$_2$Cl$_2$, saturated solutions in CH$_3$CN were treated with saturated solutions of diiodine in CH$_2$Cl$_2$ (I$_2$:Ni = 5:1) and the mixtures cooled to -20°C. Dark green, reflective needle crystals separated and these consistently had the composition $Ni(L-L)_2I_6$. However, crystallisation of a mixture of $Ni\{C_6H_4(PMe_2)\}_{2}I_2$ and $I_2$ from neat CH$_2$Cl$_2$ produced a very small number of black, triclinic crystals of composition $Ni(ligand)_{2}I_{10}$, the structure of which was determined (below) by X-ray crystallography as $[Ni\{C_6H_4(PMe_2)\}_{2}] (I_3)_2 (I_2)_2$.

Preliminary X-ray data on the hexaiodide showed it to be monoclinic, but when the presence of $I_3^-$ groups in the decaaiodide was established the full X-ray structure of the hexaiodide was not pursued, since it is likely to be $[Ni\{C_6H_4(PMe_2)\}_{2}I(I_3)_2]$. All chemical evidence obtained for these complexes indicates that oxidation to nickel(III) has not occurred. In
particular the magnetic moments in the solid state and in solution
(Table 4.31) are very low ($\mu_{\text{eff}} \leq 0.3$ BM) and probably attributable
to temperature-independent paramagnetism. Their diffuse reflectance
spectra show the characteristic bands due to $I_3^-$ at ca. 28,000
and 34,000 cm$^{-1}$. Other absorptions at lower energy are
difficult to assign, as one would expect the planar nickel(II)
cation absorptions and the singlet-triplet transitions of $I_3^-$
in this region. In acetonitrile solution, conductivities displayed
suggest 1:1 electrolytes, indicating the presence of five-
co-ordinate $[\text{Ni}(L-L)_2(I_3)]^+$, although dissociation to $[\text{Ni}(L-L)_2]^+$
+ $I_2$ cannot be excluded.

Attempts to obtain Raman spectra failed owing to
decomposition of the dark materials in the laser beam, but the
other physical and spectroscopic characteristics are very similar
to those displayed by $[\text{Ni}(L-L)_2X_2]^+(L-L = o-C_6H_4(\text{AsMe}_2)_2$,
$o-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2$, $o-C_6H_4(\text{PMe}_2)_2; X = \text{Cl, Br, I})$, where
$[\text{Ni}(L-L)_2X]^+$ ions are present in solution but the solids contain
essentially planar $\text{Ni}(L-L)_2^{2+}$ units, with weak axial association
of $X^-$ groups. Further, pure samples do not display the
characteristic e.s.r. signals given by $[\text{Ni}(L-L)_2X_2]^+$ (q.v.).
A few samples did give very weak e.s.r. signals at $g = 2.0 - 2.2$,
characteristic of Ni(III) centres, although the differences in
intensity between these signals, and those due to bulk samples
of Ni(III) complexes, indicated that a very small percentage of
nickel centres was involved. Subsequently it was established
that small quantities of bromine were present in the samples
and in the diiodine used in their preparation (positive
Fuchsin-bisulphite test). Samples prepared with diiodine
from a different source gave no signals. On heating in vacuo
these complexes lost some diiodine, but decomposed to black tars
concurrently.

The successful synthesis of $[\text{Ni}(o-C_6H_4(\text{PPh}_2)_2)_2]^+$
led to attempts at reaction with $I_2$. When $\text{Ni}(L-L)_2X_2$ ($L-L =$ ary1-substituted diphosphone ligand; $X = \text{Cl,Br}$) are treated with halogen, decomposition to 1:1 complexes occurs (q.v.), and the reaction of this complex with diiodine gave indeterminate products and was not pursued.

Structure of $\text{Ni}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}^+I_2$

Crystals suitable for X-ray examination were grown initially by mixing a saturated solution of $\text{Ni}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}^+I_2$ in CH$_3$CN (10 cm$^3$) with a five-fold molar excess of $I_2$ in CH$_2$Cl$_2$ (15 mL) and cooling to -20°C. The initial precipitate was not sufficiently crystalline, but after two weeks, some well-formed crystals were evident.

Preliminary photographic examination was performed, at room temperature using Weissenburg and oscillation techniques, by Dr. L. R. Gray. The crystal, in a 0.2 mm diameter Lindemann tube, was initially mounted along the needle axis and an oscillation photograph gave the real cell dimension $a = 11.36 \, \text{Å}$. A zero-level Weissenburg photograph gave the reciprocal cell dimensions $1/b^* = 11.52 \, \text{Å}$ and $1/c^* = 7.88 \, \text{Å}$, with $\alpha = 87.4 \, \text{Å}$. This allowed calculation of the real cell volume ($V \approx 1027 \, \text{Å}^3$). Since an oscillation photograph about $a$ had no mirror symmetry and a zero-level Weissenburg photograph about $a$ also exhibited no symmetry, it was likely that the crystal was triclinic, with space group $P\bar{1}$ or $P\bar{1}1$. No attempt was made to find the remaining cell dimensions.

Precise cell dimensions were obtained from the setting angles for 25 accurately-centred reflections on an Enraf-Nonius CAD-4 diffractometer. Difficulty was experienced in measuring the density of the crystals (by flotation in CH$_2$I$_2$/
BrCH₂CH₂Br) as the density appeared to vary from crystal to crystal. At this stage, analytical data on the bulk sample isolated from the same reaction mixture as the crystal, suggested the composition

$$\text{Ni(L-L)}_2\text{I}_6 \left(\text{C}_{20}\text{H}_{32}\text{NiP}_4\right)\text{(found: C = 19.7, H = 2.5%. Calc. for C}_{20}\text{H}_{32}\text{NiP}_4: C = 19.75, H = 2.65%)}. $$

Subsequently it became apparent that the crystal studied had the composition C₁₀₂₀H₃₂I₁₀NiP₄, and that this material was isolated exclusively when the reaction Ni(o-C₆H₄(PMe₃)₂)I₂ + I₂ was carried out in CH₂Cl₂ solution. These crystals had an observed density of 2.77 g cm⁻³ (flotation). Later, a crystal of composition Ni(L-L)₂I₆ grown from neat CH₃CN solution was found to be monoclinic.

Crystal Data

$$\left[\text{Ni(o-C₆H₄(PMe₃)₂)}\right]_2\text{I}_2\cdot\text{I}_2\cdot\text{I}_2 = \text{C}_{20}\text{H}_{32}\text{I}_{10}\text{NiP}_4. $$

M = 1724.1 Triclinic: a = 9.672(2), b = 12.369(2), c = 9.574(3)

$$\alpha = 106.55(2)^\circ, \beta = 107.70(2)^\circ, \gamma = 99.48(1)^\circ, U = 1005.6 \text{ Å}^3, Z = 1 \text{ (D flotation) = 2.77(3) g cm}^{-3}, D_{calc} = 2.846 \text{ g cm}^{-3} , $$

F(000) = 770, μ (Mo-Kα) = 82.3 cm⁻¹, λ (Mo-Kα) = 0.7107 Å, space group P₁ from the structure analysis.

Solution of the structure

Full data collection, employing an Enraf-Nonius CAD-4 diffractometer, took place on a crystal of dimensions 0.50 x 0.15 x 0.25 mm, sealed in a Lindemann capillary, at room temperature, 1.5 ≤ θ ≤ 25.0°. Monitoring of three check reflections (1, -1, 1; -2, -7, 4 and -4, -2, 16) on a time basis revealed no significant deterioration during data collection. Of 3680 reflections recorded, using graphite-monochromated Mo-Kα radiation, 3542 were unique. Of these, 628 had $F ≤ 4σ(F)$ and were treated as "less-thans" and discarded, leaving 2914 reflections that were used in the refinement. An empirical psi-scan absorption correction was applied to the data. Examination
of the distribution of 'E's' suggested the centrosymmetric space group (i.e. \( P\overline{1} \)) scaled (incorrectly) for \( \text{Ni}(L-L)_2I\).  

Attempts at solution using the computer programmes SHEXL\(^{38}\) and MULTAN\(^{39}\) both yielded a single, identical, solution with a high figure of merit, with linear \( I_3^- \) groups. When this was introduced into structure factor calculations a number of peaks (retrospectively, probably \( I_2 \) units) were revealed, but no fragment identifiable as \( \text{Ni(ligand)}_2^{2+} \) could be observed. The (incorrect) scaling of the \( F\)'s made a calculated I-I single weight vector too large, and the apparent number of such structures in the Patterson map forced attention to the space group \( P\overline{1} \). Inspection showed a number of vector triangles having in common one vector, length 2.8 \( \AA \) (I-I bonded distance). This cast doubts on the chemical formulation \( \text{Ni}(L-L)_2I_6 \) for the particular crystal on which the experiments were performed and it became clear that there were more than six I's per molecule. With nine iodine atoms included (\( R = 0.23 \)), a poor image of the \( \text{Ni(ligand)}_2 \) unit was finally observed in the electron density synthesis, and the location of all iodines, with Ni, P and C atoms, proceeded smoothly from that point, by structure factor and electron density calculations.

In the space group \( P\overline{1} \) the nickel atom must lie on a centre of symmetry. Transformation of the co-ordinates such that Ni was at \((0,0,0)\) showed the atoms of the structure conformed well, and thus refinement was continued in \( P\overline{1} \). Least squares refinement with all non-H atoms anisotropic gave \( R = 0.1058 \). An empirical weighting scheme of the type \( W = 1/(\sigma^2(F) + AF^2) \), where \( A \) was chosen to make \( \Sigma W \), approximately constant as a function of \( F \), was introduced (\( A = 0.0002 \)) at this point. A difference electron density synthesis yielded most of the hydrogen atoms and these were introduced in geometrically-calculated positions (\( d(C-H) = 1.08 \AA \)).
with separate (refined) isotropic temperature factors for the phenyl-H's and methyl-H's. Final least-squares refinement gave $R = 0.0320$ and $R_w = 0.0349$ and a difference electron-density map revealed no further significant features. The number of parameters was 174 and the ratio reflections-parameters was 16.7.

The final atomic co-ordinates are presented in Table 4.36. Atomic scattering factors for neutral atoms and anomalous dispersion terms were from SHELX (P,C,H) and published tables (I,Ni). All calculations were performed using an ICL 2970 computer with the programs SHELX, MULTAN, ORTEP, PLUTO, XANADU and various local programs.

Structure of Ni\{\text{-C}_6H_4(PMe}_2\}_2\text{-I}

The environment of the nickel atom is shown in Figure 4.33 and the molecular packing diagram in Figure 4.35. Figure 4.34 displays the arrangement of iodine atoms. Selected bond lengths and angles are in Table 4.37.

The structure determination revealed a square planar arrangement about nickel, composed of the four phosphorus atoms of the chelated diphosphine ligands. The NiP$_4$ unit is necessarily planar in P and the benzene rings are at 14.4° to the NiP$_4$ plane. This planar geometry is characteristic of d$^8$Ni(II), consistent with the chemical evidence. Ni(III) and Ni(IV) are usually octahedrally co-ordinated (q.v.). The Ni-P bond lengths (2.210(2) and 2.200(2) Å) are normal for Ni$^{II}$-P$_{trans}$ in planar complexes and can be compared with 2.206(7) Å in $trans$-[Ni(PMe$_3$)$_2$Cl(CH$_2$SiMe$_3$)]$^{44}$ and 2.200(2) Å in $trans$-[Ni(PMe$_3$)$_2$Cl(CO$_2$Me)]$^{45}$. Rather longer bond lengths are found in the isoelectronic $^{11}$Cu$^{III}$\{\text{-C}_6H_4(PMe}_2\}_2\text{-Cl}\text{(ClO}_4\}_2$ (2.263(2) Å average), and
Figure 4.33.
An ORTEP plot of the co-ordination environment about Ni in \([\text{NiC}_6\text{H}_4\text{(PMe}_2\text{)}_2\text{I}_2]_2\), showing the atom numbering scheme. (50% probability thermal ellipsoids). H-atoms excluded for clarity.
Figure 4.34. View of $[\text{Ni} \sigma-C_6H_4(\text{PMe}_2)_2]_2[I_3]_2 \cdot 2[I_2]$ showing Ni, P and I atoms only, indicating the iodine catenation arrangement, from approximately perpendicular to the 110 plane. Symmetry labels correspond with those in Table 4.37.
Figure 4.35. Packing diagram for [Ni(C6H4(PMe2)3)2][I3]2·2[I2] viewed from the c direction and excluding H atoms for clarity.
Table 4.36. Final atomic co-ordinates for \([\text{NiC}_6\text{H}_4(\text{PMe}_2)_2]^3_2\] \((I_3)_2, 2(I_2)\).
<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Bond Length/Angle (Å/deg)</th>
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</thead>
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<td>I(1)-I(2)</td>
<td>2.728(1) Ni-P(1) 2.210(2)</td>
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<tr>
<td>I(3)-I(4)</td>
<td>2.910(1) Ni-P(2) 2.200(2)</td>
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<tr>
<td>I(4)-I(5)</td>
<td>2.932(1)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.819(7) P(2)-C(3) 1.808(7)</td>
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<tr>
<td>P(1)-C(2)</td>
<td>1.816(7) P(2)-C(4) 1.801(7)</td>
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<td>P(1)-C(11)</td>
<td>1.818(7) P(2)-C(16) 1.859(7)</td>
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<tr>
<td>C(11)-C(12)</td>
<td>1.397(9) C(14)-C(15) 1.394(10)</td>
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<td>C(12)-C(13)</td>
<td>1.384(11) C(15)-C(16) 1.379(10)</td>
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<td>C(13)-C(14)</td>
<td>1.370(11) C(16)-C(11) 1.362(9)</td>
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<td>I(5)......I(1II)</td>
<td>3.576(1) P(1)....P(2) 3.02</td>
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<td>95.8(1)</td>
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<td>Ni-P(1)-C(11)</td>
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<td>C(1)-P(1)-C(2)</td>
<td>103.5(4) C(3)-P(2)-C(4) 103.8(4)</td>
</tr>
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<td>C(1)-P(1)-C(11)</td>
<td>105.2(3) C(3)-P(2)-C(16) 104.6(3)</td>
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<tr>
<td>C(2)-P(1)-C(11)</td>
<td>102.1(3) C(4)-P(2)-C(16) 102.9(4)</td>
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<tr>
<td>P(1)-C(11)-C(12)</td>
<td>123.0(5) P(2)-C(16)-C(15) 121.9(5)</td>
</tr>
<tr>
<td>P(1)-C(11)-C(16)</td>
<td>117.2(5) P(2)-C(16)-C(11) 116.6(5)</td>
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Internal ring angles in the range 118.9(7) to 121.5(6)

CONTINUED.....
continued....

\begin{verbatim}
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I(3)-I(4)-I(5)  178.8(1)  I(2^{II})-I(1^{II})...I(5^{IV})  164.7(1)
I(4)-I(5)...I(2^{II})  104.0(1)  I(1^{II})...I(5^{IV})-I(4^{IV})  82.6(1)
I(4)-I(5)...I(5^{III})  161.1(1)
\end{verbatim}

Torsion angle P(1)-C(11)-C(16)-P(2) is 1.5°

[Symmetry codes: I  -x,-y,-z
II  -x,-l+y,1-z
III  1-x,-l+y,1-z
IV  x,y,1+z ]
### Table 4.38 Ni II-I Bond Distances in Low Spin Complexes (Soft Donors)

<table>
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<th>Ni II-I (Å)</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Et₂PCH₂CH₂PEt₂)₂]I</td>
<td>2.797(3)</td>
<td>Square pyramid, axial Ni-I bond.</td>
<td>48</td>
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<tr>
<td>[Ni{PhP(o-C₆H₄SMe)₂}I₂]</td>
<td>2.567, 2.514</td>
<td>I-trans-P and I-trans-S resp. Square pyramid, 2xI's in equatorial positions</td>
<td>64</td>
</tr>
<tr>
<td>[Ni{P(OMe)₃}₃]I₂</td>
<td>2.657, 2.664</td>
<td>Trigonal bipyramidal, equatorial I's.</td>
<td>63</td>
</tr>
<tr>
<td>[Ni(Ph₂CH₂CH₂S(CH₂)₃SCH₂CH₂PPh₂)I]BPh₄</td>
<td>2.649</td>
<td>Square pyramid. Axial Ni-I bond.</td>
<td>62</td>
</tr>
<tr>
<td>[Ni(N(CH₂CH₂PPh₂)₃]I</td>
<td>2.71(1)</td>
<td>Trigonal bipyramidal, axial I</td>
<td>49</td>
</tr>
<tr>
<td>[Ni(Ph₂PCH₂CH₂OCH₂)₂I₂]</td>
<td>2.505(6), 2.485(6)</td>
<td>P₂I₂ donor set. Geometry intermediate between square planar and tetrahedral.</td>
<td>50</td>
</tr>
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</table>
[Co$^{III}$(C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]ClO$_4$(2.251 Å (av.)) but these are probably due to the higher co-ordination numbers of the metal centre. The internal dimensions of the ligand (Table 4.37) were unexceptional.

The closest approach of an iodine atom to the nickel, that of I(3), is 3.491(1) Å, which may indicate negligible bonding. Normally, Ni(II)-I bond lengths range from ca 2.4 - 2.8 Å, depending on the trans ligand and the co-ordination number of the metal (Table 4.38). Even the weakly associated iodides in [Ni$^{II}$C$_6$H$_4$(AsMe$_2$)$_2$I$_2$]$_3$ are at 3.215(2) Å. However, Stephenson estimated the nickel-iodine electrostatic interaction (i.e. non-bonded distance) to be ≈ 3.77 Å. If this is correct, a certain degree of interaction does occur, although it is very weak.

The nature of any interaction between the polyiodide units is of great interest, as structural data on complexes containing the higher polyiodides (i.e. I$_5^-$, I$_7^-$, I$_8^{2-}$ etc.) are rare. Here, the difficulty of distinguishing essentially bonding and non-bonding distances becomes apparent. A limiting value of 3.30 Å has been proposed by Coppens. On that basis the structure consists of approximately linear (178.8°), unsymmetrical I$_3^-$ groups (I(3)-I(4) = 2.910(1), I(4)-I(5) = 2.932(1) Å) lying at 21° to the NiP$_4$ plane, and diiodine molecules (I(1)-I(2) = 2.728(1) Å) whose bond length is very slightly longer (ca 7σ) than in solid diiodine (2.715(2) Å). The I$_2$ units link neighbouring I$_3^-$ units asymmetrically (Figure 4.34).

The alternative description of the polyiodide unit, as consisting of I$_5^-$ units, becomes possible if the intra-molecular I...I distinction is set at ca 3.5 Å. While I$_5^-$ has not been structurally identified in a metal complex previously, other than in "partially oxidised" species, it has been studied
with large organic cations. The antibiotic valinomycin, an ionophore, has been crystallised 'carrying' a potassium ion, the resulting cations being stabilised by an equal distribution of $I_3^-$ and $I_5^-$ ions\(^{52}\). In this structure (although interest was focused mainly on the cation) the $I_5^-$ unit was found to be linear and essentially isolated (Figure 4.39). In (trimesic acid\(^+\) $H_2O\)\(^{15a}\), it is again linear, but with some interaction with neighbouring ions. In $[NMMe_4]I_5$, the V-shaped ions also interact with neighbouring ions\(^{53}\). However, despite these differences all these $I_5^-$ ions may be described as consisting of $I_2^-I^-I_2$ units (see Figure 4.39).

In (phenacetin)\(_2H_{15}^{54}\), zig-zag chains are found which consist essentially of $I_3^-......I_2$ units (Figure 4.39). The distance between these units (3.549(3)Å\(^{54}\) is somewhat larger than that found in the present case (3.442(1) Å) suggesting a weaker interaction but otherwise there is considerable similarity. The network of "secondary" bonds is, however, different (compare Figures 4.34 and 4.39).

### 4.32 Other complexes

The treatment of $[Ni\{o-C_6H_4(AsMe_2)_2\}Cl_2]CIO_4$ (q.v.) in water with KI gave green-black Ni(ligand)$_2I_3$ as reported by Nyholm. This material was found to be diamagnetic both in the solid state (Gouy measurements) and in $CH_3CN$ solution (Evans n.m.r. method)\(^{32}\). Also, both as a solid and in solution, no e.s.r. signal could be resolved for the complex. This effectively rules out any nickel(III) formulation, and although the complex was poorly soluble, the electronic spectrum (Table 4.31) contains

* trimesic acid is 1,3,5-$C_6H_3(COOH)_3$, phenacetin is $CH_3CONHC_6H_4^-OCH_2CH_3-P$. 
Figure 4.39 (see overleaf)
Figure 4.39 Structurally characterised I₅ units.

(A) \([\text{K(Valinomycin)}]_{2}(I_{5}^{-})\)\(^{52}\)

(B) \((\text{Phenacetin})_{3}H_{5}I_{5} (I_{5} \text{ units only})\)\(^{54}\)

(C) \([\text{NMe}_{4}]I_{5}^{-}\)\(^{53}\)

In A, the \(I_{5}^{-}\) ions are linear and do not interact significantly with each other. In C, the V-shaped ions do interact weakly with each other (3.63 Å), but in A and C, the ions are both essentially \(I_{2}...I^{-}...I_{2}\). In B, the essentially separate \(I_{5}^{-}\) ions consist of \(I_{2}...I_{3}\) with a very weak interaction between these components (3.54 Å). (All distances in B are Å).
bands assignable to a nickel(II) planar environment and in particular, does not contain the band at ca 12,000 cm\(^{-1}\) which might be anticipated for a nickel(III) bis-(diarsine) complex (q.v.). The form of the polyiodide species present in this complex cannot be determined with the available spectral data, but the diffuse reflectance spectrum does not support the presence of I\(_3^−\), whilst qualitative spectra run in CH\(_2\)Cl\(_2\) solution are not incompatible with the superimposition of the spectra Ni(L-L)\(_2\)I\(_2^+\)I\(_2\) (Table 4.31).

\[\text{[Ni\((\sigma-C_6H_4(PMe_2)(AsMe_2))_2\text{Cl}_2\)]ClO}_4\] was also treated with an aqueous solution of KI. The product, Ni(ligand)\(_2\)I\(_3\), appeared more insoluble than the diarsine complex, but spectral, analytical and magnetic moment data obtained (Table 4.31) suggest similarity with Ni\((\sigma-C_6H_4(AsMe_2)_2\)\(_2\)I\(_3\).

Reaction of the corresponding Ni(IV) complexes with aqueous KI might be expected to yield a different product, with the greater number of oxidation equivalents available, but Nyholm\(^{33}\) proposed that the same material was produced, although as both the starting material and product are very sparingly soluble in water he could not obtain a pure sample.

Treatment of a trifluoroacetic acid solution of \[\text{[Ni\((\sigma-C_6H_4(AsMe_2)_2\)\text{Cl}_2\)]ClO}_4\] with aqueous KI did give a sample of Ni(ligand)\(_2\)I\(_3\), which was in all respects identical to that obtained from the nickel(III) complex.

Preliminary attempts to grow crystals of these materials by slow addition of aqueous KI to a solution of \[\text{[Ni\((\sigma-C_6H_4(AsMe_2)_2\)\text{Cl}_2\)]^+}\] failed. When dilute solutions of the reactants were employed, so that immediate precipitation did not occur, \[\text{[Ni(diarsine)\(_2\)I\(_2\]}\], identified by analysis and spectral comparison with a genuine sample, eventually crystallised.
The nickel(0) complex [Ni(o-C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2}]\textsubscript{2}(CO)]\textsubscript{2}, when treated with diiodine in dry CH\textsubscript{2}Cl\textsubscript{2} under anaerobic conditions (Schlenk techniques) gave black Ni(ligand)\textsubscript{4}. This was somewhat moisture sensitive and in polar solvents (MeOH, acetone) dissolved with concurrent rearrangement to Ni(ligand)\textsubscript{2}I\textsubscript{2}. Its electronic spectrum (diffuse reflectance) suggests that nickel(II), not nickel(IV), is present. The rearrangement in solution is typical of other 1:1 nickel(II) complexes of this ligand.

When [Ni(o-C\textsubscript{6}H\textsubscript{4}(AsPh\textsubscript{2})\textsubscript{2}]\textsubscript{2} was treated with diiodine, a black powder of composition Ni(ligand)\textsubscript{4} were isolated. This has similar spectral and magnetic properties to Ni(o-C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2})I\textsubscript{4} and probably has a similar structure. Both complexes are very likely, in view of the similar \(d^8\) metal centre, and 'soft' donor ligands, to consist of planar Ni(L-L)I\textsubscript{2} units linked by diiodine I...I...I, as found in [Pd(cis-Ph\textsubscript{2}PCH:CHPPh\textsubscript{2})I\textsubscript{4}]\textsuperscript{26} and [Pd{o-C\textsubscript{6}H\textsubscript{4}(SPh)\textsubscript{2}]I\textsubscript{4}]\textsuperscript{27}. (Figure 4.22 shows the mode of I-I\textsubscript{2} interaction).

The complexes Ni(L-L)I\textsubscript{2} (L-L = Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}, Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}, cis-Ph\textsubscript{2}AsCH:CHAsPh\textsubscript{2}, o-C\textsubscript{6}H\textsubscript{4}(PPh\textsubscript{2})\textsubscript{2}) and Ni(PEt\textsubscript{3})I\textsubscript{2} were also treated with diiodine under standard conditions in CH\textsubscript{2}Cl\textsubscript{2} (1:5 Ni:I\textsubscript{2}, -20°C). Only the black, diamagnetic Ni(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})I\textsubscript{6} was isolated. The complex [Ni(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})I\textsubscript{2}] gave a brown product of indeterminate composition. [Ni(Ph\textsubscript{2}AsCH\textsubscript{2}CH\textsubscript{2}AsPh\textsubscript{2})I\textsubscript{2}] decomposed, presumably to organo-arsenic (V) derivatives and NI\textsubscript{2}. The other complexes were recovered unchanged, although in most cases, colour changes indicative of polyiodide formation in solution were observed.

The material Ni(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})I\textsubscript{6} loses diiodine rapidly at room temperature, and in one preparation a material of
approximate composition Ni(Ph₂PCH₂CH₂PPh₂)I₄ was isolated. However, this could not be obtained pure. In common with [Ni(o-C₆H₄(AsPh₂)₂)I₄], heating Ni(Ph₂PCH₂CH₂PPh₂)I₆ in vacuo caused clean reversion to the diiodide.

A particularly poor diffuse reflectance spectrum was obtained for [Ni(Ph₂PCH₂CH₂PPh₂)I₆] which turned sticky upon grinding in dry BaSO₄. The broad bands at ca 28,700 and 35,000 cm⁻¹ (Table 4.31) lend support to the formulation [Ni(ligand)(I₃)₂].

Another ligand capable of stabilising nickel(III) and nickel(IV) is Me₂PCH₂CH₂PMe₂ (q.v.). Additional interest in this ligand was lent by the report by Chatt of [Ni(Me₂PCH₂CH₂PMe₂)₂I₂]Cl. However, on duplication of the reaction (refluxing Ni(Me₂PCH₂CH₂PMe₂)₂I₂ with aqueous/ethanolic HCl in air) a brown solid was deposited. Although this had reasonable C and H analyses for "Ni(L-L)₂I₃" as reported by Chatt, it also had an intense band at 1120 cm⁻¹ in the i.r. spectrum, attributable to the presence of a phosphine oxide. On prolonged reflux in excess aqueous/ethanolic HCl the material was completely decomposed and yellow crystals of Me₂P(O)CH₂CH₂P(O)Me₂ were recovered on concentration.

The reaction of [Ni(Me₂PCH₂CH₂PMe₂)I₂] with diiodine in CH₂Cl₂ under the standard conditions gave a small number of unstable black diamagnetic crystals of approximate composition "Ni(ligand)I₃" (Found : C = 16.8, H = 3.8, I = 74.8%. Calc. for C₆H₁₆I₃NiP₂ : C = 17.1, H = 3.82, I = 75.3%).

The complexes [Ni(Me₂SbCH₂CH₂SbMe₂)₂X]ClO₄ were instantly decomposed in solution or as suspensions in CCl₄ by X₂ (X = Cl, Br) (q.v.). The di-iodide analogue [Ni(Me₂Sb(CH₂)₃SbMe₂)₂]I, when treated with diiodine in CH₂Cl₂,
also decomposed, rather more slowly, to give organoantimony (V) residues ('H n.m.r.; \( \delta = 2.2 \) (s,Me) probably Me\(_2\)Sb(I\(_2\))(CH\(_2\))\(_3\) Sb(I\(_2\))Me\(_2\)) and nickel(II) iodide. No apparent formation of a polyiodide occurred.

4.4 Conclusions

No evidence for the formation of nickel(III) iodo-complexes has been obtained with neutral ligands in contrast with previous claims in the literature\(^{12,13}\). Since the lowest measured oxidation potential for the Ni(II)-Ni(III) couple with group Vb ligands was found to be 0.69V (for Ni(Me\(_2\)PCH\(_2\)CH\(_2\)PMe\(_2\))\(_2\)Cl\(_2\) in CH\(_3\)CN at 25°C, vs. S.H.E. with Et\(_4\)NCl as supporting electrolyte)\(^{57}\) and the potential of the couple I\(_2^-\)I\(^-\) in 0.55\(^{58}\)V, this is not surprising.

The reaction of Ni(II) iodo-complexes with diiodine invariably gives polyiodides except (as in the case of Me\(_2\)SbCH\(_2\)CH\(_2\)CH\(_2\) SbMe\(_2\)) where the ligand becomes oxidised, whilst treatment of a pre-formed nickel(III) or nickel(IV) complex with KI in water leads to reduction. Attempts at analogous reactions in anhydrous conditions, for example treatment of [Ni\(_{12}\)C\(_6\)H\(_4\)(PMe\(_2\))(AsMe\(_2\))\(_2\)Cl\(_2\)]\(_2\) in CH\(_3\)CN with (C\(_6\)H\(_5\))\(_4\)NI, also led to polyiodide formation, although less well-defined products resulted than in aqueous solution.

Using the available data from the X-ray crystallographic studies on [Ni\(_{12}\)C\(_6\)H\(_4\)(PMe\(_2\))\(_2\)]\(_2\)(I\(_3\))\(_2\).2(I\(_2\)) and the Pd(II) complexes of soft donor ligands\(^{26,27}\), some tentative remarks may be made about the nature of the polyiodide interactions in these similar (d\(_8\) planar 'soft' donor ligands) environments. In the nickel complex, the bond between I\(_3^-\) and I\(_2\) units is so long (3.442 Å), and the I-I bond in the I\(_2\) unit so little lengthened, that it is not very meaningful to describe the unit as "I\(_5^-\)."
In both the Pd(II) polyiodides also, the interaction between I\textsuperscript{2-}
co-ordinated to Pd(II) and linking I\textsubscript{2} units, is very weak, as already noted, so that description of the anions as "I\textsubscript{4}\textsuperscript{2-}" is again hardly justified when these units are compared with other I\textsubscript{4}\textsuperscript{2-} ions found in the literature \textsuperscript{19}. The weakness of these bonds, in the only materials capable of giving crystals stable enough for data collection could explain why the other Ni(II) complexes were recovered unchanged on treatment with I\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}. Only the M(ligand)\textsubscript{2}I\textsubscript{6} complexes (ligand = \textsuperscript{o}C\textsubscript{6}H\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}, \textsuperscript{\textomega}C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2}, \textsuperscript{o}C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})(PMe\textsubscript{2}) (PMe\textsubscript{2}); M = Pd, Ni) were indefinitely stable. All the other complexes decomposed at varying rates.

Whilst in the case of the dithio- and diselenahexane complexes this could reasonably be attributed to hydrolysis, rather than I\textsubscript{2} loss, in all other cases, diiodine was slowly evolved by the complexes on standing. Two conclusions may tentatively be drawn from these observations, viz:

(a) I\textsubscript{3}\textsuperscript{-} ions form where the metal is at least notionally six co-ordinate, whether the I\textsuperscript{-} ion was originally co-ordinated (as in Ni(MeECH\textsubscript{2}CH\textsubscript{2}EMe\textsubscript{2})\textsubscript{2}I\textsubscript{2}; E = S,Se) or only weakly associated (as in [Ni(\textsuperscript{o}C\textsubscript{6}H\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2})\textsubscript{2}](I\textsubscript{3})\textsubscript{2}.2I\textsubscript{2}.

(b) Where the metal is four co-ordinate, M(ligand)I\textsubscript{4} usually forms (Ni(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})I\textsubscript{6} is very unstable) and in view of the two Pd(II) X-ray structures \textsuperscript{26,27} it is tempting to suggest that all these complexes have a similar structure with I\textsubscript{2} units bridging the co-ordinated iodide ions.
References


(b) P. Coppens. Ibid., 1 333.


58. Chemical Rubber Company Handbook of Chemistry and Physics (47th Edn.).


CHAPTER 5

SOME COMPLEXES OF NICKEL(IV) WITH NEUTRAL LIGANDS
5.1 Introduction

The increase in stability of high oxidation states on progressing from the 3d to the 4d and 5d metals is well illustrated by M(IV) \((M = \text{Ni}, \text{Pd, Pt})\). While Pd(IV)\(^1\) and Pt(IV)\(^2\) complexes of neutral Group Vb donor ligands have recently been studied extensively, the only Ni(IV) complexes of such ligands yet prepared are Ni\([\sigma-C_6H_4(\text{AsMe}_2)\_2]_2 X_2\)\([\text{ClO}_4]_2\) \((X = \text{Cl, Br})\) made by Nyholm\(^4\) (Chapter 2, page 82) and \([\text{Ni}[\sigma-C_6H_4(\text{PMe}_2)\_2]_2\text{Cl}_2][\text{ClO}_4]_2\) made more recently by Warren and Bennett\(^3\). No systematic attempt to examine the effects of varying the donor atom or the ligand backbone upon these chelate complexes had been made. Very little spectroscopic data has been published for those complexes which have been synthesised, and, probably due to their highly oxidising nature, no structural data has been obtained.

Results (5.2)

The syntheses of the Ni(IV) complexes \([\text{Ni}(L-L)_2 X_2]^{2+}\) \((L-L = \sigma-C_6H_4(\text{AsMe}_2)\_2, \sigma-C_6H_4(\text{PMe}_2)\_2, X = \text{Cl, Br})\) had been achieved by concentrated nitric acid oxidation of Ni(II) or Ni(III) precursor complexes in the presence of a few drops of concentrated hydrohalic acids\(^3,4\), and also by chlorination of finely-divided \([\text{Ni}(L-L)_2][\text{ClO}_4]_2\), suspended in \(\text{CCl}_4\)\(^3\).

During this study it was found that the successful preparation of analytically pure samples of the Ni(IV) complexes was critically dependent on the method of isolation used. For example, preliminary attempts to prepare \([\text{Ni}[\sigma-C_6H_4(\text{AsMe}_2)\_2]\text{Cl}_2][\text{ClO}_4]_2\) by the published method (which involves the dilution of a conc. \(\text{HNO}_3/\text{conc. HClO}_4\) solution of the Ni(IV) complex with water to precipitate the product)\(^4\) gave products contaminated with nitrogen (C, H and N analyses; weak \(\nu_{\text{NO}}\) in the infra red spectra) and Ni(III) (e.s.r. spectral evidence). It was found that the purest products were
obtained by the oxidation (CHNO₃/CHX 10:1) of a suspension of 
[Ni(L-L)₂][ClO₄]₂ in a small volume of oxidant, at -20°C.
Where the Ni(IV) complexes were particularly soluble in the 
acid mixture (L-L = diphosphine ligands; see Table 5.1) precipitation 
of the product with 70% HClO₄ at ca 0°C also yielded satisfactory 
materials. For L-L = Me₂PCH₂CH₂PMe₂, the Ni(IV) complex could not 
be precipitated by HClO₄ (70%), or by HPF₆ (60%) or HBF₄ (42%). It 
was eventually prepared, as an extremely hygroscopic and oxidising 
purple-pink solid, by Cl₂/CCl₄ oxidation of [Ni(Me₂PCH₂CH₂PMe₂)₂] 
[BF₄]₂ in a Schlenk apparatus. Bromine, however, was not a strong 
enough oxidant to allow the corresponding bromide to be made in 
this way. All the complexes, once isolated, were stored at -20°C 
under dry nitrogen, in which condition they were stable for a few 
days. Measurements were made on freshly-prepared samples, 
and Nujol mulls (infra red) and BaSO₄ mulls (diffuse reflectance) 
were prepared in an efficient (< 10 p.p.m. H₂O) glove box.

Other variations attempted during the preparations 
of the complexes involved the inert anion employed. As high 
oxidation state metal perchlorates are potentially explosive, 
efforts were made to isolate the Ni(IV) materials by precipitation 
with HPF₆ and HBF₄, as the most concentrated aqueous solutions 
available. Commercial HPF₆ was found to give more insoluble salts 
than HClO₄, but these were impure, probably because the commercial 
acid itself contains a large proportion of impurities. Unfortunately, 
HBF₄ gave unsatisfactory products, containing much Ni(III) (e.s.r. 
evidence), probably as a result of the aqueous solution being more 
dilute than HClO₄. The acid CF₃SO₃H was also tried, but the 
Ni(IV)-CF₃SO₃⁻ salts were not precipitated.

* CARE! Explosion hazard. No explosions were experienced in 
this work, but high oxidation state metal perchlorates are often 
dangerous.
Complexes obtained in an analytically satisfactory state, their analyses and physical data, are included in Table 5.1.

Properties of the Complexes (5.3)

To enable attempts to obtain solution data, a wide variety of solvents were assessed for the Ni(IV) complexes. The complexes were either insoluble in, or were reduced by, all organic solvents tried (viz. purified and dried CH₂Cl₂, C₆H₄Cl₂; insoluble. CH₃CN, C₆H₅NO₂, CH₃NO₂, C₂H₅OH, CH₃COOH, propylene carbonate; complex decomposed on dissolution, usually to Ni(III)). They did, however, dissolve in concentrated HCl (with decomposition) and trifluoroacetic acid. Decomposition was slowest in the latter solvent.

Freshly prepared samples of [Ni(L-L)₂X₂][ClO₄]₂ (L-L = o-C₆H₄(PMe₂)₂, o-C₆F₄(PMe₂)₂, o-C₆H₄(AsMe₂)(PMe₂)) were diamagnetic (μₑffective < 0.6 B.M., Gouy Method) and exhibited no resolvable e.s.r. signals. (The latter is particularly significant since the corresponding Ni(III) cations required only low microwave power and receiver gain settings for spectra to be observed when polycrystalline powders were used). However, while the complexes of o-C₆H₄(AsMe₂)₂ were also diamagnetic as measured by the Gouy method, weak e.s.r. spectra were resolved. Interestingly, these spectra differed from those obtained using bulk Ni(III) samples. For the Ni(IV) material, the Ni(III) impurity gave an axial (2g-value) spectrum (g₁ = 2.133, linewidth derivative peak-to-peak 37G; g₂ = 2.016). The bulk Ni(III) material gives a rhombic (3 g-value) spectrum (see Chapter 3.3, page 161). This behaviour has been observed before for the Ni(III) complex diluted into a Co(III) host lattice, where the rhombic spectrum is observed for concentrations of > 10% Ni(III) and the axial (g₁ = 2.14, g₂ = 2.08) spectrum is observed for ca 5% Ni(III). It is thought
TABLE 5.1  ANALYTICAL  DATA

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<th>Complex</th>
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<th>C&lt;sup&gt;a&lt;/sup&gt; (a)</th>
<th>H&lt;sup&gt;b&lt;/sup&gt;</th>
<th>X%</th>
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<td>27.3(27.7)</td>
<td>2.8(3.0)</td>
<td>7.9(8.2)</td>
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</tr>
<tr>
<td>[Ni&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>dk green</td>
<td>50.0(29.6)</td>
<td>4.2(4.0)</td>
<td>8.5(8.7)</td>
</tr>
<tr>
<td>[Ni&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>dk green</td>
<td>26.2(26.6)</td>
<td>3.7(3.6)</td>
<td>—</td>
</tr>
<tr>
<td>[Ni&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>dk blue</td>
<td>26.9(26.7)</td>
<td>3.6(3.6)</td>
<td>—</td>
</tr>
<tr>
<td>[Ni&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>green</td>
<td>23.8(24.3)</td>
<td>3.0(3.2)</td>
<td>—</td>
</tr>
<tr>
<td>[Ni&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(BF&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>violet</td>
<td>22.0(23.9)</td>
<td>5.5(5.3)</td>
<td>—</td>
</tr>
<tr>
<td>[Pd&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(ClO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>deep yellow</td>
<td>26.4(26.2)</td>
<td>2.7(2.6)</td>
<td>7.6(7.8)</td>
</tr>
<tr>
<td>[Co&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>light violet</td>
<td>34.5(34.1)</td>
<td>3.4(3.4)</td>
<td>—</td>
</tr>
<tr>
<td>[Co&lt;sup&gt;2+&lt;/sup&gt; - C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>light violet</td>
<td>35.7(35.8)</td>
<td>1.8(1.8)</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Calculated value in parenthesis.  (b) Compound is highly unstable and the analysis reflects this.
to be due to deviation from ideal $D_{4h}$ symmetry in the crystal structure of the bulk Ni(III) complex, which does not occur at suitable dilution in a diamagnetic host. After a few days storage, all the Ni(IV) complexes gradually develop the rhombic spectra of the corresponding Ni(III) complexes, as the sample is progressively reduced to Ni(III).

Work on the nickel complexes of the 1,2-dithiolenes, $[\text{Ni}(S_2C_2R_2)_2]$, which are probably best described as Ni(II) complexes of ligand radical anions $S_2C_2R_2^-$, based on X-ray crystallographic studies (see Chapter 2, page 46), has led to the suggestion that $[\text{Ni}^{2+}_\text{II}-C_6H_4\text{AsMe}_2\text{X}_2]$ is effectively a Ni(II) complex of $\sigma-C_6H_4\text{AsMe}_2\text{X}_2$. Although there is also evidence in the literature that this is not the case*, and during this study electronic spectroscopy lent further weight to the plausibility of the $d^6$ configuration (q.v.), attempts were made to grow crystals suitable for an X-ray study, to probe the change in metal-ligand (especially metal-halogen) bond lengths during the progression Ni(II) $\rightarrow$ Ni(III) $\rightarrow$ Ni(IV).

As the complexes decomposed in organic solvents it was necessary to adapt the synthetic method so that crystallisation on addition of conc. HClO$_4$ to the conc.$\text{HNO}_3$ solution proceeded more slowly. Unfortunately, from many attempts, rarely were suitably large crystals obtained, and preliminary X-ray examination showed that these were of poor crystallinity. The reproducibility of these crystal-growing attempts was poor, unlike the previous method used to grow crystals of (e.g.): $[\text{Ni}(\text{cis-Ph}_2\text{PCHCHPPh}_2)\text{Br}_3]$. $C_7H_8$ (Chapter 3.2, page 146), so that further refinement of partially-

* Far infra-red spectroscopy shows that $\nu_{\text{Ni-X}}$ increases greatly with the progression Ni(III) $\rightarrow$ Ni(IV) for $[\text{Ni}^{2+}_\text{II}-C_6H_4\text{AsMe}_2\text{X}_2]$ $\rightarrow$ Ni(IV), while $\nu_{\text{Ni-As}}$ is not greatly changed, consistent with the progression $d^7$ $\rightarrow$ $d^6$, see Chapter 2.
successful attempts failed.

In a typical attempt to obtain crystals, \([\text{Ni}\left(\text{C}_6\text{F}_4\text{PMe}_2\right)_2\text{Cl}_2] (0.25\text{g})\) was dissolved in conc. \(\text{HNO}_3\) (5 ml) and conc. \(\text{HCl}\) (2 drops) at -20°C (CCl\(_4\) slush bath). Conc. \(\text{HClO}_4\) (5 drops) was added with stirring. The solution was rapidly filtered through a fine-porosity glass frit and stored at -20°C for 24 hours, during which time needle-shaped crystals developed. These were examined under the microscope. They were light purple in colour and appeared to extinguish, but were very small, and preliminary Weissenburg photography gave disappointing results, (very diffuse spots). Work is currently under way on adapting the EXAFS technique to this problem (see Discussion, page 247).

**Spectroscopic Results (5.4)**

Careful comparison of the far i.r. spectra of corresponding chloro- and bromo- complexes, and of the \(\text{Ni(III)}\) analogues, reveal the presence of single, medium-intensity bands at ca 420 cm\(^{-1}\) (X = Cl) and ca 310 cm\(^{-1}\) (X = Br) (Table 5.2) assignable as \(v_{\text{Ni-X}}\) (Blu) consistent with a \(\text{trans-D}_{2h}\) structure for the cations. This is comparable to values obtained for \([\text{Ni}\left(\text{C}_6\text{H}_4\text{AsMe}_2\right)_2\text{X}_2]\text{ClO}_4\) by the metal-isotope substitution technique. The large increase in \(v_{\text{Ni-X}}\) on oxidation from \(\text{Ni(III)}\) to \(\text{Ni(IV)}\) is also consistent with removal of a \(\sigma\)-antibonding e.g. electron \(t^6_{2g}e^1\text{Ni(III)} \rightarrow t^6_{2g}e^0\text{Ni(IV)}\) and provides a strong argument for a metal-centred oxidation (Table 5.2).

Electronic spectra were recorded by diffuse reflectance (BaSO\(_4\) as diluent and reference) and on CF\(_3\)COOH solutions (Table 5.3). Even in the latter, decomposition is rapid; often two processes occur. One is reduction to \(\text{Ni(III)}\) (electronic spectral evidence) but the other, which occurred only for the diphosphine ligands, involves reprecipitation of the
Table 5.2. A Comparison of $\nu_{M-X}$ for $d^6$ and $d^7$ complexes $[M(L)_2X_2]^{n+}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$d^7\nu_{M-X}$ (n=1) cm$^{-1}$</th>
<th>$d^7\nu_{M-X}$ (n=2) cm$^{-1}$</th>
<th>M-X Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(PMe_2)}_2Cl_2]^+$</td>
<td>263</td>
<td>425</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(PMe_2)}_2Br_2]^+$</td>
<td>180</td>
<td>306</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6F_4(PMe_2)}_2Cl_2]^+$</td>
<td>235</td>
<td>425</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6F_4(PMe_2)}_2Br_2]^+$</td>
<td>183</td>
<td>315</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(PMe_2)(AsMe_2)}_2Cl_2]^+$</td>
<td>248</td>
<td>416</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(PMe_2)(AsMe_2)}_2Br_2]^+$</td>
<td>189</td>
<td>306</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(AsMe_2)}_2Cl_2]^+$</td>
<td>260</td>
<td>408</td>
<td>2.425(3)(c)</td>
<td>26</td>
</tr>
<tr>
<td>$[\text{Ni}{\sigma-C_6H_4(AsMe_2)}_2Br_2]^+$</td>
<td>193</td>
<td>311</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Me}_2PCH_2CH_2PMe}_2}_2Cl_2]^{n+}$</td>
<td>248</td>
<td>b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd}{\sigma-C_6F_4(PMe_2)}_2Cl_2][\text{ClO}_4]_2$</td>
<td>-</td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd}{\sigma-C_6H_4(PMe_2)}_2Cl_2][\text{ClO}_4]_2$</td>
<td>-</td>
<td>b</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>$d^7\nu_{M-X}$ (n=0) cm$^{-1}$</th>
<th>$d^7\nu_{M-X}$ (n=1) cm$^{-1}$</th>
<th>M-X Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co}{\sigma-C_6H_4(PMe_2)}_2Cl_2]^+$</td>
<td>(a)</td>
<td>399</td>
<td>2.253(1)(c)</td>
<td>3</td>
</tr>
<tr>
<td>$[\text{Co}{\sigma-C_6H_4(AsMe_2)}_2Cl_2]^+$</td>
<td>(a)</td>
<td>386</td>
<td>2.256(3)(c)</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{Co}{\sigma-C_6F_4(PMe_2)}_2Cl_2]^+$</td>
<td>(a)</td>
<td>398</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Notes: (a) There is some dispute as to whether the Co(II) complexes are four-, five- or six-co-ordinate. No $\nu_{\text{Co-Cl}}$ is detected down to 200 cm$^{-1}$.
(b) Could not be positively identified; obscured by ligand modes.
(c) The bond shortening in $d^6$ complexes compared with $d^7$ complexes is notable.
## Electronic Spectra of d^6 complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( E_{\text{max}}(10^3 \text{ cm}^{-1})^a )</th>
<th>( E_{\text{max}} 10^3 \text{ cm}^{-1}(\text{emol dm}^3 \text{ cm}^{-1}\text{Mol}^{-1})^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Br}_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>16.8sh, 17.8, 23.2, 25.2, 26.2</td>
<td>18.25(500), 27.78(14700)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Br}_2\text{CIO}_4]^2_2)</td>
<td>14.6sh, 16.85, 23.15, 26.45</td>
<td>17.18(1470), 27.03(11600)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>16.9sh, 18.0, 24.6, 26.7</td>
<td>18.59(-)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{CIO}_4]^2_2)</td>
<td>16.7, 24.5</td>
<td>17.24(-)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2)_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>15.9sh, 17.5(br), 24.9</td>
<td>17.12(970)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2)_2\text{Br}_2\text{CIO}_4]^2_2)</td>
<td>16.3, 24.6, 29.9</td>
<td>16.45(1550)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{AsMe}_2)_2\text{CIO}_4]^2_2)</td>
<td>15.7sh, 16.5, 24.4, 26.6</td>
<td>16.90(2850), 26.88(13700)</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{C}_6\text{H}_4(\text{AsMe}_2)_2\text{Br}_2\text{CIO}_4]^2_2)</td>
<td>16.2, 24.2, 26.2</td>
<td>decomposes</td>
</tr>
<tr>
<td>([\text{Ni}^{II} - \text{PCH}_2\text{CH}_2\text{PMe}_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>16.9sh, 17.6, 24.5(b)</td>
<td>decomposes</td>
</tr>
<tr>
<td>([\text{Pd}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>22.8sh, 24.3</td>
<td>24.51(~ 1800)</td>
</tr>
<tr>
<td>([\text{Co}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2\text{CIO}_4]^2_2)</td>
<td>-</td>
<td>17.86(102), 27.17(5240)(c)</td>
</tr>
<tr>
<td>([\text{Co}^{II} - \text{C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2\text{PF}_6]^2_2)</td>
<td>-</td>
<td>17.79(63), 26.88(5550)(c)</td>
</tr>
</tbody>
</table>

(a) diffuse reflectance.  
(b) CF_3CO_2H solution, emol values approximate.  
(c) MeCN solution.
Ni(IV) complex (presumably as the CF$_3$COO$^-$ salt).

The spectra both solid and solution, consist of one moderate intensity band at ca 16-19 × $10^3$ cm$^{-1}$ and more intense bands at > 25 × $10^3$ cm$^{-1}$. In $D_{4h}$ symmetry the first band can be assigned to the first spin-allowed transition of a $d^6$ ion, namely $^1A_1 ightarrow ^1E$, and the remainder to $^1T_2$ charge transfer. The d-d transition shifts to higher energy Br<Cl, and

$$\sigma-C_6H_4(AsMe_2)_2 < \sigma-C_6H_4(PMe_2)(AsMe_2)_2 < \sigma-C_6H_4(PMe_2)_2$$

$$< \sigma-C_6F_4(PMe_2)_2.$$  However it is not possible simply to draw conclusions about the spectrochemical ordering of the ligands on this data, since in ligand-field theory, this transition corresponds to $10Dq-C^-$, involving the Racah parameter C, and the tetragonal parameter $D_t$ in addition to $D_q$. Since it is evident that the higher-energy d-d bands are obscured by the charge transfer transitions, any analysis of the relative importance of these terms is precluded, although the ordering of the energies fits that expected on comparison with the similar $d^6$ ion, Co(III), where the same ordering occurs, including the highest position for $\sigma-C_6F_4(PMe_2)_2$ in the series. The relative magnitudes of 10Dq, C and $D_t$ for Co(III) should be comparable to Ni(IV). The position of $\sigma-C_6F_4(PMe_2)_2$ is anomalous since from the electrochemical results and observation of the shelf-life of its Ni(IV) complex it is clearly not the best $\sigma$-donor ligand. Presumably, the decrease in 10Dq expected as a result of the electron-withdrawing perfluoroaryl ligand backbone is more than offset by a similar reduction in C caused by the interaction of the phosphorus with the F $\pi$-orbitals.

As electronic spectral data on the complexes $\text{trans-}[\text{Co}(L-L)_2X_2]^+(L-L = \sigma-C_6H_4(AsMe_2)_2, \sigma-C_6H_4(PMe_2)(AsMe_2), \sigma-C_6F_4(PMe_2)_2)$ was scarce, these complexes were prepared by adaptations of literature methods for $\text{trans-}[\text{Co}(\sigma-C_6H_4(AsMe_2)_2)_2Cl_2]Cl$. 

and their electronic spectra were recorded in CH₃CN solution. In profile, they are similar to the Ni(IV) spectra - consistent again with the d⁶ configuration for the Ni(IV) complexes. In Table 5.3, data obtained for the Ni(IV) complexes is compared with that for the isoelectronic Co(III), Pd(IV) and Pt(IV) complexes.

Cyclic voltammetry proved most useful in the study of the Ni(IV) complexes. Whereas difficulty had previously been experienced in obtaining cyclic voltammograms for the Pt(II)-Pt(IV) and Pd(II)-Pd(IV) oxidations, the Ni(III)-Ni(IV) waves were usually readily obtained and electrochemically reversible judging from the parameters usually used to assess this (Chapter 7, page 293). The reason for this difference is that in order to observe the Pt(II) or Pd(II) 2-electron oxidations, a large excess of chloride ions was necessary to drive the equilibrium

\[
[M^{II}(L-L)_2]^{2+} \rightleftharpoons [M^{II}(L-L)_2Cl]^+ \rightleftharpoons [M^{II}(L-L)_2Cl_2]^{10}
\]

to the right, and the metal oxidation occurred as a shoulder on the Cl⁻→½Cl₂ oxidation wave. However the Ni(III) - Ni(IV) system had the advantage that the co-ordination number was constant, so that Bu₄NBF₄ could be used as support electrolyte. The conditions used, and results obtained, for the electrochemical experiments are given in Table 5.4. It can be seen that the small differences in redox potentials observed with changes in the ligand for the process Ni(II)→Ni(III)⁺e become more marked for the process Ni(III)→Ni(IV)⁺e. In particular, while the difference in redox potential for the Ni(II)→Ni(III)⁺e process between the complexes of o-C₆H₄(PMe₂)₂ and o-C₆F₄(PMe₂)₂ is 0.12V, (Chapter 3.3, page 176), that for the process Ni(III)→Ni(IV)⁺e is 0.22V. (Table 5.4). Also of significance is that the effect of the perfluoroaryl backbone in the above case is somewhat
### TABLE 5.4 ELECTROCHEMICAL DATA

<table>
<thead>
<tr>
<th>Starting Complex</th>
<th>Ip(\text{av})Ni^{II}/Ni^{IV}(a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2]\text{Cl}_2)</td>
<td>-</td>
<td>e</td>
</tr>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2]\text{Cl}_2)</td>
<td>1.18</td>
<td>e, g</td>
</tr>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2]\text{Cl}_2)</td>
<td>1.26</td>
<td>f</td>
</tr>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2]\text{Cl}_2)</td>
<td>1.40</td>
<td>e, g</td>
</tr>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2]\text{Cl}_2)</td>
<td>1.30</td>
<td>f</td>
</tr>
<tr>
<td>([\text{Ni}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2]\text{Br}_2)</td>
<td>1.23</td>
<td>f</td>
</tr>
</tbody>
</table>

(a) Volts \(\pm 0.01\).  
(b) 0.1M Et\(_4\)NCl in CH\(_2\)CN as supporting electrolyte.
(c) 0.1M Bu\(_4\)NBF\(_4\) in CH\(_2\)CN as electrolyte.  
(d) 0.1M Et\(_4\)NClO\(_4\) in CH\(_2\)CN as electrolyte.  
(b) and (c) at carbon electrode, potentials versus standard calomel electrode (SCE).  
(d) at Pt Electrode versus Ag/AgClO\(_4\) - literature values converted to SCE by adding +0.46.  
(e) this work.  
(f) Reference 3.
Figure 5.5. Cyclic Voltammograms

(a) \([\text{Ni(o-C}_6\text{H}_4\text{PMe}_2)_2\text{Cl}_2]^+ \rightleftharpoons [\text{Ni(o-C}_6\text{H}_4\text{PMe}_2)_2\text{Cl}_2]^{2+}\]

(b) \([\text{Ni(o-C}_6\text{F}_4\text{PMe}_2)_2\text{Cl}_2]^+ \rightleftharpoons [\text{Ni(o-C}_6\text{F}_4\text{PMe}_2)_2\text{Cl}_2]^{2+}\]

recorded on ~2mM solutions in 0.1M Bu^4NBF_4/CH_3CN solution, using Ni(II) starting material and proceeding via the Ni(II)-Ni(III) waves (< 1.0V) (see Chapter 3.3, page 176), showing the difference in potential due to the substitution of a perfluoroaryl backbone in the diphosphine ligand.
Table 5.6. $^1$H n.m.r. Data for $d^6$ Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H n.m.r., solvent and conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni}(\sigma-\text{C}_6\text{H}<em>4\text{PM}</em>{2})_2\text{Cl}_2][\text{ClO}_4]_2$</td>
<td>$\delta = 2.1$ (broad). (conc. $\text{HNO}_3$, room temperature)</td>
<td>a.</td>
</tr>
<tr>
<td>$[\text{Ni}(\sigma-\text{C}_6\text{F}<em>4\text{PM}</em>{2})_2\text{Cl}_2][\text{ClO}_4]_2$</td>
<td>$\delta = 2.4$ (broad). (conc. $\text{HNO}_3$, room temperature)</td>
<td>a.</td>
</tr>
<tr>
<td>$[\text{Co}(\sigma-\text{C}_6\text{H}<em>4\text{PM}</em>{2})_2\text{Cl}_2][\text{PF}_6]$</td>
<td>$\delta = 2.3$ (broad) (CD$_2$Cl$_2$, room temperature)</td>
<td>a.</td>
</tr>
<tr>
<td>$[\text{Co}(\sigma-\text{C}_6\text{F}<em>4\text{PM}</em>{2})_2\text{Cl}_2]\text{Cl}$</td>
<td>$\delta = 2.0$ (broad) ((CD$_3$)$_2$SO, room temperature)</td>
<td>a.</td>
</tr>
<tr>
<td>$[\text{Pd}(\sigma-\text{C}_6\text{F}<em>4\text{PM}</em>{2})_2\text{Cl}_2][\text{ClO}_4]_2$</td>
<td>$\delta = 2.1$ (broad) (conc. $\text{HNO}_3$, room temperature)</td>
<td>a.</td>
</tr>
<tr>
<td>$[\text{Pd}(\sigma-\text{C}_6\text{H}<em>4\text{PM}</em>{2})_2\text{Cl}_2][\text{ClO}_4]_2$</td>
<td>$\delta = 1.9(t)(2J_{\text{P-H}};5\text{Hz})$</td>
<td>b.</td>
</tr>
</tbody>
</table>

(a) this work  
(b) reference 1.
more significant than the effect of substituting As for P in the ligand. (Figure 5.5).

Only irreversible and uninterpretable oxidation processes were seen on attempts to record the Ni(III) → Ni(IV) wave for [Ni(Me₂PCH₂CH₂PMe₂)₂Cl₂]⁺, although, as noted earlier, it is possible to generate the Ni(IV) species chemically. Possibly, the Ni(IV) complex is generated electrochemically, then, undergoes fast secondary reactions with the solvent; it was observed that the solid Ni(IV) complex was very hygroscopic, turning green and sticky within 30s of exposure to air.

Attempts were made to obtain ¹H n.m.r. spectra of the more stable complexes, in particular those of o-C₆H₄(PMe₂)₂, in solution in conc. HNO₃. Unfortunately, in these conditions, only broad, weak signals could be observed, although data was obtained for [Pd{o-C₆F₄(PMe₂)₂}Cl₂][ClO₄]₂ and some representative Co(III) complexes (Table 5.6 overleaf).

Owing to the lack of resolution of any coupling and the broadness of the observed bands, stereochemical predictions based on these spectra are not possible.

Discussion (5.5)

Ni(IV) complexes of the type [Ni(L-L)₂X₂][ClO₄]₂ (X = Cl, Br) were obtained only for the ligands o-C₆H₄(AsMe₂)₂, o-C₆H₄(AsMe₂)(PMe₂), o-C₆H₄(PMe₂)₂, o-C₆F₄(PMe₂)₂ and (X = Cl only) Me₂PCH₂CH₂PMe₂. These ligands combine strong σ-donor power with small steric demands. The LFSE contribution to the stability of these (t₂²g e°) ions is maximised by strong σ-bonding, and a π-acceptor component is unlikely to be important in view of the high metal oxidation state. That the most stable complexes are formed with the o-phenylene-backboned ligands is
a further example of the ability of this rigid backbone to resist ligand dissociation. In contrast, the instability of the complex [Ni(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2][\text{BF}_4]_2 may be due to the flexibility of the alkyl backbone, since in lower oxidation states (including Ni(III); see Chapter 3.3, page 176) there is often little difference in stability between complexes of \(\text{o-C}_6\text{H}_4\text{(PMe}_2)_2\) and \(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\).

Preliminary attempts were made to obtain \(\text{cis-}[\text{Ni(L-L)}_2\text{X}_2]^{2+}\) by the treatment of conc. HNO\(_3\) solutions of the Ni(IV) complexes with conc. aqueous AgNO\(_3\), imitating, in suitably oxidising conditions, the isolation of purple \(\text{cis-[Co\{o-C}_6\text{H}_4\text{(AsMe}_2)_2\}_2\text{X}_2]^n^+\) \((X = \text{NO}_3, \text{Cl}, \text{H}_2\text{O} \text{ etc}; n = 1,3)^{12,13}\). However, although colour changes were occasionally observed which suggested some reaction, the trans-complexes were always recovered by precipitation with 70\% HClO\(_4\). Since it is thought that isomerisation of the kinetically inert cis-Co(III) complexes proceeds via a Co(II) intermediate, and the reduction to Ni(III) is so facile, the failure to isolate cis-Ni(IV) complexes may be due to a similar mechanism operating, involving a Ni(III) intermediate.

The incorporation of other, softer donor atoms, such as -SbMe\(_2\) or weaker \(\sigma\)-donors such as -SMe, in complexes of Ni(IV) was attempted by the same strategy that gave some successful results for Ni(III) \(^{11}\) viz. the use of \(\text{o-C}_6\text{H}_4\text{(PMe}_2\text{)(SbMe}_2)\) and \(\text{o-C}_6\text{H}_4\text{(PMe}_2\text{)(SMe)}\). These ligands were chosen because of the success of both the \(\text{o-C}_6\text{H}_4\) backbone and the -PMe\(_2\) group in promoting stability in the Ni(IV) complexes. However, nitric acid oxidation of \(\text{Ni\{o-C}_6\text{H}_4\text{(PMe}_2\text{)(SbMe}_2)\}_2\text{X}_2\) or \([\text{Ni(o-C}_6\text{H}_4\text{(PMe}_2\text{)(SbMe}_2)\}_2\text{Br}_2]\text{ClO}_4\) resulted only in instantaneous decomposition, even at -20\(^\circ\)C, and a similar result was obtained for the high-spin Ni(II) complexes \([\text{Ni\{o-C}_6\text{H}_4\text{(PMe}_2\text{)(SMe)}\}_2\text{X}_2]\) \((X = \text{Cl}, \text{Br})\). Not surprisingly, the complex \([\text{Ni\{o-C}_6\text{H}_4\text{(SbMe}_2)\}_2\text{ClO}_4\}_2\) was also decomposed by nitric acid.
Treatment of [Ni(L-L)]^{2+} or [Ni(L-L)_2X]^+ (L-L = o-C_6H_4(PPh_2)_2, Ph_2PCH_2CH_2PPh_2; X = Cl,Br) with conc. HNO_3 at -20°C gave a light green solution and a dark, sticky solid. On slow warming to room temperature a vigorous, exothermic reaction with evolution of nitrous fumes invariably occurred. Decanting off the acid and washing the solid with 70% HClO_4 revealed that this material was largely unchanged Ni(II) complex, while attempts to precipitate a product from the acid with 70% HClO_4 or conc. HPF_6 also failed. In view of the failure to produce [Ni(L-L)_2X_2]^+ with these ligands these results were not unexpected.

Efforts to obtain [Ni(L-L-L)_2X]^+ by conc. HNO_3/HX oxidation of [Ni(L-L-L)_2X]^+ (L-L-L = Me As(CH_2CH_2CH_2AsMe_2)_2, PhP(CH_2CH_2PPh_2)_2) also failed. Although Pt(IV) complexes of this type can be made, only one impure Pd(IV) complex was obtained, and the failure to obtain Ni(IV) analogues is consistent with the stability trends already discussed (Chapter 3.3, page 86). Interestingly, attempts to make [Ni(H_2NCH_2CH_2NH_2)_2Cl_2]^2+ failed, although it is present in the mixed-valence material [Ni^{II}(L-L)_2] [Ni^{IV}(L-L)_2Cl_2]Y_4 (Y = Cl,ClO_4), and Co(III), Pd(IV) and Pt(IV) analogues exist. Although H_2NCH_2CH_2NH_2 is high in the spectrochemical series for Co(III), it is somewhat lower than o-C_6H_4(AsMe_2)_2^{14}, which in turn is lower than o-C_6H_4(PMe_2)_2^{13}. As is evident from the electrochemical results obtained in this, and other, studies, small differences in the electronic properties of ligands lead to more pronounced effects on the stability of high oxidation state complexes, and this may explain why [Ni(H_2NCH_2CH_2NH_2)_2Cl_2] is decomposed by conc. HNO_3. The mixed valence structure undoubtedly stabilises the Ni(IV) material in this case, and it has previously been noted that the corresponding Pd(IV) and Pt(IV) materials [M(diamine)_2 Cl_2]^2+ (M = Pd,Pt) are also much more stable in similar mixed-valence complexes. Further details, including the spectroscopic properties of Ni(II)-Ni(IV) mixed valence complexes, are discussed in Chapter 6, page 269.
The general rule observed for Ni(II), Pd(IV) and Pt(IV), that these oxidation states prefer to bind at least sufficient halide ions for neutrality (see Chapter 3.2, and references 1, 2 and 11), does not apply to Ni(IV), since attempts to prepare Ni(L-L)X₄ (L-L = o-C₆H₄(AsMe₂)₂, Ph₂PCH₂CH₂PPh₂, cis-Ph₂PCHCHPPh₂) from Ni(II) or Ni(III) precursors with conc. HNO₃ all failed, resulting in decomposition.

For Pd(IV) and Pt(IV), the complexes M(L-L)X₄ are formed preferentially with weaker σ-donors. Thermogravimetric analysis ¹,² established that these materials decompose cleanly on heating to the square planar M(II) species, with reductive elimination of X₂. Decomposition temperatures were much lower for the Pd complexes than the corresponding Pt complexes. It may be that the Ni(IV) complexes are too unstable towards reductive elimination to exist. The relatively low position of X⁻, and the aryl phosphine ligands, in the spectrochemical series would not promote any great stability in such complexes.

The green material obtained by prolonged exposure of [Ni(Et₂PCH₂CH₂P Et₂)Cl₇] to Cl₂¹⁵ (Chapter 2, page 82) is therefore presumably a phosphine oxide complex, not a Ni(IV) complex as previously postulated.

The failure to obtain crystals suitable for an X-ray structural determination was disappointing, as crystal structures of analogous Ni(II) and Ni(III) complexes exist ¹⁶,¹⁷ and a comparison of the series Ni(II), Ni(III), Ni(IV) would have been interesting. Currently, attempts are in progress to obtain structural information for selected examples of the Ni(IV) complexes by a technique not requiring crystalline material, namely EXAFS (Extended X-ray Absorption Fine Structure analysis).
Conclusions (5.6)

This study has established the limits of stability of complexes of Ni(IV) with the neutral, Group Vb ligands. Only with \( \text{C}_6\text{H}_4(\text{PMe}_2)_2 \), \( \text{C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2) \), \( \text{C}_6\text{H}_4(\text{AsMe}_2)_2 \), \( \text{C}_6\text{F}_4(\text{PMe}_2)_2 \), and \( \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2 \) was it possible to isolate \([\text{Ni}(\text{L-L})_2\text{X}_2]^{2+} \) (\( \text{X} = \text{Cl}, \text{Br} \)). It has also demonstrated that their description as genuine Ni(IV) complexes is valid spectroscopically by comparison with isoelectronic Co(III), Pd(IV) and Pt(IV) systems. However, the assignment of the spectroscopic data would be even firmer if crystallographic examination of a Ni(IV) complex had succeeded. With this in mind, an application has been made, and granted, for utilisation of the newly-instigated SERC service which provides for the use of facilities at the Synchrotron Radiation Service at Daresbury, Warrington. This is to enable EXAFS (Extended X-ray Absorption Fine Structure) analysis to be carried out on selected examples of Ni(IV) (and Fe(IV), see Chapter 8, page 363) complexes. This technique allows the determination of limited structural data without the necessity for crystalline samples*, providing that suitable 'model' compounds, necessary for testing the EXAFS solutions, have been the subject of X-ray crystallography. For \([\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)_2)_2\text{Cl}_2]^{2+} \), such compounds do fortunately exist, for example \([\text{Et}_4\text{N}]_2[\text{NiCl}_4] \), \([\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)_2)_2] (\text{I}_3)_2 2\text{I}_2 \) and \([\text{Ni}(\text{C}_6\text{H}_4(\text{AsMe}_2)_2)_2\text{Cl}_2])^{2+} \).

* For reviews of the technique, its theory and applications, see references 18, 19, 20 and 24.
References


CHAPTER 6

Chemistry of Ni(III) and Ni(IV) with Diamine Ligands
6.11 Introduction

It has been known for some time that Ni(II) complexes of diamine ligands may be oxidised under various conditions to yield either light brown materials of composition Ni(L-L)$_2$X$_3$ (L-L = diamine ligand; X = Cl, Br) with magnetic moments corresponding to one unpaired electron, or dark green materials, also of composition Ni(L-L)$_2$X$_3$, with low magnetic moments ($\mu_{\text{eff}} \approx 0.8$ B.M.). Satisfactory explanations of the differences between the two types were not forthcoming at the time. More recently, Japanese workers suggested that the former complexes are 'genuine' (D$_{4h}$) Ni(III) and the latter type are Ni(II) - Ni(IV) mixed valence class II$^{1,2}$ compounds. This was disputed by Papavassiliou and Layek$^3$ who assigned a Ni(II) - Ni(IV) structure to "Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$Cl$_2"$, (which had previously been classified as 'genuine Ni(III)'$^{1,2,3}$) and suggested that the earlier Japanese and Russian materials were 'ligand-deficient'. As Ni(II) - Ni(IV) mixed-valence materials had not been characterised until the recent Japanese study$^3$, a short review of developments in the chemistry of the better-known (and presumably analogous) Pt and Pd systems is included.

6.12 Linear Chain Mixed Valence Complexes of Pd and Pt

(a) General Characteristics.

Unlike Ni(II), whose four-co-ordinate complexes with weaker-field ligands are tetrahedral, Pd(II) and Pt(II) four co-ordinate complexes are invariably square planar, and diamagnetic. Some of these complexes can be obtained as linear chain materials. One of the oldest examples is [Pt(NH$_3$)$_4$][PtCl$_4$] which is known as Magnus' Green Salt (MGS) and was first obtained in 1828. The green colour is surprising as the constituent ions, both square planar, are colourless ([Pt(NH$_3$)$_4$]$^{2+}$) and light pink ([PtCl$_4$]$^{2-}$).
The structure of the salt consists of stacks of alternating anions and cations, and the colour is thought to result from metal-metal interactions. Analogues with, for example, \([\text{Pt(CN)}_4]^{2-}\) and \([\text{Pt}(2,2'-\text{bipyridyl})_2]^{2+}\), exist. The strength of the metal-metal interaction has been related to the strength of colour of the materials, which range from dark green through purple to light pink\(^5\). Similar, although much weaker, interactions between metal centres occur in other Pt(II) complexes, for example in cis-\([\text{Pt(NH}_3)_2\text{Cl}]\), \([\text{Pt(NH}_3)_4]^{2+}\) etc. However, none of these displays significantly anomalous electrical properties due to metal-metal interactions.\(^5\)

The combination of square planar M(II) cations (M = Pd, Pt) with M(IV) octahedral species with trans halide ligands can also give materials with 'stacked' structures, this time with alternating M(II) and M(IV) units. The oldest example, known as Wolfram's Red Salt\(^7\), is \([\text{Pt(NH}_2\text{Et})_4][\text{Pt(NH}_2\text{Et})_4\text{Cl}_2]\). The principal structural feature of such materials is a linear Pt\(^{\text{II}}\).....Cl-Pt\(^{\text{IV}}\)-chain\(^8\),\(^9\) (Figure 6.121). This gives rise to their unusual anisotropic electronic characteristics. As in all other solids of this type, the principal feature in single-crystal low temperature and high pressure spectra of Wolfram's red, and its bromo-analogue, is an intense transition polarised parallel to the chains and attributed to an electron transfer from a filled \(d_z^2\) orbital of the Pt(II) unit to an empty \(d_z^2\) orbital on a neighbouring Pt(IV) unit.\(^11\) Resonance Raman spectra, using excitation into this transition reveal many progressions in different vibrations, especially at low temperatures. The most significant of these is in the symmetric stretch of the Cl-Pt\(^{\text{IV}}\)-Cl unit.\(^12\)

Beginning with the efforts of Kida\(^10\), a large number of analogous complexes have now been synthesised, with various mono- and diamine ligands, and many of these have been characterised
by X-ray crystallography. These can be classified according to the degree of disorder in the structures. If two distinct Pt (or Pd) sites are observable by X-ray diffraction, this indicates three-dimensional order in the crystal, and such materials are ascribed to class II of the Robin and Day Scheme. These show strong H-bonding between the amine ligands and counter ions outside the chain, for example as in \([\text{Pt(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2][\text{Pt(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_2]\) \([\text{ClO}_4]\)_4^n, as shown in Figure 6.122, and this may be responsible for such order. Other examples only show one-dimensional order—that is, along the \(\text{Pt}^{\text{II}}\)...\(\text{Cl} - \text{Pt}^{\text{IV}}\)-unit, with each 'stack' disordered relative to other 'stacks'. An example is \([\text{Pt(NH}_2\text{Et)}_4]\) \([\text{Pt(NH}_2\text{Et)}_4\text{Br}_2]\)\(\text{Br}_4\), Figure 6.122. Much rarer is three-dimensional disorder, which is probably due to significant numbers of defects in the 'stacks', consisting of Pt(III) or Pd(III) sites. Although no e.s.r. signals have been resolved for the latter category, it is possible that strong coupling of Pt(III)-X sites occurs, preventing observation of the signal.

* Compounds containing atoms of the same metal in more than one oxidation state were classified by Robin and Day\(^{13}\) as follows; in class I compounds the valences are firmly trapped at different co-ordination sites, with no significant interaction between them. Class III compounds have virtually complete valence delocalisation and no distinction between sites can be made. Class II compounds are intermediate, in that while distinct valency is preserved, there is sufficient orbital overlap between adjacent metal atoms to permit electron transfer between the two sites. A typical feature of such complexes is the intervalence charge-transfer band in the electronic spectrum, mentioned earlier.
Figure 6.121. A diagramatic representation of the structure of Wolfframs Red Salt ([Pt(EtNH₂)₄][Pt(EtNH₂)₄Cl₂]Cl₄). Crystal water and chloride positions outside the chain are omitted. The bridging chlorides are drawn in fixed positions but are statistically disordered in the crystal. From reference 5.
Figure 6.122
(see overleaf)
Figure 6.122 (opposite)

(A) A projection of the Pt$^{IV}$-Br...Pt$^{II}$ chain of (three-dimensionally-ordered) [Pt(en)$_2$][Pt(en)$_2$Br$_2$][ClO$_4$] into the bc plane. Hydrogen bonds between the ClO$_4^-$ ions and -NH$_2$ groups on the ligand (N-O $\leq$ 3.0 Å) are indicated by dotted lines. Circles indicate the centres of atomic positions.

(B) ORTEP plot of (a) a chain of [Pt(EtNH$_2$)$_4$][Pt(EtNH$_2$)$_4$Cl$_2$][Br$_4$]$_4$, rotated 20° around the a axis and 40° around the c axis. The bromine positions drawn are statistically half-occupied. (b), (c), the same plot showing the two possible bromine arrangements along one chain. The bromine positions shown are fully-occupied and (a) is the superimposition of (b) and (c). This is a one-dimensionally ordered structure. From reference 5.
In a period where increasing interest in one-dimensional metals is in progress, investigation of the electrical properties of these materials has been of importance. Depending upon the halide ions present, and the nature of the ligands, nearly all the mixed valence materials show increasing conductivity with increasing pressure.\(^{11}\) (At the same time, the wavelength of the polarised intervalence charge transfer transition increases with increasing pressure\(^ {11}\)). Both these observations are a consequence of the gradual reduction in the inequivalence of the M(II) and M(IV) sites with compression along the chain direction.\(^5\) However, the electrical conductivities, even under pressure, are much lower than those encountered with, for example, the partially-oxidised bis(oxalato)platinum or tetracyanatoplatinum salts.\(^5\)

Another consequence of the one-dimensional ordering is the variation in colours of the complexes with particle size. For example, large crystals of Wolfram's Red are actually green, and on grinding, turn red, then purple-blue.\(^5\)

(b) Specific examples

To illustrate more fully the nature of mixed-valence complexes of the type \([\text{M(L-L)}_2\text{M(L-L)}_2\text{X}_{\text{n}}\text{X}_{\text{n}}]\), the syntheses and properties of certain examples of the many compounds now in the literature will be outlined.

Crystals suitable for X-ray or resonance Raman investigations are usually obtained by slow diffusion between solutions containing M(II) complexes and M(IV) complexes.\(^8,9,12\) (In this respect, Pt enjoys the advantage of a reasonably stable +4 oxidation state, whereas Pd(IV) complexes are less stable, making crystal growing somewhat harder). For example, crystals of \([\text{Pt(H}_2\text{N}(\text{CH}_2)_3\text{NH}_2)_2]\text{[Pt(H}_2\text{N}(\text{CH}_2)_3\text{NH}_2)_2\text{X}_{\text{n}}\text{X}_{\text{n}}]\text{Y}_{\text{n}}\) (\(X = \text{Cl}, \text{Br}, \text{I}; Y = \text{ClO}_4, \text{BF}_4\))\(^15\) were grown by diffusion in this way. The Pt\(^{\text{IV}}\)-X to Pt\(^{\text{II}}\)...X bond length ratio increases in the order
Cl < Br < I, indicating a tendency in this order to a Pt(III) complex. 15 The resonance Raman spectra of the complexes, when recorded upon single crystals with polarised light, the electric vector of which is parallel to the conducting axis, show long progressions in the symmetric X-PtIV-X symmetric stretch. 15 Apparently the six-membered chelate ring in these complexes does not hinder isolation of the mixed-valence complexes, compared with the more conventional five-membered rings encountered in, for example, [Pt(H₂NCHRCH₃NH₂)₂][Pt(H₂NCHRCH₂NH₂)₂X₂](ClO₄)₄ (R = H, Me, Et). Another system involving an unusual ligand, recently characterised, utilises an unsubstituted tetraaza macrocycle ((14)aneN₄ - see Chapter 2, Figure 2.4, page 64) with which the complex [Pd(macrocycle)][Pd(macrocycle)Cl₂](ClO₄)₄ is obtained. 17 In general, Pd(II)-Pd(IV) complexes are rather more recent than their Pt analogues, and [Pd(H₂NCH₂CH₂NH₂)₂] [Pd(H₂NCH₂CH₂NH₂)₂Cl₂][ClO₄]₄, for example, was first made in 1973. 18 Its crystal structure shows one-dimensional order 19 and the corresponding Pt complex is isomorphous. As in the neutral mixed-valence complex [Pd(NH₃)₂Cl₂][Pd(NH₃)₂Cl₄], the Pd(IV) complex in these compounds is considerably stabilised compared with the pure Pd(IV) material, and the mixed-valence materials have an almost infinite shelf-life. Complexes of Pd(IV) are generally rather unstable.

6.13 Ni(III) and Ni(II)/(IV) Complexes - Earlier Literature

Russian workers 2 found that passing chlorine through a methanol solution of Ni(en)₂Cl₂ or [Ni(en)₃]Cl₂ (en = H₂NCH₂CH₂NH₂) produced a brown-yellow precipitate of composition Ni(en)₂Cl₃, while brown Ni(en)₂Br₃ was the product of the oxidation of Ni(en)₂Br₂ with Br₂ in CCl₄ suspension. Both these complexes were demonstrated to possess one oxidising equivalent in redox reactions with Fe(II) and both had magnetic moments corresponding to one unpaired electron.
Dilute acids with weakly co-ordinating anions (20% HClO₄, dilute HNO₃) replaced one halide ion as expected, giving [Ni(en)₂X₂]Y (X = Cl, Br; Y = ClO₄, NO₃). Concentrated acids, however, gave dark green, lustrous materials of composition [Ni(en)₂X]Y₂. (Y = ClO₄, NO₃, HSO₄).²

Later, complexes of the analogous ligand pn (pn = H₂NCH(CH₃)CH₂NH₂) were made similarly, but Ni(pn)₂Cl₂ was dark green and essentially diamagnetic.¹

In view of the complex chemistry of the nickel(II) diamine systems, e.s.r. studies were undertaken.²⁰,²¹,²² It was found that [Ni(en)₂Cl₂]Y (Y = Cl, ClO₄, NO₃, HSO₄) exhibited e.s.r. spectra typical of D₄h systems, with g₁ < g₂; g₂ ≈ 2.0.²¹ Also, when this complex was dissolved in 40% HF, hyperfine coupling to F was observed in the g₁ region, corresponding to the formulation [Ni(en)₂F₂]⁺ (trans).²¹ The e.s.r. spectra of polycrystalline samples of the en and pn complexes obtained earlier were found to fall into two categories. The materials of μ eff ca 1.8 - 2.0 B.M. showed strong, sharp signals (2 or 3 g-values) and the dark green, nearly diamagnetic complexes showed only weak, broad signals.²² In HCl solutions, all the complexes of en gave signals characteristic of [Ni(en)₂Cl₂]⁺. Interestingly, although hyperfine interactions due to the axial halide ions could be observed, no ¹⁴N hyperfine coupling could be resolved. In this respect, of course, the compounds differ from the otherwise similar [Ni(L-L)₂X₂]⁺ (L-L = o-C₆H₄(EMe₂); E = P, As) where a hyperfine pattern rich in P or As character is seen (Chapter 3.3, page 167). The observation of one halogen-sensitive infrared band in the spectra of [Ni(en)₂X₂]⁺ (X = Cl; 218 cm⁻¹, X = Br; 162 cm⁻¹)²³ supported the D₄h structure suggested by e.s.r. measurements.
In spite of all the complexes made, their chemical transformations and e.s.r. spectra, no explanation was offered to account for the two categories of oxidation products until Japanese workers re-examined the earlier compounds, and synthesised further examples of Ni(L-L)$_2$Cl$_3$ (L-L = H$_2$N(CH$_2$)$_2$NH$_2$(pd), 1,2-C$_6$H$_{10}$(NH$_2$)$_2$ (cyn), H$_2$NCH(Me)CH(Me)NH$_2$ (btn)). They suggested that while Ni(en)$_2$Cl$_3$ and Ni(pd)$_2$Cl$_3$ were genuine Ni(III) complexes, all the other Ni(L-L)$_2$Cl$_3$ complexes were mixed-valence materials [Ni(L-L)]$^+$[Ni(L-L)$_2$Cl$_2$]Cl$^-$, thus accounting for their low magnetic moments (the planar Ni(II) and octahedral d$^6$ Ni(IV) units being diamagnetic) and very weak e.s.r. signals. The diffuse reflectance spectra of these compounds showed a band at ca $16 \times 10^3$ cm$^{-1}$, absent in [Ni(en)$_2$Cl$_2$]Cl, and assigned to the intervalence (Ni(IV)$\rightarrow$Ni(II)) charge transfer.

Resonance Raman experiments were carried out on Ni(pn)$_2$X$_3$,$^4$ showing the progression expected for a mixed-valence compound, in $\nu$ sym $- \nu^+$ (X = Cl only; no progression was seen for X = Br as the energy of excitation was said to be higher than that of the intervalence charge transfer band). The symmetric Ni-Cl stretch occurred at ca 260 cm$^{-1}$, and similar results were obtained for Ni(en)$_2$Cl$_3$.$^2$ The Russian workers$^2$ had earlier demonstrated that this existed in both forms, (Ni(III) - yellow brown, $\mu_{\text{eff}}$ = 1.8 B.M., and a dark green, diamagnetic form), and that studied in the Raman experiments is clearly a mixed-valence complex. It was suggested, however, that the brown-yellow Ni(III) form was a 'ligand deficient' material, made only in non-anhydrous conditions.$^4$

6.14a Results and Discussion

The aim of this study was to discover whether it was truly possible to make pure Ni(en)$_2$Cl$_3$ in both Ni(III) (D$_{4h}$) and Ni(II)-Ni(IV) mixed-valence forms - a unique type of isomerism - and to elucidate the factors which favour formation of Ni(III) or
Ni(II) - Ni(IV) complexes with this, and other, diamine ligands, which had not been satisfactorily explained\(^1\),\(^2\),\(^3\),\(^4\). If the Ni(III) complexes were indeed genuine, contrary to the recent suggestion\(^4\), it was hoped to characterise them more fully for comparison with the data obtained for \([\text{Ni}(L-L)_2X_2]^+\) (\(L-L = \Sigma C_6H_4(\text{EMe}_2)_2; E = \text{P,As}\)).

Early preparations of \(\text{Ni(en)}_2\text{Cl}_3\) involved the rapid passage of chlorine via a Pasteur pipette into a saturated solution of \(\text{Ni(en)}_2\text{Cl}_2\) in 'technical' grade methanol (i.e. containing ca 1\% \(H_2O\)). This yielded the brown-yellow powder first obtained by the Russian workers\(^1\),\(^2\). After filtration, washing with \(CCl_4\) and drying in vacuo, the analyses (C, H, N and Cl) corresponded well with the formulation \(\text{Ni(en)}_2\text{Cl}_3\) (Table 6.141) and no bands due to water, co-ordinated or not, could be observed in the infra-red spectrum. The spectroscopic and magnetic properties of the complex were entirely consistent with a Ni(III) complex, \([\text{Ni(en)}_2\text{Cl}_2]\text{Cl}\), although the insolubility of the material restricted measurements to the solid state (Table 6.142).

Attempts were made to obtain the Ni(II) - Ni(IV) mixed valence form of \(\text{Ni(en)}_2\text{Cl}_3\). This was eventually achieved by passing a stream of chlorine heavily diluted with nitrogen through a solution of \(\text{Ni(en)}_2\text{Cl}_2\) in methanol-ethanol (1:1 by volume; solvents dried by reflux over, and distillation from, their respective magnesium alkoxides). It was a dark green-black solid, which also analysed well for \(\text{Ni(en)}_2\text{Cl}_3\), and had a low, but significant, magnetic moment (0.8 B.M.). An e.s.r. spectrum was only observable with high spectrometer sensitivity.

In view of the above results, attempts were made to obtain both forms of other complexes. Bromination of \(\text{Ni(en)}_2\text{Br}_2\)
under a variety of conditions (Br₂/CCl₄ suspension; Br₂-methanol, slow passage of dilute Br₂ vapour through methanol-ethanol solutions of Ni(en)₂Br₂) gave only the dark brown [Ni(en)₂Br₂]Br (Tables 6.141, 6.142), a Ni(III) complex. It is possibly significant that, although no electronic or other spectral data for the supposed Ni(II)-Ni(IV) form of the complex is available⁴, no progressions in νNi-Br were seen in the resonance Raman spectrum.⁴ The material isolated could in fact have been the Ni(III) complex⁴. But, in view of the delicate balance between Ni(III) and Ni(II)-Ni(IV) complexes in the chloride, the existence of the Ni(II)-Ni(IV) bromo-complex cannot certainly be ruled out.

Similarly, varying the conditions of synthesis for Ni(pn)₂Cl₃ (pn = H₂NCH₂CH(Me)NH₂) did not affect the product, which spectroscopic and physical data (Tables 6.141, 6.142) showed was a Ni(II)-Ni(IV) mixed-valence complex.

Similar efforts to obtain both forms of Ni(pd)₂X₃ failed; only Ni(III) complexes were isolated with this ligand.

The observations of the Russian workers, that repeated treatment of Ni(L-L)₂X₃ (L-L = diamine ligand) with concentrated mineral acids yielded Ni(L-L)₂X₂Y (Y = NO₃, ClO₄, HSO₄) was confirmed, and spectroscopic and physical data shows that these are better formulated as [Ni(L-L)]₂[Ni(L-L)₂X₂]Y₂. Interestingly, dilute acids merely bring about metathesis, and the formation of [Ni(III)(L-L)₂X₂]Y (L-L = en.²⁴), and it was also found that treatment of [Ni(en)₂]Cl₄ (Y = Cl,ClO₄) with 30% HCl yields the Ni(III) complex.¹²⁴ Details of these interconversions are given in Figure 6.143.

Evidently, the confusion in the literature over the two forms of Ni(L-L)₂X₃ arises from the similar methods of preparation
<table>
<thead>
<tr>
<th>Complex</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(en)}_2\text{Cl}_2]\text{Cl}$</td>
<td>16.9(16.8)</td>
<td>5.4(5.6)</td>
<td>19.5(19.6)</td>
<td>1.87</td>
</tr>
<tr>
<td>$[\text{Ni(en)}_2\text{Cl}_2]\text{ClO}_4$</td>
<td>13.5(13.8)</td>
<td>4.8(4.6)</td>
<td>15.2(16.0)</td>
<td>1.97</td>
</tr>
<tr>
<td>$[\text{Ni(pd)}_2\text{Cl}_2]\text{Cl}$</td>
<td>23.2(23.0)</td>
<td>6.2(6.4)</td>
<td>17.6(17.9)</td>
<td>1.98</td>
</tr>
<tr>
<td>$[\text{Ni(en)}_2\text{Br}_2]\text{Br}$</td>
<td>11.6(11.5)</td>
<td>3.7(3.9)</td>
<td>13.6(13.4)</td>
<td>1.80</td>
</tr>
<tr>
<td>$[\text{Ni(pd)}_2\text{Br}_2]\text{Br}$</td>
<td>16.2(16.1)</td>
<td>4.5(4.5)</td>
<td>12.3(12.5)</td>
<td>2.06</td>
</tr>
<tr>
<td>$[\text{Ni(en)}_2]\text{[Ni(en)}_2\text{Cl}_2]\text{Cl}_4$</td>
<td>17.0(16.8)</td>
<td>5.5(5.6)</td>
<td>19.4(19.6)</td>
<td>0.90</td>
</tr>
<tr>
<td>$[\text{Ni(en)}_2]\text{[Ni(en)}_2\text{Cl}_2]\text{ClO}_4$</td>
<td>11.8(11.6)</td>
<td>3.9(3.9)</td>
<td>13.4(12.7)</td>
<td>1.1</td>
</tr>
<tr>
<td>$[\text{Ni(pn)}_2]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni(pn)}_2]\text{Cl}_2\text{Cl}_4$</td>
<td>23.2(23.0)</td>
<td>6.4(6.4)</td>
<td>18.0(17.9)</td>
<td>0.95</td>
</tr>
<tr>
<td>$[\text{Ni(pn)}_2]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni(pn)}_2]\text{Br}_2]\text{Br}_4$</td>
<td>15.9(16.1)</td>
<td>4.6(4.5)</td>
<td>12.4(12.4)</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6.142. Spectroscopic Results

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu/\text{cm}^{-1})</th>
<th>(E_{\text{max}}/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(en)_2Cl_2]Cl</td>
<td>214s</td>
<td>778vbr, 530w (sh), 438 (sh), 420, 374, 354 (sh), 306</td>
</tr>
<tr>
<td>[Ni(en)_2Cl_2]ClO_4</td>
<td>215s</td>
<td>800br, 530vws (sh), 382 (sh), 366 (sh), 336, 274 (sh)</td>
</tr>
<tr>
<td>[Ni(pd)_2Cl_2]Cl</td>
<td>216s</td>
<td>826, 530w (sh), 420br, 380, 354 (sh), 322 (sh), 302 (sh)</td>
</tr>
<tr>
<td>[Ni(en)_2Br_2]Br</td>
<td></td>
<td>850, 560 (sh), 405 (sh), 380, 250</td>
</tr>
<tr>
<td>[Ni(pd)_2Br_2]Br</td>
<td></td>
<td>950 (sh), 850br, 576 (sh), 510br, 442br (sh), 394 (sh), 378 (sh), 352 (sh)</td>
</tr>
<tr>
<td>[Ni(en)_2Ni(en)_2Cl_2]Cl_4</td>
<td>254s</td>
<td>800 (sh), 720 (sh), 670 (sh), 640, 612 (sh), 558, 412, 370, 344, 328 (sh)</td>
</tr>
<tr>
<td>[Ni(en)_2Ni(en)_2Cl_2][ClO_4]_4</td>
<td>ca 250 (sh)</td>
<td>838w, 580s, 450 (sh), 358, ca 280 (sh)</td>
</tr>
<tr>
<td>[Ni(pd)_2Ni(pd)_2Cl_2]Cl_4</td>
<td>250s</td>
<td>794w (sh), 720 (sh), 648s, 622 (sh), 558 (sh), 422, 378, 322</td>
</tr>
<tr>
<td>[Ni(pd)_2Ni(pd)_2Br_2]Br_4</td>
<td>204s</td>
<td>1 000, 970 (sh), 770 (sh), 690br (sh), 616 (sh), 446, 382</td>
</tr>
<tr>
<td>[Ni((\alpha)-C_6H_4(PMe_3)(NMe_2))]Br_2ClO_4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni((\alpha)-C_6H_4(PMe_3)(NMe_2))]Cl_2ClO_4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Polythene plates, 400—180 cm\(^{-1}\), Nujol mulls. Bands assigned to \(\nu(\text{Ni}-\text{X})\) (\(\text{Ni}^{III}\) complexes) or \(\nu(\text{Ni}^{IV}-\text{X} \cdots \text{Ni}^{III})\) (mixed-valence \(\text{Ni}^{III}-\text{Ni}^{IV}\) complexes). * Diffuse reflectance, with dried BaSO_4 as diluent and reference. * Recorded at room temperature. Spectra recorded on powders in quartz tubes except for the \(\text{Ni}^{III}-\alpha\)-C_6H_4(PMe_3)(NMe_2) complexes which were generated in situ by addition of X_2-CCl_4 to a CH_2Cl_2 solution of the appropriate \(\text{Ni}^{III}\) complex. Linewidths/G (derivative peak to peak) are shown in parentheses.
Figure 6.143. REACTIONS OF $\text{Ni(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\text{)}_2\text{Cl}_3$ 

\[
\begin{align*}
\text{[Ni}^{\text{II}}\text{(en)}_2\text{.Ni}^{\text{IV}}\text{(en)}_2\text{Cl}_2]\text{[ClO}_4\text{]}_4 \quad \text{70% HClO}_4 \quad \text{6 M HCl} \\
\rightarrow \quad \text{[Ni}^{\text{III}}\text{(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\text{)}_2\text{Cl}_2]\text{Cl} \\
\rightarrow \quad \text{conc H}_2\text{SO}_4 \quad \text{6 M HCl} \\
\rightarrow \quad \text{[Ni(en)}_2\text{.Ni(en)}_2\text{Cl}_2]\text{[HSO}_4\text{]}_4 \\
\rightarrow \quad \text{[Ni}^{\text{III}}\text{(en)}_2\text{Cl}_2]\text{NO}_3 \\
\rightarrow \quad \text{Ni(en)}_2\text{Cl}_2 \quad \text{Ni(en)}_2\text{Cl}_2 \quad \text{Ni(en)}_2\text{Cl}_2 \quad \text{Cl}_4 \\
\text{MeOH:EtOH} \\
(1:1), \text{dry solvents} \\
\rightarrow \quad \text{[Ni}^{\text{II}}\text{(en)}_2\text{.Ni}^{\text{IV}}\text{(en)}_2\text{Cl}_2]\text{Cl}_4 \\
\text{9:10 Cl}_2:\text{N}_2 \text{ slow stream} \\
\text{6 M HCl} \\
\rightarrow \quad \text{[Ni}^{\text{III}}\text{(en)}_2\text{Cl}_2]\text{ClO}_4 \\
\text{6 M HCl} \\
\rightarrow \quad \text{[Ni}^{\text{III}}\text{(en)}_2\text{Cl}_2]\text{NO}_3
\end{align*}
\]
(mixtures are obtained by small fluctuations in reaction conditions) and from the fact that the preparations used by previous workers have not been described in detail. Preparations used in this study are given in Chapter 7, page 326. An impure, mainly Ni(III) material "[Ni(en)$_2$Cl$_2$]Cl" is sometimes isolated with a greenish hue due to the presence of some Ni(II) - Ni(IV) form (electronic spectral evidence) while the Ni(II) - Ni(IV) form was never free of at least a trace of e.s.r. activity. In one sample, rather badly contaminated with Ni(III), an interesting e.s.r. spectrum (Figure 6.144, page 270) was obtained. While the pure Ni(III) complexes showed no hyperfine coupling as polycrystalline solids, this sample exhibits clear coupling in the $g_{\perp}$ region to two chloride nuclei (7 lines; $^{35}/^{37}$Cl; I = 3/2) - a consequence of the Ni(III) sites responsible being effectively 'doped' into a diamagnetic host lattice, in a manner reminiscent of the observance of an axial spectrum of [Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$Cl$_2$]$^+$ impurities in a Ni(IV) complex (Chapter 5, page 239).

(b) **Spectroscopic Properties**

The far infra red spectra showed the presence of one halogen-sensitive band at ca 215 cm$^{-1}$ (Ni(III) chlorides) or 250 cm$^{-1}$ (Ni(II) - Ni(IV) complexes), assigned to $\nu_{\text{Ni-X}}$ ($B_1u$) for the Ni(III) complexes and $\nu_{\text{Ni}^\text{IV}-\text{X} \ldots \text{Ni} \ldots}$ ($B_1u$) in the mixed valence materials. The far infra red spectra of Ni(en)$_2$Cl$_3$ (both forms) are compared in Figure 6.145. The nickel-bromine stretching frequency in the Ni(III) complexes is too low in frequency ($\lt 180$ cm$^{-1}$) to be observed with the available instrument, but a band at ca 200 cm$^{-1}$ in [Ni(pn)$_2$][Ni(pn)$_2$Br$_2$]Br$_4$ is tentatively assigned to $\nu_{\text{Ni}^\text{IV}-\text{X} \ldots \text{Ni} \ldots}$ in this complex (Table 6.142). Figure 6.146 compares the far infra red spectra of the Ni(III) and Ni(II)-Ni(IV) forms of Ni(en)$_2$Cl$_3$.

As anticipated from similar spectra of Pd and Pt analogues, the diffuse reflectance spectra of the Ni(II)-Ni(IV)
Figure 6.144

EPR Spectrum of Ni$^{III}$\(_{(en)}\)\(_2\)Cl\(_3\) in a Ni(II)/Ni(IV) host lattice
complexes are dominated by an intense intervalence charge transfer band \( \text{d}_{2\text{Ni(IV)}} \leftrightarrow \text{d}_{2\text{Ni(II)}} \) at \( \text{ca} \ 16 \times 10^3 \text{ cm}^{-1} \) (Tables 6.142, Figure 6.146). The Ni(III) complexes, by comparison, display a very weak band at lower energy, characteristic of D\(_{4h}\) d\(^7\) complexes such as [Ni(2,3-dimethyl-1,4,8,11-tetra-azacyclotetradecane)\(X_2\)]\(\text{ClO}_4\)\(^2\) (Chapter 2, page 65) or [Ni(Me\(_2\)PCH\(_2\)CH\(_2\)PMe\(_2\))\(_2\)Cl\(_2\)]BF\(_4\)\(^2\) (Chapter 3, page 167). Typical examples are compared in Figure 6.146.

Generally, the e.s.r. spectra are typical of those observed for D\(_{4h}\) low-spin d\(^7\) complexes \( g_\| = 2.0, g_\perp = 2 - \frac{\epsilon \alpha^2 \lambda}{E_g} \) where \( \lambda = -715 \text{ cm}^{-1} \) for Ni\(^{3+}\), \( E_g \) is the \( g \) - \( e \) separation energy (cm\(^{-1}\)) and \( \alpha \) is the d\(_2\) orbital coefficient in the molecular orbital of the unpaired electron. In practice, \( g_\perp \approx 2.2 \) for the Ni(III) complexes. (Table 6.142). Weak, broad signals were obtained for all samples of the Ni(II) - Ni(IV) form of \( \text{Ni(en)}_2 \)\(_2\)\(\text{Cl}_3\), but none were evident for the corresponding pn complexes.

The insolubility of all the complexes in this study restricted the collection of spectroscopic data, and also precluded the successful growing of crystals for X-ray study, although such a study would be of great interest for [Ni(en)\(_2\)][Ni(en)\(_2\)\(\text{Cl}_2\)]\(\text{Cl}_4\), for example. Crystal growing by diffusion of separate solutions of Ni(II) and Ni(IV) complexes was not possible; although the Ni(IV) complexes must be generated at least transiently in solution to enable 'stack' formation with planar Ni(II) entities, all efforts to isolate a Ni(IV) complex (e.g. chlorination at \( \text{ca} \ - 80^\circ \text{C} \), or use of K\(_2\)S\(_2\)O\(_8\) as oxidant) failed. Presumably the stabilisation of Ni(IV) in the mixed valence materials is even more marked than for the Pd(IV) analogues.

6.15 Complexes of Other N-donor Ligands

Commercial availability of the tetraazamacrocyclic 1,4,8,11-tetraazacyclotetradecane (CYCLAM)\(^2\) made the synthesis
Figures 6.145 (below) and 6.146 (above)

Diffuse-reflectance spectra of $[\text{Ni}^{III}(\text{en})_2\text{Cl}_2]\text{Cl}$ (---); $[\text{Ni}^{IV}(\text{en})_2\text{Ni}^{III}(\text{en})\text{Cl}_2]\text{Cl}_4$ (· · · ·); $[\text{Ni}(\text{pd})_2\text{Cl}_2]\text{Cl}$ (-----), and $[\text{Ni}(\text{pn})_2\text{Cl}_2]\text{Cl}$ (---) in the range 300—850 nm. Barium sulphate was used as diluent and reference.

Far-i.r. spectra (350—180 cm$^{-1}$) of (a) $[\text{Ni}^{III}(\text{en})_2\text{Cl}_2]\text{Cl}$ and (b) $[\text{Ni}^{II}(\text{en}),\text{Ni}^{IV}(\text{en})_2\text{Cl}_2]\text{Cl}_4$ in Nujol mulls.
of its Ni(III) complexes attractive for comparisons with the other systems. Data obtained for these complexes was entirely consistent with the literature and will not be reported here. However it should be noted that attempts to form a Ni(II) - Ni(IV) complex with this ligand failed, although a Pd(II) - Pd(IV) complex has been synthesised and its structure determined crystallographically.

The Ni(II) complexes of N,N'-alkylated diamines, \([\text{Ni(Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]\text{Cl}_2\)\] and \([\text{Ni}o-C_6\text{H}_4(\text{NMe}_2)_2]\text{Cl}_2\) were unaffected by chlorine and were decomposed by nitric acid. This is probably a consequence of the weak field exerted by these ligands, which in turn is due to long Ni-N bonds owing to the alkyl substituents' steric effects. The failure of chlorine or nitric acid to oxidise cis-[Ni(L-L)\_2X\_2] (L-L = 1,10-phenanthroline or 2,2'-bipyridyl) was a little surprising in view of the ready electrochemical oxidation of the \([\text{Ni}(L-L)_3]^{2+}\) species to \([\text{Ni}(L-L)_3]^{3+}\).

Nickel(II) complexes of the 'hybrid' ligand \(o-C_6\text{H}_4(\text{PMe}_2)(\text{NMe}_2)\) were oxidised in situ by halogen in CH\(_2\)Cl\(_2\) solution in e.s.r. tubes, and the spectra examined. The complex \([\text{Ni}(L-L)_2]\text{BF}_4\) formed a transient Ni(III) complex, the e.s.r. of which was typical of trans-[Ni(L-L)\_2X\_2]\(^+\) species (Table 6.142), confirming that the -NMe\(_2\) groups were co-ordinated to Ni(III) in this case. If they had dissociated, one would have anticipated the broad signal (X = Cl, Br) seen, for example, in the spectrum of \([\text{Ni}o-C_6\text{H}_4(\text{PMe}_2)(\text{OME})_2\text{Br}_3\] (OME groups unco-ordinated; see Chapter 3.1, page105). The planar 1:1 complex \([\text{Ni}o-C_6\text{H}_4(\text{PMe}_2)(\text{NMe}_2)]\text{Br}_2\) did give the familiar four-line coupling to one \(^7\)Br nucleus on treatment with Br\(_2\) in CH\(_2\)Cl\(_2\). Both these complexes, though very unstable and not isolated as solids, further illustrate the remarkable effect of the \(o-C_6\text{H}_4(\text{PMe}_2)\)-group on the isolation of high oxidation state complexes, noted elsewhere (Chapter 3.3, page181; Chapter 5, page247). In contrast, Ni(II) complexes of the amine-arsine,
\(-C_6H_4(\text{AsMe}_2)(\text{NMe}_2)\)\(^{33}\) were instantly decomposed by halogens, or by nitric acid. Only one other instance of \(-\text{NMe}_2\) co-ordination to Ni(III) is known - the complexes \([\text{Ni(C_6H_3(CH_2NMe_2)_2-O,0')}X_2]\)\(^{37}\).

6.16 Conclusions

This study has demonstrated that it is possible to obtain \(\text{Ni(en)}_2\text{Cl}_3\) in both Ni(III) and Ni(II)-Ni(IV) mixed valence forms. Despite further attempts to duplicate this observation with similar ligands, no other examples of this unique isomerism were found. The 1,2-diamines substituted at either, or both, carbons gave exclusively Ni(II) - Ni(IV) complexes, while only Ni(III) complexes were obtained for 1,3-propanediamine. The \(-\text{NMe}_2\) group is too weak a \(\sigma\)-donor to promote the oxidation to Ni(III) except in the presence of the powerful \(\sigma\)-donor \(-\text{PMe}_2\) group in neutral ligands.

The conclusion that it is possible to synthesise Ni(II)-Ni(IV) mixed valence complexes \([\text{Ni(L-L)}_2][\text{Ni(L-L)}_2\text{X}_2]\)\(^4\) is of great interest. Preliminary measurements of conductivity,\(^3\) and the lower energy of the intervalence charge transfer band in the Ni(II)-Ni(IV) complexes, suggest a lesser autonomy of Ni(II) and Ni(IV) sites compared with the Pd(II)-Pd(IV) and Pt(II)-Pt(IV) analogues,\(^5\), and this may lead to further investigation of the Ni systems, with emphasis on their potential electrical (semiconductor) properties.

The reasons why the ligands with 'branched chain' backbones favour Ni(II)-Ni(IV) formation, while en and pd \((\text{H}_2\text{N(CH}_2)_3\text{NH}_2)\) favour Ni(III) formation (\([\text{Ni(en)}_2][\text{Ni(en)}_2\text{Cl}_2]\)\(\text{Cl}_4\) is converted to the Ni(III) form in 30% HCl) are very unclear. Presumably, relative solubilities, and the precise consitution of the methanol or methanol-ethanol solutions after halogenation, bear some relation to the product formed. The preparation of Ni(II)-Ni(IV) materials by treatment of \(\text{Ni(en)}_2\text{Cl}_3\) with concentrated
mineral acids, of formula \([\text{Ni(en)}_2]_4[\text{Ni(en)}_2\text{Cl}_2]_4\) \((Y = \text{NO}_3, \text{HSO}_4, \text{ClO}_4)\), together with the hydrogen bonding observed in X-ray crystallographic studies of Pd and Pt analogues, suggests that hydrogen bonding to these anions could be important in the formation of Ni(II)-Ni(IV) chains from \(D_{4h}\) Ni(III) cations.

The mechanisms by which the Ni(III) or Ni(II)-Ni(IV) complexes are formed are obscure. X-ray crystallography has established a cis-octahedral halide-bridged dimeric structure for the Ni(L-L)_2X_2 complexes, of formula \([\text{Ni}_2(L-L)_2X_2]X_2\), and in boiling methanol, molecular weight measurements showed that this structure is preserved for L-L = en. However, to allow for the formation of the Ni(II)-Ni(IV) 'stacks', or the \(D_{4h}\) Ni(III) complexes, \([\text{Ni}(L-L)_2]^{2+}\) or \([\text{Ni}(L-L)_2(H_2O)_2]^{2+}\) must exist in solution, even if only as a very small equilibrium concentration.

**Note added in proof**

Japanese workers have recently measured the Cl 2p and Ni 2p \(3/2\) binding energies in Ni(pn)_2Cl_3, concluding that they support the mixed valence formulation for this compound, and have also synthesised new mixed valence complexes of tetraazamacrocyclic ligands \([\text{Ni}(L)][\text{Ni}(L)\text{Br}_2]\text{ClO}_4\) \((L = [13]-, [14]-,\) and \([15]-\text{ane-N}_4;\) see page 56 for details of ligand structure).

6.2 Fluoride Complexes of Nickel(II)

6.21 Introduction

In the course of e.s.r. measurements on the Ni(III) diamine complexes \([\text{Ni}(L-L)_2X_2]X\) \((X = \text{Cl, Br}; L-L = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)\) dissolved in various aqueous media and frozen to -196°C, Russian workers found that hyperfine coupling to the axial (trans) halide ligands
could be resolved in the $g_{II}$ region, depending on the nature of the medium. In 40% HF, the coupling could be assigned to two $^{19}F$ ligands - that is, in this acid, the species $^{\text{trans}}[\text{Ni(en)}_2F_2]^+$ is formed. ($^{19}F; I = \frac{3}{2}, 100\%$).

With the equipment available for the current study, it was not possible to investigate such strongly polar solvents as 40% HF - indeed, even measurements in $\text{CH}_3\text{CN}$ were difficult (Chapter 3, page 167), so it was desired to investigate the synthesis of a solid Ni(III)-fluoro complex.

However, although the co-ordination chemistry of NiX$_2$ ($X = \text{Cl, Br, I}$) has been widely and extensively studied (Chapter 2, page 27), that of NiF$_2$ is virtually non-existent. It was therefore necessary to attempt the preparation of some representative Ni(II) fluoro-complexes with N-donor ligands and to investigate their spectroscopic properties, before carrying out oxidation experiments.

In this section, a short review of relevant aspects of fluoride-containing co-ordination compounds is included for comparison with the Ni(II) work.

6.22 Fluoride-containing Co-ordination Complexes

Papers describing metal complexes with fluoride as co-ligands are very sparse, especially by comparison with the analogues with chloride, bromide and iodide. Several factors probably contribute to this scarcity, both practical and theoretical. An example of the former type is the insoluble nature and chemical inertness of MF$_2$ ($M = \text{Fe, Co, Cu, Ni}$) lattices, due to their high thermo-dynamic stability. This, coupled with the fact that $F^-$ is a poor $\sigma$-donor (and its low position in the spectrochemical series), makes
the synthesis of complexes of MF₂ more challenging in many cases than complexes of MX₂ (X = Cl, Br, I). For example, the complexes [PtF(PRPh₂)₃][HF₂] (R = Ph or Me) were synthesised by the action of HF on [Pt(PRPh₂)₄] at -80°C. Recently, the thermal decomposition of hydrated metal tetrafluoroborate salts in the presence of certain ligands was found to yield fluoro-complexes in some cases. For example, heating [M(H₂O)₆][BF₄]₂ (M = Co, Cu) with 3,5-dimethylpyrazole(L) yielded '[MFL₂BF₄]' or MF₂L₂ depending on conditions. The former were dimers, [L₂MF₂ML₃]²⁺ with trigonal bipyramidal (M = Co) or square pyramidal (M = Cu) geometry.

Other complexes with similar ligands have been prepared by the same general method, and the area has recently been reviewed. The tetramers, in particular, are interesting; they consist of a cubic core with M and F at alternate corners. Subsequently it was discovered that identical products could be obtained by heating a suspension of hydrated metal fluoride with the appropriate ligands in an inert solvent. This route has also sufficed for the preparation of some Cu(II)-diamine complexes Cu(L-L)₂F₂, although the Cu-F interaction is very weak in these d⁹ complexes.

Although heating a mixture of [Ni(H₂O)₆][BF₄]₂ with the tridentate analogue of en, HN(CH₂CH₂NH₂)₂ (dien), in inert solvents resulted only in decomposition to NiF₂ and dien adducts of BF₃, the complex [Ni(en)₂(H₂O)(BF₄)]BF₄ is easily formed by loss of H₂O from [Ni(en)₂(H₂O)₂](BF₄)₂ - a rare example of co-ordinated BF₄⁻ and an example of possible intermediates in the formation of fluoro-complexes by the tetrafluoroborate decomposition route.

Ion-exchange, using Dowex resin, is another method of overcoming the reluctance of metal fluorides to react with ligands.
Octahedral, violet \([\text{Ni}(\text{meso-Me}_6\text{[14]aneN}_4)\text{F}_2]5\text{H}_2\text{O}\) was prepared by passing square planar, yellow \([\text{Ni}(\text{meso-Me}_6\text{[14]aneN}_4)](\text{ClO}_4)_2\) through a Dowex 1X8 column in the \(\text{F}^-\) form. The crystal structure established that the \(\text{F}^-\) ions were co-ordinated, rather than \(\text{H}_2\text{O}\) which is higher in the spectrochemical series, probably because the \(\text{H}_2\text{O}\) hydrogen-bonds to the amine protons.

6.23 Nickel(II) Fluoride Complexes - Results and Discussion

The reaction of a suspension of \(\text{NiF}_2.4\text{H}_2\text{O}\) (Ventron, reagent grade) with various diamines (1:3 mole ratio) in refluxing methanol gave pink-violet coloured solutions. After filtration from unreacted \(\text{NiF}_2\), removal of the solvent or precipitation with diethyl ether generally gave \([\text{Ni}(\text{L-L})_2\text{F}_2]\), in an unsolvated form, in good yield, as pink or blue powders.

On treatment of methanol solutions of these complexes with 0.5 mole equivalents of \(\text{NiF}_2.4\text{H}_2\text{O}\) with further refluxing, colour changes (pink-violet to dark blue) were noted, and the \(\text{NiF}_2\) dissolved. After filtration, precipitation with acetone or 2-propanol yielded blue materials analysing as \(\text{Ni}(\text{L-L})_2\text{F}_2\). (Analytical and physical data for all the complexes is shown in Table 6.231).

Similar reactions with diimine ligands \((\text{L-L} = \text{2,2'-bipyridyl}, \text{1,10-phenanthroline})\) also gave \([\text{Ni}(\text{L-L})_3\text{F}_2]\) and \([\text{Ni}(\text{L-L})_2\text{F}_2]\), as light pink and green powders respectively. Prolonged reflux was necessary for the formation of \([\text{Ni}(\text{L-L})_3\text{F}_2]\) in methanol with these ligands, followed by careful precipitation with 2-propanol and cooling to \(-20^\circ\text{C}\), otherwise the green \([\text{Ni}(\text{L-L})_2\text{F}_2]\) precipitated preferentially. Although the tris-ligand complexes were easily generated in water (cf the corresponding chlorides and bromides\(^{41}\)) they could not be isolated free of water of crystallisation even after drying in \textit{vacuo} at 80°C.
Attempts to prepare complexes of stoichiometry Ni(L-L)X₂ (L-L = en, pn) by refluxing NiF₂·4H₂O and the ligand (1:1 ratio) in methanol, or reaction of [Ni(L-L)₃]F₂ with NiF₂, 4H₂O in methanol or ethanol, failed. Only mixtures of Ni(L-L)₂F and NiF₂ were isolated by these procedures. However, the more sterically-demanding ligand Me₂NCH₂CH₂NMe₂ (tmen) easily formed Ni(tmen)F₂ on refluxing NiF₂·4H₂O with the ligand in 2-propanol, as a pale green solid.

The electronic spectra of the complexes [Ni(L-L)₃]F₂ (L-L = diamine)(Table 6.232) are similar to those of the analogues [Ni(L-L)₃]X₂ (X = Cl, Br, NO₃), and are typical of the octahedral 3d⁸ ion. Three main bands are observed in the diffuse reflectance and solution spectra, at ca 11, 18.5 and 25 x 10³ cm⁻¹, assigned (Figure 6.233) as due to \( ^3A_{2g} \rightarrow ^3T_{2g} \), \( ^3T_{1g} \) (\( ^3F \)) and \( ^3T_1 \) (\( ^3P \)) respectively.

Figure 6.233. Correlation diagram for triplet states of 8a₅d configuration.
Table 6.23 | Analytical and Physical Data for the Nickel(l1) Fluorides

<table>
<thead>
<tr>
<th>Complex</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%F</th>
<th>λR.</th>
<th>μe</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(en)₃]F₂</td>
<td>26.0(26.0)</td>
<td>8.5(8.7)</td>
<td>30.1(30.5)</td>
<td>12.3(11.7)</td>
<td>-</td>
<td>7.80</td>
<td>Light blue-pink</td>
</tr>
<tr>
<td>[Ni(pn)₃]F₂</td>
<td>34.1(33.9)</td>
<td>9.6(9.6)</td>
<td>26.1(26.5)</td>
<td>11.0(11.9)</td>
<td>-</td>
<td>2.85</td>
<td>Pink</td>
</tr>
<tr>
<td>[Ni(pd)₃]F₂</td>
<td>33.8(33.9)</td>
<td>9.6(9.6)</td>
<td>26.6(26.5)</td>
<td>11.0(11.9)</td>
<td>e</td>
<td>3.16</td>
<td>Light blue</td>
</tr>
<tr>
<td>Ni(en)₂F₂</td>
<td>21.8(22.2)</td>
<td>7.6(7.6)</td>
<td>26.0(25.9)</td>
<td>19.0(17.1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pn)₂F₂</td>
<td>29.2(29.4)</td>
<td>8.3(8.2)</td>
<td>22.8(23.0)</td>
<td>18.2(18.6)</td>
<td>p</td>
<td>360,376</td>
<td>Light pink</td>
</tr>
<tr>
<td>Ni(pd)₂F₂</td>
<td>29.5(29.4)</td>
<td>8.2(8.2)</td>
<td>23.2(23.3)</td>
<td>21.1(21.4)</td>
<td>e</td>
<td>2.94</td>
<td>Light pink</td>
</tr>
<tr>
<td>[Ni(bipy)₃]F₂</td>
<td>64.6(63.7)</td>
<td>4.7(4.7)</td>
<td>15.0(15.0)</td>
<td>10.0(10.0)</td>
<td></td>
<td></td>
<td>Light pink</td>
</tr>
<tr>
<td>[Ni(phen)₃]F₂</td>
<td>68.6(67.8)</td>
<td>3.7(3.7)</td>
<td>13.1(13.1)</td>
<td>23.2(23.2)</td>
<td></td>
<td></td>
<td>Light pink</td>
</tr>
<tr>
<td>[Ni(bipy)₂F₂]</td>
<td>50.0(50.0)</td>
<td>3.9(3.9)</td>
<td>13.1(13.1)</td>
<td>23.2(23.2)</td>
<td></td>
<td></td>
<td>Light green</td>
</tr>
<tr>
<td>[Ni(phen)₂F₂]</td>
<td>62.8(63.0)</td>
<td>3.3(3.3)</td>
<td>12.4(12.4)</td>
<td>23.2(23.2)</td>
<td></td>
<td></td>
<td>Light green</td>
</tr>
<tr>
<td>[Ni(tmed)F₂]</td>
<td>33.3(33.3)</td>
<td>3.3(3.3)</td>
<td>13.1(13.1)</td>
<td>23.2(23.2)</td>
<td></td>
<td></td>
<td>Green</td>
</tr>
</tbody>
</table>

(a) Calculated values in parentheses.
(b) * ca 1.5% difficulties were experienced with the "Alizarin Fluoride Blue" method of F analyses, which could have been caused by incomplete release of F⁻ ions during complex decomposition procedures.
(c) Measured at 298K by Gouy method; * ca 0.05 R.M.
(d) Complexes probably formulated [Ni₂(1-L)₂F₂]⁺; see text.
(e) Region obscured by ligand bands.
(f) *bipy* is 2,2'-bipyridine; *phen* is 1,10-phenanthroline.
(g) Assignment, based on comparison with spectra of chloro-complexes, somewhat tentative.
Table 6.23: Electronic Spectroscopic Data for the Nickel(II) Fluorides

<table>
<thead>
<tr>
<th>Complex</th>
<th>Diffuse Reflectance Spectra</th>
<th>Solution Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(en)₂]F₂</td>
<td>17.0 (sh), 18.2, 29.2, 35.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.7(4.7), 12.7(6.5)(sh), 18.5(9.5), 25.0(7.8), 29.6(19.6)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Ni(phen)₃]F₂</td>
<td>9.7(sh), 12.4, 17.4 (w,sh), 19.0, 24.9 (sh), 30.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18.2(16.8), 29.1(28.9)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Ni(pd)₂]F₂</td>
<td>12.5, 17.8, 28.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.6(8.5), 18.3(5.0), 29.4(15.4)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(en)₂F₂</td>
<td>18.1, 28.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.3(25.3), 27.9(39.0)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(pd)₂F₂</td>
<td>8.53(sh), 10.87, 17.84, 28.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10.2(3.0), 17.1(9.8), 27.6(16.0)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(bipy)₃F₂</td>
<td>18.9, 21.3(sh), 25.1(sh), 30.1(sh), 32.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.0(4.0), 19.2(5.3), 26.3(6.5), 32.7(10), 39.1(13.8), 41.3(62.8)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(pzpy)₃F₂</td>
<td>18.7, 25.1(sh), 30.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.0(7.8), 27.6(12.2)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(bipy)₂F₂</td>
<td>18.9, 21.3(sh), 25.1(sh), 30.1(sh), 32.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>12.3(3.6), 19.1(9.1), 29.2(1220)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(phen)₂F₂</td>
<td>19.2, 25.1(sh), 30.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.8(7.0), 13.1(sh)(3.4), 17.5(5.8), 23.3(sh)(7.3), 34.0(900)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(bipy)₂F₂</td>
<td>13.2, 17.0, 23.7, 28.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.9(7.0), 12.3(3.4)(sh), 18.0(6.0)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(pd)₂F₂</td>
<td>13.2, 16.9, 24.4(sh), 27.0(sh), 29.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.0(3.6), 13.3(sh)(5.2), 14.8(7.0), 25.8(3.6), 29.4(6.9), 30.9(8.5)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(phen)₂F₂</td>
<td>11.3, 16.9, 24.4(sh), 27.0(sh), 29.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.7(sh)(3.2), 10.7(3.4), 17.0(7.8), 27.6(12.2)</td>
</tr>
</tbody>
</table>

(a) Recorded on PE 554 and SF 700 machines - experimental details in Chapter 7, page 281.
(b) Recorded on a Beckman spectrophotometer at the University of Reading by Dr.D.Rice.
(c) Methanol solution.
(d) H₂O solution.
Sometimes, additional bands appear as shoulders on the main absorptions, particularly on the lowest energy maxima. As pointed out by Jorgensen, this area (11.0 - 13.0 \times 10^3 \text{ cm}^{-1}) corresponds to the energetic crossover point of the $^3T_{2g}$ and $^1E_g$ energy levels. These two levels cannot actually coincide; their minimum separation is $2k$ where $k$ is the energy of the interacting off-diagonal elements. The spin forbidden transition to the $^1E_g$ level will 'borrow' intensity from the spin allowed transition to the $^3T_{2g}$ level. Thus the shoulder may be due to the spin-forbidden transition to $^1E_g$.

Again, the spectra of the complexes Ni(L-L)$_2$F$_2$ (L-L = diamine) are notably similar to those of Ni(L-L)$_2$X$_2$ (X = Cl, Br, I). Since these complexes exhibit the halide-bridged dimeric structure [Ni$_2$(L-L)$_4$X$_2$]X$_2$, with $C_{2v}$ symmetry at the metal, it is very likely that the fluorides are similar, precluding any detailed analysis of the spectra. The similarity of the methanol solution spectra to those of the solids indicates that the structure is probably maintained in solution; this is the case for [Ni$_2$(L-L)$_4$X$_2$]X$_2$ (X = Cl) as indicated by molecular weight measurements.

Solution and diffuse reflectance spectra, together with molecular weight and conductivity studies, suggest that the complexes Ni(L-L)$_2$X$_2$ (L-L = 2,2'-bipyridyl;1,10-phenanthroline; X = Cl, Br) are monomeric and pseudo-octahedral with, most probably, $C_{2v}$ symmetry (cis-halides). On the basis of spectral comparison, a similar structure is probable for Ni(L-L)$_2$F$_2$.

Finally, the electronic spectra of Ni(tmen)F$_2$ are strongly indicative of tetrahedral co-ordination and the coincidence of bands in the diffuse reflectance and solution spectra suggest a monomeric structure. Magnetic moment determinations (Gouy or Evans method) were consistent with this, and all the other, formulations (Table 6.23).
6.24 Oxidation Reactions

A major difficulty with the oxidation of these fluoro-complexes is that common oxidants (for example, Cl₂, HNO₃, Br₂) give potential donor ligands (Cl⁻, Br⁻, NO₃⁻) of comparable or significantly higher position in the spectrochemical series than F⁻. An oxidant was required, therefore, which did not exhibit this undesirable tendency, but which could be used in solution in organic solvents, enabling oxidation of nickel(II) complexes either in solution or in suspension in an inert solvent. Obviously, the very reactive and powerfully oxidising elemental fluorine could not be used as it would almost certainly oxidise the organic ligands.

Recently, a report was published describing the product of careful fluorination of aqueous solutions of M₂SO₄ (M = Cs, Rb), which yielded MSO₄F as a white solid (Caesium fluoroxysulphate). This was soluble without immediate decomposition in dry, acetamide-free CH₃CN.

A sample of CsFOSO₃ was synthesised by the published procedure and stored at -20°C in a plastic container. Its reactions with examples of the Ni(II) diamine complexes were studied. Aqueous solutions of the complexes were seemingly unaffected - only a small amount of decomposition was noted. Suspensions of the complexes were then treated with CsFOSO₃ in CH₃CN (electrochemical grade; see Chapter 7, page 294). Immediate reaction ensued, the blue Ni(L-L)₂F₂ complexes turning pale green. However, the products had no e.s.r. signal and their diffuse reflectance spectra were inconsistent with a Ni(II)-Ni(IV) mixed valence complex; no intervalence charge transfer band could be observed and only the weak bands consistent with pseudo-octahedral high-spin Ni(II) were present. Infra red spectra of the crude products
showed significant changes in the ligand modes, indicating that the oxidant had reacted with the ligand.

Solutions of the diamine complexes in methanol were treated with solid CsFOSO$_3$. No reaction occurred even after several hours stirring at room temperature. Similar results were obtained with the di-imine complexes and with [Ni(tmen)F$_2$]. Attempts to use other oxidants (e.g., K$_2$S$_2$O$_8$, HNO$_3$, Ce(SO$_4$)$_2$) under various conditions also failed.

The results of this study are therefore necessarily inconclusive. It is possible that with a more selective oxidant, Ni(III) and/or mixed valence Ni(II)-Ni(IV) fluoro-complexes could be synthesised. The negative results with the FOSO$_3^-$ ion were due mainly to the fact that it is too powerful an oxidant. A limited range of oxidants which are essentially mild fluorinating agents exist, some of which (e.g., XeF$_2$) could be of use.
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CHAPTER 7: EXPERIMENTAL DETAILS
7.1 Physical Measurements

Infra-red Spectra

Infra-red spectra were recorded for nujol mulls between sodium chloride or potassium bromide discs (4000 - 600 or 4000 - 400 cm\(^{-1}\) respectively), or between polythene plates, previously checked for transparency in the region (500-170 cm\(^{-1}\)), using a Perkin-Elmer 580B infra-red spectrometer.

The nujol was dried by heating it under nitrogen with sodium pellets until the sodium melted. It was then stirred for thirty minutes, cooled and stored over the sodium. Assignments of bands as predominantly metal-halogen stretches were made by careful comparison, where practicable, of a series of isostructural halide and ligand derivatives.

Nuclear Magnetic Resonance Spectra

Routine \(^1\)H n.m.r. spectra (of, for example, ligands and ligand derivatives) were recorded on Perkin-Elmer R12 or R24 spectrometers (60 MHz, continuous wave) using tetramethylsilane as internal reference.

\(^{19}\)F and \(^{31}\)P n.m.r. spectra were recorded on a Bruker 360 MHz spectrometer, referenced to external \(\text{C}_6\text{F}_{6}\) and 85% \(\text{H}_3\text{PO}_4\) respectively.

Electronic Spectra

Solution spectra were obtained using matched 1 cm path length quartz cells on a Perkin-Elmer 554 spectrometer over the range ca 13,000-40,000 cm\(^{-1}\). A few near infra-red spectra were recorded using a Pye-Unicam SP700 spectrometer (8,000-15,000 cm\(^{-1}\)).
Molar extinction coefficients were calculated using the Beer-Lambert Law:

\[ A = \varepsilon l = \log_{10} \frac{I_0}{I} \]

where
\[ c = \text{concentration (mol dm}^{-3}\text{)} \]
\[ l = \text{pathlength of sample (cm)} \]
\[ A = \text{absorbance}, \]
\[ I_0, I = \text{intensities of incident and transmitted radiation; respectively} \]
\[ \varepsilon = \text{molar extinction coefficient (dm}^2\text{mol}^{-1}\text{cm}^{-1}) \]

Diffuse reflectance spectra were measured with the appropriate spectrometer attachments (38,000 - 13,000 cm\(^{-1}\)). Barium sulphate (dried in vacuo at 80°C) was used as diluent and reference. Near infra-red diffuse reflectance spectra were measured using nujol mulls spread on filter paper, with a pure nujol-soaked paper as reference, in the solution attachment of the SP700 spectrometer. Nujol mulls between glass plates, mounted on Ba SO\(_4\) compacted in the sample compartment, were employed for air- or moisture-sensitive samples which were prepared in a dry box (q.v.).

**Molar Conductivities**

The conductivities of ca 10\(^{-3}\) M solutions were determined at 293K using a Pye Conductance Bridge (Catalogue No. 11700). A glass cell fitted with 1 cm\(^2\) platinised electrodes was employed. The cell constant was determined by measuring the conductance (1/R; R = resistance) of various concentrations of aqueous KCl. The specific conductance of KCl as a function of temperature was obtained from a standard text.\(^1\)
Cell constant \((\text{cm}^{-1})\) = resistance \((\Omega)\) x specific conductivity \((\text{cm}^{-1} \text{ cm}^{-1})\).

Molar conductivity \((\Lambda_N)\) \(\text{cm}^2 \text{ mol}^{-1}\) =
\[
\frac{\text{conductance} \times 10^3 \times \text{cell constant}}{\text{molarity of solution}}
\]

**Magnetic Measurements**

Solid state magnetic susceptibilities were obtained using a Gouy balance and used to calculate the magnetic moment \((\mu)\) at 293K.

\[\mu \text{ (Bohr Magnetons)} = 797.5 \sqrt[3]{\chi_M} \text{T}\]

Hg[Co(SCN)₄] was used as calibrant and molar susceptibilities were corrected for diamagnetism using Pascal's Constants.² Solution measurements were made using the method of Evans,³ which employs the shift in the resonance of proton signals in the solvent in which a paramagnetic substance is dissolved, relative to the resonance of the pure solvent.

**Mass Spectra**

Mass spectra were recorded at 70 eV on an AEI MS30 by the Mass Spectral service of this Department.

**Elemental Analysis**

Carbon, hydrogen and nitrogen analyses were performed on an F and M Analyser Model 185 by Dr. W. Levason. Halide was determined by AgNO₃ conductimetric titration⁴ which determines ionic
halide only. (That is, not organohalide or chlorine in ClO$_4^-$ ions). Complexes were decomposed by warming in dilute ammonia solution (in the presence of Na$_2$S$_2$O$_3$ as a mild reducing agent in the case of Ni(III), Ni(IV) and polyiodide complexes). Fluorine was determined spectrophotometrically using the 'Alizarin Fluorine Blue' reagent. $^5$

**Thermogravimetric Analysis**

Thermogravimetric measurements were performed at the Royal Military College of Science, Shrivenham, using a Stanton-Redcroft TG/750/770 with a STA/780 thermal analyser under dynamic argon atmosphere.

7.2 Electrochemical Measurements

Electrochemical measurements, made with the assistance of Mr. D. Pearce, were recorded using a Hi-Tek D.T. 2101 potentiostat and a Hi-Tek PPR1 waveform generator. Current-potential and current-time responses were recorded using a Hewlett-Packard 7015A chart recorder. The cyclic voltammetric measurements were made employing a carbon working electrode (area 0.064 cm$^2$), a platinum wire secondary electrode and a standard calomel electrode (SCE) as reference. A two-compartment three-electrode cell utilising a Luggin capillary for probing the working compartment from the reference compartment was used throughout. Electrochemical reversibility was assessed by measuring the difference in potential of the oxidation and reduction components of the observed wave (which under ideal conditions should be ca 60 mV, but which can range from 65-80 mV for an electrochemically reversible process) and the relative heights of each component of the wave (the ratio of which should be approximately unity for a reversible process). Rigorous assessment of reversibility by the observation of the variation in these
parameters with scan rate was not performed as the time available for electrochemical experiments was limited.

Acetonitrile for electrochemical work was purified by the following method: Acetonitrile (Aldrich reagent grade; 1.5L) was refluxed over alkaline potassium permanganate (45g KMnO₄, 15g anhydrous Na₂CO₃) overnight, then distilled under nitrogen onto fresh calcium hydride (2g). After refluxing over the calcium hydride for 3h, it was distilled off and stored under nitrogen, the first and last fractions being discarded.

Tetrabutylammonium tetrafluoroborate, Bu₄NBF₄, was prepared by mixing hot solutions of [Bu₄N]HSO₄ (Aldrich) (50g) and NaBF₄ (16g) in distilled water. The white precipitate of Bu₄NBF₄ was filtered off from the cooled solution and recrystallised from EtOH/H₂O, then dried overnight in vacuo at 80°C. Tetraethylammonium chloride was obtained commercially (Eastman-Kodak) and recrystallised twice from CH₃CN - Et₂O then dried in vacuo at 80°C.

A 0.2M solution of base electrolyte was employed throughout, and made up to .002M in the complex under investigation immediately before the experiment. Solutions were purged with dry nitrogen where necessary, and the cell was equipped for purging also.

7.3 Electron Spin Resonance Spectra

Electron spin resonance spectra were obtained using a Varian E-4 X-band spectrometer, employing 100 kHz modulation and pitch-KCl as reference. Room temperature spectra were recorded on solid samples or CH₂Cl₂ solutions in quartz glass tubes (ca 3mm internal diameter) suspended in the instrument cavity in
such a manner as to enable the cavity to be tuned with as high a microwave power as feasible, although this was not necessary for the more responsive materials. Spectra of solutions in polar solvents (CH$_3$CN or CH$_3$CN - CH$_2$Cl$_2$ mixtures) were recorded in narrow quartz tubes (ca 1 mm internal diameter). For low temperature spectra, a small Dewar flask of quartz glass with a suitably transparent section designed to fit into the microwave cavity was employed. The samples (solids or solutions) were frozen quickly to -196°C in liquid N$_2$ and placed in the Dewar, also containing liquid N$_2$. During the recording of spectra the cavity was usually purged with dry nitrogen; these Dewars are relatively inefficient and condensation absorbs microwave radiation strongly. The tubes were capped with small rubber seals to prevent the condensation of liquid oxygen onto the sample. Liquid oxygen can cause explosions, damaging or breaking the delicate (and expensive) Dewars. In recording all spectra, microwave frequency was fixed and the magnetic field varied, as is standard practise in e.s.r. spectroscopy. Spectra were recorded as first derivatives, as is also standard practise.

7.4 Inert Atmosphere Techniques

For those complexes which are oxygen- or moisture-sensitive, special techniques are required during their synthesis and isolation, and during attempts to obtain physical or spectroscopic data. During this work, use was made of Schlenk techniques employing a double-manifold (vacuum and nitrogen) system for synthesis and a large, efficient dry box for the manipulation of complexes during data collection. Specific details of the apparatus used in the present study have previously been described $^6$ and a comprehensive account of experimental techniques for the handling of air-sensitive materials is available.$^7$
7.5 Reagents

Solvents

Tetrahydrofuran (Fluka) was dried by refluxing over sodium wire, and distillation from sodium benzophenone ketal, or refluxing over sodium, distillation onto LiAlH$_4$ and further distillation therefrom. Diethyl ether and cyclohexane were dried by storage over freshly-extruded sodium wire. Methylene chloride, chloroform, carbon tetrachloride and petroleum ether (40° - 60°C boiling range) were dried by reflux over and distillation from CaH$_2$. Where necessary, alcohols were dried by reflux over magnesium turnings followed by distillation from the resultant magnesium alkoxides.

Metal Salts

The following were used as supplied; NiBr$_2$.3H$_2$O, NiCl$_2$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O, Ni(ClO$_4$)$_2$.6H$_2$O, NiSO$_4$.7H$_2$O (B.D.H. Ltd., Poole). Hexaaquonickel(II) iodide was prepared by the combination of stoichiometric amounts of Ni(NO$_3$)$_2$.6H$_2$O and NaI in warm 1-butanol. After cooling, the NaNO$_3$ was filtered off and the NiI$_2$.6H$_2$O used in solution. Hexaaquonickel(II) tetrafluoroborate was made by the addition of 42% HBF$_4$ to Ni(CO$_3$)$_4$.nH$_2$O, followed by evaporation to dryness. The [Ni(H$_2$O)$_6$](BF$_4$)$_2$ was recrystallised before use from ethanol. Cobalt(II) salts were used as supplied (BDH Chemicals Ltd., Poole).

Palladium(II) chloride and Na$_2$Pd Cl$_4$ were used as supplied (Johnson Matthey Chemicals Ltd.). The [Pd(MeCN)$_2$Cl$_2$] was prepared by refluxing PdCl$_2$ in MeCN, cooling and filtering off the yellow product.

All other reagents were of the best available
commercial grade and where necessary were purified by recognised literature procedures.

7.6 Preparation of Starting Materials; Complexes of Ni(0) and Ni(II)

7.61 Complexes of Nickel(0)

The following complexes were prepared by literature procedures, involving the combination of Ni(CO)$_4$ and the ligand in benzene or pentane under an inert atmosphere. (Great care is required in handling the very toxic Ni(CO)$_4$);

\[
[Ni(CO)]_2(o-C_6H_4(AsMe_2)_2) \quad (v_{CO} 2011, 1952 \text{ cm}^{-1} \text{ in cyclohexane})
\]

\[
[Ni(CO)]_2(o-C_6H_4(PMe_2)_2) \quad (v_{CO} 1990, 1927 \text{ cm}^{-1} \text{ in cyclohexane})
\]

\[
[Ni(CO)]_2(Me_2PCH_2CH_2PMe_2) \quad (v_{CO} 1989, 1929 \text{ cm}^{-1} \text{ in cyclohexane})
\]

Satisfactory C and H analyses were obtained for these materials.

Attempts to circumvent the use of the toxic carbonyl by refluxing [Ni(CO)$_2$(PPh$_3$)$_2$]$^*$ with the ligands in benzene failed; the products had unsatisfactory C and H analyses and their infrared spectra were inconsistent with the required dicarbonyls.

$^*$ [Ni(CO)$_2$(PPh$_3$)$_2$] may be prepared easily by the reduction of [Ni(PPh$_3$)$_2$I$_2$] with CO in an autoclave under moderate pressure.

A sample of this Ni(0) complex was kindly supplied by Dr. K.C. Smith.
7.62 Synthesis of Nickel(II) Complexes

During the course of this study, a very large number of nickel(II) complexes was prepared to enable a wide range of complexes to be investigated in attempts at the preparation of high oxidation state materials or polyiodides. Although electronic spectra, infra red and far-infra red spectra, C and H analyses and (where necessary) magnetic moments, conductivity measurements and $^1$H n.m.r. spectra were recorded for all of these materials for comparison with the spectra of oxidation products, this data will not be reproduced here in detail. Tables 7.62 (1-4) summarise the spectroscopic properties of the Ni(II) complexes and references to their preparation. Only those complexes not previously synthesised will be described here.

7.621 Ni(L)$_2$X$_2$

(a) Preparation of new complexes, and modified synthesis of known complexes

Dibromobis(triethylarsine)nickel(II) [Ni(AsEt$_3$)$_2$Br$_2$]

A suspension of powdered anhydrous NiBr$_2$ (0.6 g, 2.7 mmol) in dry CH$_2$Cl$_2$ (25 cm$^3$) was treated with AsEt$_3$ (0.8 g, 5 mmol) under nitrogen. After stirring for 48 hours, the dark green solution was filtered (Schlenk stick) and the solvent slowly removed in vacuo yielding dark green-brown crystals. These were filtered off and dried in vacuo. 1.09 g, 80%. The corresponding chloride was made similarly as a purple-red powder.

Dibromobis(dimethylamine)nickel(II) [Ni(NMe$_2$H)$_2$Br$_2$]

The ligand (2 cm$^3$) was distilled in vacuo on to anhydrous
NiBr₂ (3.3 g, 15 mmol). After shaking at room temperature for 1 hour, the excess Me₂NH was removed in vacuo and the green powder stored under N₂.

**Dibromobis(2-dimethylphosphinoanisole)nickel(II) [Ni(o-C₆H₄(PMe₂)(OMe))₂Br]**

The ligand (0.34 g, 2 mmol) was added to a deoxygenated solution of NiBr₂.3H₂O (0.272 g, 1 mmol) in warm methanol (6 cm³). After cooling to -10°C, the reflective red crystals were filtered off, washed with diethyl ether and dried in vacuo 0.4 g, 72%.

**Dibromobis(tri-n-propylphosphine oxide)nickel(II) [Ni(Pr₃P=O)₂Br₂]**

The ligand (0.35 g, 2 mmol) was added to a warm solution of NiBr₂.3H₂O in 1-butanol (0.272 g, 1 mmol; 20 cm³). Triethyl orthoformate (2 cm³) was added and the mixture refluxed for thirty minutes. Solvent was removed in vacuo, leaving a sticky blue oil. All attempts to solidify this by stirring with diethyl ether and other inert solvents, or recrystallisation at low (-80°C) temperatures failed. Electronic spectra were recorded of the oil. The corresponding chloride was similarly prepared, also as an oil. Both complexes are moisture-sensitive and decomposed by donor solvents.

(b) Comments

The infra-red and electronic spectra of the [Ni(L)₂X₂] (L = trialkylphosphine; X = Cl, Br, I) were entirely consistent with the literature examples, described in Chapter 2, confirming their stereochemistry as trans-planar. Similarly, for L = dialkylarylpophosphate, this description applies. Earlier authors have described [Ni(Ph₂PMe)₂Cl₂] as exclusively planar in the solid state, while the corresponding bromide is tetrahedral. Electronic and infra red spectra
(Table 7.621) confirm these assignments, although in solution in
CH₂Cl₂ it is clear that an equilibrium between planar and tetrahedral
forms exists for the bromide.

The new complexes of Et₃As are clearly analogous to
those of Et₃P, except that the "d-d" transitions are shifted to
lower energy, indicative of the lower ligand field of the arsine.

Finally, the electronic spectra of the complexes
of Pr₃P = 0 are entirely consistent with the expected tetrahedral
gometry.

7.622 Ni(L-L)X₂

(a) New complexes; preparative methods

Dibromo(o-methylthiophenylidiphenylphosphine)nickel(II),
[Ni{q-C₅H₄(PPh₂)(SMe)Br₂}

Anhydrous NiBr₂ (0.65g, 3 mmol) was stirred for 2 days
with the ligand (0.62g, 2 mmol) in CH₂Cl₂ (50 cm³) during which
time a deep purple-red solution formed. Unreacted NiBr₂ was
filtered off, the solution concentrated to ca 15 cm³, cyclohexane
(15 cm³) slowly added and the mixture cooled to -20°C overnight.
The red-purple crystals were filtered off, recrystallised from
CH₂Cl₂/C₆H₁₂ and dried in vacuo. 0.84g, 80%.

Dichloro(1,4-bis(diphenylphosphino)butane)nickel(II),
[[Ni(Ph₂P(CH₂)₄PPh₂Cl₂)]₃]

To a solution of the ligand (0.85g, 2 mmol) in 1-butanol
(30 cm³) was added NiCl₂·6H₂O (0.48g, 2 mmol) in the same solvent
(15 cm³). The mixture was refluxed briefly whereupon a light purple
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<tr>
<th>Complex</th>
<th>T.R. (cm⁻¹)</th>
<th>Electronic Spectra 10³ cm⁻¹ (λ, dm³ mol⁻¹ cm⁻¹)</th>
<th>Analysesμ</th>
<th>Referenceμ</th>
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<tr>
<td>[Ni(PMe₃)₂Cl₂]</td>
<td>400 vs</td>
<td>21.00(490), 22.93(12,600), 37.3(1560)(sh)</td>
<td>25.1(25.6)</td>
<td>2, 3, 10</td>
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<tr>
<td>[Ni(PMe₃)₂Br₂]</td>
<td>310 μm</td>
<td>18.12(1080), 21.55(650), 26.18(5500), 40.98(20,000)</td>
<td>19.4(19.4)</td>
<td>2, 3, 10</td>
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<td>[Ni(PMe₃)₂Cl₂]</td>
<td>400 vs</td>
<td>20.92(470), 27.32(16,200), 35.2(sh)(5000)</td>
<td>39.3(39.4)</td>
<td>2, 3, 10</td>
</tr>
<tr>
<td></td>
<td>208 μg</td>
<td>36.8(77)</td>
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<td>[Ni(PMe₃)₂Br₂]</td>
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<td>[Ni(PMe₃)₂Br₂]</td>
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<td>[Ni(PPh₃)₂Cl₂]</td>
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<td>[Ni(PPh₃)₂Br₂]</td>
<td>5(300μg(br)</td>
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<td>410 vs</td>
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<td>47.6(47.7)</td>
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<td>[Ni(PPh₃)₂Br₂]</td>
<td>311 vs</td>
<td>19.40(120), 25.64(5000), 35.7(sh)(2000)</td>
<td>38.7(38.9)</td>
<td>6, 14</td>
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<td></td>
<td>242(br)</td>
<td></td>
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<tr>
<td>[Ni(PPh₃)₂Cl₂]</td>
<td>409 vs</td>
<td>20.46(510), 27.17(13,600), 40.00(11,700)</td>
<td>52.6(52.0)</td>
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<td>44.6(44.6)</td>
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<td>[Ni(PCy₃)₂Cl₂]</td>
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<td>18.8(160), 25.0(710), 39.4(121000)</td>
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<td>[Ni(PCy₃)₂Br₂]</td>
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<td>17.30(164), 21.1(sh)(160)</td>
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<td>6, 14</td>
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<th>Compound</th>
<th>ν&lt;sub&gt;Ni-X&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;Ni-Me&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;Ni-P&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<td>300 (br)</td>
<td>19.30(160), 25.50(1300), 34.9(250)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>43.3(43.3), 48.1 (4.7)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>[Ni(Ph&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;CMe&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Ph)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
<td>405 (s&lt;sup&gt;b&lt;/sup&gt;)</td>
<td>19.5 (2h)&lt;sup&gt;b&lt;/sup&gt;, 25.3(26.7)&lt;sup&gt;b&lt;/sup&gt;, 35.2&lt;sup&gt;b&lt;/sup&gt;, 46&lt;sup&gt;b&lt;/sup&gt;,</td>
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<td>[Ni(Ph&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;CMe&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Ph)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
<td>287 (br)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.8(210), 18.9(310), 17.9(3400), 36.2&lt;sup&gt;b&lt;/sup&gt;(3900)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>17.4, 18.5, 25.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>55.1 (51.9), 4.7 (4.1)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>8.8, 11.0, 18.7&lt;sup&gt;b&lt;/sup&gt;, 18.0, 25.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>65.9 (65.9), 4.7 (4.7)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>265 (br)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.0, 10.8, 14.9&lt;sup&gt;b&lt;/sup&gt;, 17.1, 22.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>56.1 (58.2), 4.2 (4.1)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>-</td>
<td>7.3 (29), 13.3&lt;sup&gt;b&lt;/sup&gt;, 15.5 (400), 20.8 (22)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>31.5 (31.8), 6.4 (6.7)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>18.05 (400), 21.8 (200), 39.7 (20000)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>22.1 (22.1), 5.9 (5.6)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>[Ni(dpmm)&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;]</td>
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<td>15.3, 15.1, 15.3&lt;sup&gt;b&lt;/sup&gt;, 20.6&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>[Ni(dpmm)&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>218</td>
<td>16.56 (480), 22.3 (220), 27.6 (20000), 37.1 (24700)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>26.4 (26.7), 5.4 (5.3)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>[Ni(dpmm)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>-</td>
<td>13.3, 14.8, 23.7&lt;sup&gt;b&lt;/sup&gt;, 15.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.5 (15.5), 4.4 (4.5)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>23.8, 11.6&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>22.7, 11.1&lt;sup&gt;b&lt;/sup&gt;, 36.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
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</table>

(a) -Me groups non-co-ordinated; see Chapter 3.
(b) The samples prepared in this study contain either tetrahedral or square-planar isomers depending on X; see Experimental section.
(c) Red, square planar form (c) tetrahedral form; see Experimental section.
(d) Obtained only as oils, in a impure form; hence no analyses or f.t.r. data.
(e) ν<sub>Ni-X</sub> except (g) ν<sub>Ni-P</sub>.

(h) ν<sub>Ni-X</sub> tetrahedral form.
(i) References from Chapter 2.
(j) CH<sub>2</sub>Cl<sub>2</sub> solutions except (k) diffuse reflectance spectra.
(k) Found (calc.).
(l) in acetone.
(m) qualitative spectra in CH<sub>2</sub>Cl<sub>2</sub>.
### Table 7 622 Ni(II)

<table>
<thead>
<tr>
<th>Complex</th>
<th>I.R. (cm⁻¹)</th>
<th>Electronic Spectra $10^3$ cm⁻¹ (λ, dm⁻¹ mol⁻¹ cm⁻¹)</th>
<th>Analyses</th>
<th>Colour</th>
<th>References</th>
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<tbody>
<tr>
<td>[Ni(P₂C₂H₂P₂P₂H₂)Cl₂]</td>
<td>311(s), 355(m)</td>
<td>21.3(1600), 30.5(sh) (1100)</td>
<td>58.2(58.4), 4.2(4.1)</td>
<td>Red-purple</td>
<td>27(1)</td>
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<tr>
<td>[Ni(P₂C₂H₂P₂P₂H₂)Br₂]</td>
<td>275(m), 261(w)</td>
<td>20.4(1900), 28.3(670), (sh), 30.9(1000)</td>
<td>49.8(49.8), 3.6(3.7)</td>
<td>Purple</td>
<td>27(1)</td>
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<td>[Ni(P₂C₂H₂P₂P₂H₂)Cl₂]</td>
<td>341, 327(s)</td>
<td>23.8(1170), 31.5(2600),(sh), 32.2(17,800)</td>
<td>59.2(59.2), 4.7(4.5)</td>
<td>Orange</td>
<td>26(1)</td>
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<td>[Ni(P₂C₂H₂P₂P₂H₂)Br₂]</td>
<td>21.2(2500), 26.5(460)</td>
<td>347, 312</td>
<td>50.3(50.65), 3.8(3.9)</td>
<td>Dark Red</td>
<td>26(1)</td>
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<td>[Ni(P₂C₂H₂P₂P₂H₂)Cl₂]</td>
<td>21.4(670), 25.9(500),(sh), 33.0(7600),(sh)</td>
<td>347, 312</td>
<td>50.3(50.65), 3.8(3.9)</td>
<td>Dark Red</td>
<td>26(1)</td>
</tr>
<tr>
<td>[Ni(P₂C₂H₂P₂P₂H₂)Cl₂]</td>
<td>20.6(820), 25.5(2100), 33.3(11,000)</td>
<td>23.8(2000), 36.1(27,000)</td>
<td>59.2(59.4), 4.2(4.2)</td>
<td>Orange-brown</td>
<td>30</td>
</tr>
<tr>
<td>[Ni(P₂C₂H₂P₂C₂H₂P₂H₂)Br₂]</td>
<td>333, 312(a)</td>
<td>21.2(1900)</td>
<td>50.9(50.8), 3.4(3.6)</td>
<td>Brown</td>
<td>30</td>
</tr>
<tr>
<td>[Ni(P₂C₂H₂P₂C₂H₂P₂H₂)Cl₂]</td>
<td>328, 289(a)</td>
<td>12.3, 18.4, 19.4, 25.5(sh), 26.6</td>
<td>60.3(60.5), 5.0(5.1)</td>
<td>Light grey</td>
<td>E</td>
</tr>
<tr>
<td>[Ni(P₂C₂H₂P₂C₂H₂P₂H₂)Br₂]</td>
<td>255, 231(s)</td>
<td>11.4, 16.9, 18.3, 24.4, 29.4</td>
<td>52.5(52.1), 4.4(4.4)</td>
<td>Light green</td>
<td>28</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂C₂H₂P₂H₂)Cl₂]</td>
<td>364, 337(s)</td>
<td>21.1(1500), 26.0(700), 34.7(24,000)</td>
<td>61.9(62.5), 4.4(4.2)</td>
<td>Yellow</td>
<td>31(1)</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂C₂H₂P₂H₂)Br₂]</td>
<td>294, 252(m)</td>
<td>19.7(600), 23.6(380), 29.3(sh)(12,000)</td>
<td>53.9(54.1), 3.2(3.6)</td>
<td>Orange</td>
<td>31(1)</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂C₂H₂P₂H₂)(SMe₂)Cl₂]</td>
<td>300, 282(ω)</td>
<td>18.8(900), 24.4(760), 31.7(sh)(3900)</td>
<td>51.8(52.1), 3.7(3.9)</td>
<td>Red-purple</td>
<td>46</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂P₂C₂P₂H₂)(SMe₂)Cl₂]</td>
<td>294(s), 286(ω)</td>
<td>21.2(1500), 26.0(700), 34.7(24,000)</td>
<td>43.6(43.4), 3.0(3.3)</td>
<td>Purple</td>
<td>E</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂P₂C₂P₂H₂)(SMe₂)Br₂]</td>
<td>248(br) (M)</td>
<td>19.8, 25.0, 27.2(sh), 38.8</td>
<td>28.6(28.7), 3.7(3.8)</td>
<td>Orange</td>
<td>E</td>
</tr>
<tr>
<td>[Ni(P₂C₂H₂P₂C₂H₂P₂H₂)(SMe₂)Cl₂]</td>
<td>362, 317(m)</td>
<td>23.2(1200), 34.3(3300), 40.7(12,600)</td>
<td>26.0(25.8), 6.0(5.8)</td>
<td>Yellow-Orange</td>
<td>34</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂C₂P₂H₂)(SMe₂)Br₂]</td>
<td>302, 262 (M)</td>
<td>Insoluble</td>
<td>17.7(17.8), 4.1(4.0)</td>
<td>Red-brown</td>
<td>34</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂P₂C₂H₂P₂H₂)(SMe₂)Br₂]</td>
<td>219, 255</td>
<td>19.0(700), 28.1(6500)(sh), 34.0(7100)(sh)</td>
<td>51.0(50.8), 3.2(3.4)</td>
<td>Purple</td>
<td>32</td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂P₂C₂H₂P₂H₂)(SMe₂)Br₂]</td>
<td>18.7(1500), 24.8(1600), 34.0(18,000)</td>
<td>47.0(47.3), 3.6(3.7)</td>
<td>Purple</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>[Ni(C₂H₂P₂P₂C₂H₂P₂H₂)(SMe₂)Br₂]</td>
<td>18.7(1500), 24.8(1600), 34.0(18,000)</td>
<td>47.0(47.3), 3.6(3.7)</td>
<td>Purple</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>

**Continued.....**
Table 7.622 Ni(II) : Notes

(a) Includes those complexes newly synthesised in this work. This applies to all the Ni(II) Tables.

(b) $v_{\text{Ni-X}}$ except where otherwise stated; this work.

(c) Complex insoluble

(d) $\text{CH}_2\text{Cl}_2$ solution.

(e) Acetone solution.

(f) References are to preparative details only, and are from Chapter 2. In many cases, spectroscopic data has not previously been reported. For consistency, data from this study only has been included here.

(g) Non-electrolyte in $10^{-3}$ M $\text{ClCH}_2\text{CH}_2\text{Cl}$. 

\begin{table}
<table>
<thead>
<tr>
<th>Complex</th>
<th>$v_{\text{Ni-X}}$ (cm$^{-1}$)</th>
<th>$\delta$ (cm$^{-1}$)</th>
<th>$\beta$ (cm$^{-1}$)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\gamma$ (cm$^{-1}$)</th>
<th>$r$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}^{2+}$</td>
<td>34.5 (17,000)</td>
<td>26.9 (22,500)</td>
<td>33.1 (23,000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>45.1 (41.2)</td>
<td>3.1 (3.2)</td>
<td>Purple</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>43.7 (41.9)</td>
<td>3.2 (3.4)</td>
<td>Purple</td>
<td>28(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>30.1 (6500)</td>
<td>3.5 (1.5)</td>
<td>Purple</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>46.8 (45.8)</td>
<td>2.8 (2.8)</td>
<td>Purple-blue</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>39.2 (39.2)</td>
<td>2.8 (2.8)</td>
<td>Purple-blue</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>66.9 (47.2)</td>
<td>3.5 (1.5)</td>
<td>Purple</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>42.1 (42.4)</td>
<td>3.0 (2.8)</td>
<td>Dark blue</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>42.1 (42.4)</td>
<td>3.0 (2.8)</td>
<td>Dark blue</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{2+} \cdot \text{Ph}_2 \cdot \text{Ph}_2$</td>
<td>42.1 (42.4)</td>
<td>3.0 (2.8)</td>
<td>Dark blue</td>
<td>31(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$E$ = see Experimental section.

(t) tentative assignment

(o) obscured by strong ligand modes.
powder was deposited. Upon drying in vacuo this became light fawn.
1.1g, 84%.

Dichloro(o-dimethylphosphinophenyldimethylstibine)nickel(II)
[\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2); \text{Cl}_2)]

The ligand (0.145g, 0.5 mmol) in dichloromethane (5 cm$^3$) was added to NiCl$_2$.6H$_2$O (0.12g, 0.5 mmol) in ethanol (30 cm$^3$). The red solution was reduced in volume to ca 10 cm$^3$, and cyclohexane added slowly. Red-orange crystals separated, which were filtered off, rinsed with diethyl ether and dried in vacuo. 0.14g, 65%.

(b) Comments

The far infra-red and electronic spectra of the complexes [\text{Ni}(L-L)X$_2$] (L-L = \text{Ph}_2P(\text{CH}_2)_n\text{PPh}_2; n = 1,2,3; \text{cis} \text{Ph}_2\text{PCHCHPPh}_2; \text{C}_6\text{H}_4(\text{PPh}_2)_2, \text{C}_6\text{H}_4(\text{PPh}_2)(\text{SMe}), \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2; X = \text{Cl,Br}. L-L = \text{C}_6\text{H}_4(\text{AsPh}_2)(\text{PPh}_2), \text{C}_6\text{H}_4(\text{AsPh}_2)_2, \text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2, \text{cis} \text{Ph}_2\text{AsCHCHAsPh}_2, \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2; X = \text{Br, I}) confirm literature assignments (Chapter 2) of cis-square planar structure to all these complexes. The new complexes [\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)(\text{SMe}))\text{Br}_2] and [\text{Ni}(\text{C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2))\text{Cl}_2] also clearly have the same structure. The isolation of a 1:1 Ni(II) complex with the phosphine-stibine is in contrast to results obtained with the ligands \text{C}_6\text{H}_4(\text{EMe}_2)_2 (E = \text{P}, \text{E} = \text{As} or \text{E} = \text{Sb}), where only 2:1 complexes are obtained, but is not without precedent; \text{C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2) also gives a 1:1 complex with NiCl$_2$.\textsuperscript{13}, which also appears to be cis-square planar.

Although the complexes of \text{Ph}_2P(\text{CH}_2)_4\text{PPh}_2 are very insoluble, diffuse reflectance spectra suggest that both chloride and bromide are pseudotetrahedral. They are probably polymeric, and the relatively high frequency of $\nu_{\text{Ni-X}}$ (Table 7.622)
confirms that halogen bridging to give pseudooctahedral stereochemistry, as suggested by Indian workers\textsuperscript{23}, does not occur.

\[7.623 \text{Ni}(L-L)X_2 \overset{2\text{Ni}(L-L)Y} \rightarrow \text{[Ni}(L-L)Y]_2 \text{Y}_2 \overset{2\text{Ni}(L-L)Y_2} \rightarrow (a) \text{New complexes}\]

\textbf{Dibromobis(o-dimethylphosphinophenyldimethylstibine)nickel(II)}
\[\text{[Ni}(o-C_{6}H_{4}(PMe_{2})(SbMe_{2}))_{2}Br_{2}]\]

Under dinitrogen, the ligand (0.26 g, 0.8 mmol) was added to a solution of NiBr\(_2\) (0.11 g, 0.5 mmol) in ethanol (10 cm\(^3\)). The mixture was warmed to 50°C, stirred for 5 minutes and evaporated to 5 cm\(^3\). Diethyl ether was added to produce a brown solid. After cooling to -20°C, the brown solid was filtered off, and dried in vacuo. 0.14g, 40%.

\textbf{Dichlorobis(o-dimethylphosphinophenyldimethylstibine)nickel(II)}
\[\text{[Ni}(o-C_{6}H_{4}(PMe_{2})(SbMe_{2}))_{2}Cl_{2}]\]

Under dinitrogen a warm n-butanol solution (20 cm\(^3\)) of NiCl\(_2\).6H\(_2\)O, (0.17 g, 0.7 mmol) was treated with the ligand (0.4 g, 1.4 mmol). After stirring for 20 minutes, the solution was concentrated to ca 10 cm\(^3\), and cooled to -20°C overnight. The brown product was filtered off, rinsed with diethyl ether and dried. 0.27 g, 54%. The complex is insoluble in or decomposed by common solvents.

\(* X = \text{Cl,Br,I}; Y = \text{ClO}_4, \text{BF}_4; L-L = \text{bidentate ligand}.*\)
Bis(o-dimethylphosphinophenyldimethylstibine)nickel(II) perchlorate
\[ \text{[Ni}_{\sigma-C_6H_4(PMe_2)(SbMe_2)}_2]_2(C\text{ClO}_4)_2 \]

A solution of Ni(Cl\text{O}_4)_2.6\text{H}_2\text{O} (0.37 g, 1 mmol) in 2-propanol (25 cm³) was treated with the ligand (0.44 g, 1.5 mmol). A yellow-green precipitate formed rapidly, which was filtered off, rinsed with i-propanol and dried in vacuo. 0.6 g, 81%.

Bromobis(o-dimethylphosphinophenyldimethylstibine)nickel(II) perchlorate
\[ \text{[Ni}_{\sigma-C_6H_4(PMe_2)(SbMe_2)}_2\text{Br}]\text{ClO}_4 \]

The ligand (0.145 g, 0.5 mmol) was added under dinitrogen to a mixture of Ni\text{Br}_2.6\text{H}_2\text{O} (0.05 g, 0.25 mmol) and Ni(Cl\text{O}_4)_2.6\text{H}_2\text{O} (0.09 g, 0.25 mmol) in ethanol (25 cm³), and the mixture refluxed. On cooling purple crystals separated. 0.16 g, 76%.

\[ \text{[Ni}_{\sigma-C_6H_4(PMe_2)(SbMe_2)}_2\text{Cl}]\text{ClO}_4, \text{brown-purple crystals, were prepared similarly.} \]

Dibromobis(o-phenylenebis(dimethylstibine)nickel(II)
\[ \text{[Ni}_{\sigma-C_6H_4(SbMe_2)}_2\text{Br}_2] \]

Under dinitrogen the ligand (0.35 g, 0.9 mmol) was added to Ni\text{Br}_2.3\text{H}_2\text{O} (0.13 g, 0.5 mmol) in n-butanol (15 cm³) at ca. 45°C. After 10 minutes, the solution was cooled, concentrated, and diethyl ether added dropwise until crystallisation commenced. The solution was cooled to -20°C overnight, the purple powder collected and dried. 0.34 g, 75%.

Bis(1,2-bis(dimethylphosphino)3,4,5,6-tetrafluorobenzene)nickel(II) perchlorate
\[ \text{[Ni}_{\sigma-C_6F_4(PMe_2)}_2]_2(\text{ClO}_4)_2 \]

The ligand (0.54 g, 2 mmol) was syringed into a warm
solution of \([\text{Ni(H}_2\text{O)}_6]\)(\text{ClO}_4)_2\) (0.4 gm, 1.1 mmol) in propan-2-ol (50 cm\(^3\)) with stirring, when a yellow precipitate appeared immediately. This was filtered off, washed with propan-2-ol, and diethyl ether and dried in vacuo. It was recrystallised from acetonitrile-propan-2-ol (1:1 v/v). 0.71 g, 89%.

**Dichlorobis[1,2-bis(dimethylphosphino)3,4,5,6-tetrafluorobenzene]nickel(II)**

\[\text{[Ni}^{2+}\text{C}_6\text{F}_4\text{PMe}_2\text{]}_2\text{Cl}_2\]

The ligand (0.27 g, 1.0 mmol) was added to a deoxygenated solution of \(\text{Ni(H}_2\text{O)}_6\text{Cl}_2\) (0.12 g, 0.5 mmol) in ethanol (40 cm\(^3\)) and the mixture refluxed for five minutes, cooled and concentrated to ca 5 cm\(^3\). Diethyl ether (30 cm\(^3\)) was added with rapid stirring and the mixture cooled to 20\(^\circ\)C overnight. The resulting green precipitate was filtered off, washed with diethyl ether (5 cm\(^3\)) and dried in vacuo (0.073 g, 22%). On concentrating the filtrate, and cooling, dark-orange crystals were obtained, which were isolated in a similar manner. 0.098 g, 29%.

\[\text{[Ni}^{2+}\text{C}_6\text{F}_4\text{PMe}_2\text{]}_2\text{Br}_2\] was isolated in a similar manner as orange-brown crystals. 0.322 g, 85%.

**Di-iodobis(o-phenylenebis(dimethylphosphine)nickel(II))**

\[\text{[Ni}^{2+}\text{C}_6\text{H}_4\text{PMe}_2\text{]}_2\text{I}_2\]

A solution of \([\text{Ni}^{2+}\text{C}_6\text{H}_4\text{PMe}_2\text{]}_2\text{Cl}_2\) (0.33 g, 0.5 mmol) in acetonitrile (50 cm\(^3\)) was treated with NaI (0.3 g, 2 mmol) in methanol (10 cm\(^3\)). On reducing the volume of the solution, well formed orange crystals precipitated. Yield ca quantitative.
Diiodobis(o-phenylenebis(diphenylphosphine)nickel(II)

$[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PPh}_2\text{)}_2)_2\text{I}_2]$ 

A warm ethanol solution (100 cm$^3$) of $[\text{Ni}(\text{o-C}_6\text{H}_4\text{(PPh}_2\text{)}_2\text{I}_2]$ (0.75 g, 1 mmol) was treated with the ligand (0.44 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm$^3$) and the mixture boiled. Water was then added slowly to the refluxing solution, until a purple solid started to precipitate, whereupon the solution was cooled. The black-purple solid was washed and dried. 0.90 g, 76%.

Diiodobis(1,3-bis(dimethylstibino)propane)nickel(II)

$[\text{Ni(Me}_2\text{Sb(CH}_2\text{)}_3\text{SbMe}_2)_2\text{I}_2]$ 

The ligand (0.35 g, 1 mmol) was added under dinitrogen to a freshly prepared degassed solution of nickel(II) iodide (0.6 mmol) in 1-butanol (15 cm$^3$). After stirring for 10 minutes the resulting dark purple solid was filtered off (Schlenk tube) and dried. It was recrystallised under dinitrogen from MeNO$_2$/Et$_2$O, but in the presence of oxygen, some oxidation of the ligand occurs. 0.35 g, 70%.

Diiodobis(1,2-bis(dimethylphosphino)ethane)nickel(II)

$[\text{Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{I}_2]$ 

The ligand (0.3 g, 2 mmol) was syringed into a degassed solution of nickel(II) iodide (1 mmol) in 1-butanol (50 cm$^3$), with stirring. After 15 minutes, the bright orange precipitate was filtered off, rinsed with diethyl ether (2 x 15 cm$^3$) and dried in vacuo. 0.53 g, 83%.
Di-iodobis(2,5-diselenahexane)nickel(II)
[Ni(MeSeCH₂CH₂SeMe)₂I₂]

To nickel(II) iodide (1 mmol) in 1-butanol (12 cm³) was added the ligand (0.43 g, 2 mmol) by syringe. After stirring for 30 minutes, precipitation was completed by slow addition of diethyl ether (10 cm³), and the yellow malodorous solid filtered off, and rinsed with ether, (2 x 5 cm³). The complex slowly decomposes in moist air, and is best kept in sealed ampoules. 0.59 g, 79%.

Dichlorobis(o-methylthiophenyldimethylphosphine)nickel(II)
[Ni(o-C₆H₄(PMe₂)(SMe))₂Cl₂]

The ligand (.37 g, 2 mmol) was added dropwise with stirring to a degassed solution of NiCl₂.6H₂O (.24 g, 1 mmol) in warm ethanol (30 cm³). After briefly refluxing and cooling to room temperature the khaki-green precipitate was filtered off, washed with cold ethanol and diethyl ether and dried in vacuo. 0.4 g 80%. [Ni(o-C₆H₄(PMe₂)(SMe))₂Br₂] was similarly prepared. 0.38 g, 71%.

Discussion

Details of the spectroscopic properties of the new Ni(II) complexes are included in Table 7.623. Other Ni(II) complexes were prepared by established literature procedures. In all cases, analytical (C and H analyses) and spectroscopic data confirmed that the expected products were obtained. These complexes had, almost without exception, been the subjects of detailed spectroscopic studies, so that it is not proposed to include spectroscopic results obtained in this study, but merely to give references to their preparation and spectra.
The following complexes were obtained; \([\text{Ni}(L-L)_2][\text{ClO}_4]_2\) (\(L-L = \sigma-C_6H_4(\text{EMe}_2)_2\); \(E = \sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{SbMe}_2)_2\); \(\sigma-C_6H_4(\text{NMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{SbMe}_2)_2\)), \([\text{Ni}(L-L)_2X]_2\) \((X = \text{Cl, Br})\); \([\text{Ni}(L-L)_2][\text{BF}_4]\) (\(L-L = \sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{NMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\)); \([\text{Ni}(L-L)_2][\text{ClO}_4]\) (\(L-L = 1,10\)-phenanthroline, 2,2'-bipyridyl; \(X = \text{Cl, Br})\). The complexes \([\text{Ni}(L-L)_2][\text{BF}_4]\) (\(L-L = \sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{NMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\); \(\sigma-C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2\)) were also synthesised by vacuum pyrolysis of the corresponding \([\text{Ni}(L-L)_3X]_2\) (\(L-L = 1,10\)-phenanthroline, 2,2'-bipyridyl; \(X = \text{Cl, Br})\). The complexes \([\text{Ni}(L-L)_2][\text{BF}_4]\) (\(X = \text{Cl, Br})\) were available from an earlier study.

The new complexes (Table 7.623) are almost all wholly analogous to similar complexes, already well-characterised, in the literature (Chapter 2, page 36). The spectra of the complexes of \(\sigma-C_6H_4(\text{PMe}_2)_2\) are very similar to those of the \(\sigma-C_6H_4(\text{PMe}_2)_2\) complexes and suggest the presence of five-co-ordinate square pyramidal \([\text{Ni}(\sigma-C_6H_4(\text{PMe}_2)_2)X]^+\) in CH\(_3CN\) solution (\(X = \text{Cl, Br, I})\). The \([\text{Ni}(\sigma-C_6H_4(\text{PMe}_2)_2)X]^+\) is clearly planar, as expected. Similar conclusions may also be drawn from the spectra of the complexes of \(\sigma-C_6H_4(\text{PMe}_2)(\text{SbMe}_2)_2\) and \(\sigma-C_6F_4(\text{PMe}_2)_2\). For the latter ligand it is significant that the \([\text{Ni}(L-L)_2]\) can be obtained in two forms. Rapid crystallisation from ethanol yields a green, paramagnetic complex, whose electronic spectrum (diffuse reflectance), is typical of an octahedral d\(^8\) ion. Slow crystallisation gives a brown, diamagnetic material with solution spectra typical of the low-spin five co-ordinate \([\text{Ni}(L-L)_3X]^+\) found for the related \(\sigma-C_6H_4(\text{EMe}_2)_2\) (\(E = \text{P, As})\) ligands. In less polar solvents \((\text{CH}_3\text{CN, CH}_2\text{Cl}_2))\), or upon standing for ca 2 weeks, the green form reverts to the brown form (electronic spectral evidence). Attempts to synthesise an octahedral bromo-
Table 1.2.1: Nickel(II) Complexes \([\text{Ni}(L)_2X_2]\), \([\text{Ni}(L)_24]\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Analytical Data</th>
<th>Electronic Spectra [^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni}^{[2]} \text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})</em>{2} \text{Br}_{2})</td>
<td>(x = 3.8(3.9))</td>
<td>(10^{3} \text{cm}^{-1}(\varepsilon, \text{dm}^{3} \text{mol}^{-1} \text{cm}^{-1}))</td>
</tr>
<tr>
<td>(\text{Ni}(\text{Me}<em>{2} \text{PCH}</em>{2} \text{CH}<em>{2} \text{PMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(23.3(23.3))</td>
<td>(9.7, 11.8^d, 14.3, 24.3, 29.1^d (\mu_{\text{eff}} = 2.91 \text{ B.M.}))</td>
</tr>
<tr>
<td>(\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PPh}<em>{2})</em>{2} \text{Br}_{2})</td>
<td>(39.6(39.8))</td>
<td>(18.9(1300), 30.1(7300), 33.3(31,000))</td>
</tr>
<tr>
<td>(\text{Ni}(\text{Me}<em>{2} \text{Sb(CH}</em>{3})<em>{3} \text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(16.9(16.8))</td>
<td>(18.3(1200), 25.7(2220))</td>
</tr>
<tr>
<td>{\text{Ni}(\text{MeSeCH}<em>{2} \text{CH}</em>{2} \text{SeMe})<em>{2} \text{Cl}</em>{2}}</td>
<td>(13.0(12.9))</td>
<td>(18.3(3400), 20.7(3600), 32.9(1200))</td>
</tr>
<tr>
<td>(\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(33.8(34.0))</td>
<td>(19.8(4000), 20.7(3600), 32.9(1200))</td>
</tr>
<tr>
<td>(\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(30.3(31.2))</td>
<td>(26.0^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2}}</td>
<td>(27.0^d)</td>
<td></td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(29.4(29.4))</td>
<td>(19.4, 29.1^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(24.4(24.6))</td>
<td>(19.5(910), 27.5(2940)(\text{sh}), 33.3(8900))</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(43.2(43.4))</td>
<td>(12.9(\text{sh}), 14.1, 15.0, 26.6, 32.3^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(36.7(36.8))</td>
<td>(20.25(290), 32.9(2970))</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(35.7(35.9))</td>
<td>(18.8(\text{br}), 21.55, 24.4, 29.9^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(25.7(25.9))</td>
<td>(15.1(1100), 19.16(3500), 28.6(\text{sh})(6200))</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(35.4(35.9))</td>
<td>(31.9, 15.9, 16.0(\text{sh}), 24.9, 30.7^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(32.0(31.7))</td>
<td>(24.3(9000), 32.3(3800))</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Cl}</em>{2})</td>
<td>(30.1(30.1))</td>
<td>(21.2(\text{sh}), 23.4^d)</td>
</tr>
<tr>
<td>{\text{Ni}(\text{C}<em>{6} \text{H}</em>{4} (\text{PMe}<em>{2})(\text{SbMe}</em>{2})<em>{2} \text{Br}</em>{2})</td>
<td>(19.3(\text{sh}), 23.4, 26.5, 30.3)</td>
<td></td>
</tr>
</tbody>
</table>

\[^a\text{n.m.r.:} \Delta = 2.22(\text{br. singlet})(\text{CO}_{3})_{2}\text{SO}\]

\[^b\text{Continued...}\]
Notes

(a) Some of these complexes have been prepared before, but no analytical or physical data was given to support possible structural assignments. Therefore they have been included in this Table.
(b) In CH₂Cl₂, except
(c) CH₃CN solution,
(d) diffuse reflectance.
(e) diffuse reflectance; Nujol mull mounted on filter paper.
complex failed. This behaviour resembles that of $o-C_6F_4(AsMe_2)_2$ which forms only an octahedral, green chloride and a similar bromide which reverts to the brown, low spin isomer in solution.

Of the other complexes, $[Ni(o-C_6H_4(PPh_2)_2)_2]I$ and $[Ni(Me_2Sb(CH_2)_3SbMe_2)_2]I$ are formulated as low-spin five co-ordinate species, while the complexes of MeSeCH_2CH_2SeMe and $o-C_6H_4(PMe_2)(SMe)$ are clearly octahedral. Replacement of a $-EMe_2$ group ($E = P, As$ or $Sb$) by $-SMe$ is evidently sufficient to lower the ligand field to the extent that a change in spin state occurs. However, the solution spectrum in CH_2Cl_2 of $[Ni(o-C_6H_4(PMe_2)(SMe)_2)_2]X_2$ suggests that an equilibrium with the five-co-ordinate form exists.

7.624 Multidentate Ligands

(a) Preparation of new complexes

Bromo(o-phenylenebis(3-dimethylarsinopropyl)methylarsine)nickel(II)perchlorate, $[Ni(o-C_6H_4[AsMe(CH_2CH_2CH_2AsMe_2)_2]Br]ClO_4$

The ligand (0.69 g 1.25 mmol) was dissolved in CH_2Cl_2 (5 ml) and added dropwise by syringe to a hot solution of NiBr_2.3H_2O (0.275 g 1.04 mmol) in ethanol (35 cm^3). After refluxing for 2 hr, solvent volume was reduced to ca 5 cm^3. The sticky red precipitate was collected by decantation, washed thoroughly with dry diethyl ether, dried in vacuo and re-dissolved in ethanol (25 cm^3). Solid LiClO_4·H_2O (0.3 g, 2.4 mmol) was added portionwise and the mixture cooled to -20°C. The powdery red-purple precipitate was collected and dried in vacuo. It appeared rather moisture-sensitive. Attempts to purify the complex further were unsuccessful and the product had rather poor analyses (Table 7.624). This is probably due to impurities present in the crude ligand which are difficult to remove by procedures which do not cause the desired product to decompose.
The ligand (0.9 g, 1.34 mmol) was dissolved in CH₂Cl₂ (10 ml) and added dropwise to a hot solution of NiBr₂·3H₂O (0.355 g, 1.3 mmol) in ethanol (50 ml). After refluxing for 2d, the mixture was cooled slowly to -20°C and stored. One week later, the resulting shiny, crystalline product was filtered off and washed with cold ethanol and diethyl ether, then dried in vacuo. 0.9 g, 76%.

Discussion

Nickel(II) complexes with multidentate ligands have been widely studied in recent years, and the structural assignments made on the basis of data obtained in this study agree with observations in the literature in most respects.

The complexes of PhP(CH₂CH₂PPh₂)₂ (Table 7.624) are evidently five co-ordinate in the solid state and square planar in CH₃CN solution. This is in agreement with earlier work. Conductivity measurements show that the solution species are [Ni{ligand}X]⁺. In contrast, the complexes of MeAs(CH₂CH₂CH₂AsMe₂)₂ are five-co-ordinate as solids and in CH₂Cl₂ solution, while those of CH₃C(CH₂PPh₂)₂ are square bipyramidal as solids, but planar in CH₂Cl₂ solution. In this case, conductivity measurements (X = Cl) indicate that planar co-ordination is achieved by dissociation of one -PPh₂ group. For this ligand, a pure sample of [Ni{ligand}Br₂] was not obtained. The crystalline product isolated from ethanol solution appears to decompose slightly on drying in vacuo. Recrystallisation from CH₂Cl₂-ether failed to yield a purer product and instead gave an orange material with a strong band at
1110 cm$^{-1}$ in the infra red spectrum, probably due to $\nu_{\text{P=O}}$. For oxidation experiments, the Ni(II) material was isolated from 1-butanol (under N$_2$ atmosphere), dried quickly in vacuo and used immediately.

The linear and facultative tetradeinate ligand (Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$) gave a brown product with NiBr$_2$ which appears to be planar in solution and probably forms [Ni(ligand)]Br$_2$ in solution; this is consistent with the observation that [Ni(ligand)][PF$_6$]$_2$ is the sole product of the treatment of the corresponding chloride with NH$_4$PF$_6$. It is possible to make the square pyramidal [Ni(ligand)Br]$^+$ cation in the presence of ClO$_4^-$ or BPh$_4^-$ counterions, but this too appears to dissociate to the planar (P$_4$ donor set) moiety in CH$_2$Cl$_2$ (Table 7.624). These conclusions were of importance for the Ni(III) study; isolation of a d$^7$ pseudooctahedral [Ni(ligand)X$_2$]$^+$ species may conceivably have depended on the geometry of the Ni(II) precursor. (Chapter 3).

The ligands As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$ and P(CH$_2$CH$_2$PPh$_2$)$_2$ both yield trigonal bipyramidal [Ni(ligand)Br]Br (Table 7.624, electronic spectra). The arsine complex is very susceptible to displacement of the co-ordinated Br$^-$ by H$_2$O, in a fashion analogous to the reaction observed with the closely similar complexes of P(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$. 

Nickel(II) complexes of o-C$_6$H$_4$[As(Me)CH$_2$CH$_2$CH$_2$AsMe$_2$]$_2$ had not been prepared prior to this investigation. Severe difficulties were found in purifying the crude complex presumably owing to the presence of some partially-oxidised ligand (Table 7.624). The electronic spectrum of the [Ni(ligand)Br]ClO$_4$ species is similar to that of [Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$Br]ClO$_4$, suggesting a square pyramidal stereochemistry. The susceptibility of the complex to hydrolysis, in contrast to the o-C$_6$H$_4$(E=Me)$_2$ complexes, may well be due to the long, flexible propyl chains in the tetradeinate.
Table 7.624 : Notes

(a) The square brackets indicate the co-ordination environment in the solid phase as deduced from electronic spectral data. In solution, especially in polar solvents, some complexes are four-co-ordinate; see Experimental section.

(b) Analysis indicated that one mole equivalent of water was taken up during weighing. The solid complex was obtained anhydrous (i.r. spectral evidence) but is hygroscopic; see reference. Electronic spectrum is of the [Ni{Ligand} (H₂O)]²⁺ moiety.

(c) in CH₂Cl₂ solution except

(d) CH₃CN solution

(e) diffuse reflectance.

(f) butan-1-ol solution.

(g) qualitative spectrum, CH₂Cl₂ solution.

(h) from Chapter 2 (E = Experimental section) except

(j) this Chapter.
7.7 Complexes of Nickel(III)

7.71 \([\text{Ni}(L)_2X_3]\)

The syntheses of all these complexes were performed in the apparatus described in Chapter 3 (page 105), except for the PMe3 complexes which were made in conventional Schlenk apparatus. All physical measurements were made on freshly prepared samples (within ca 6 hours of preparation), which were stored at -20°C until required.

**Tribromobis(triethylphosphine)nickel(III) \([\text{Ni}(\text{PET}_3)_2\text{Br}_3]\)**

A solution of \([\text{Ni}(\text{PET}_3)_2\text{Br}_3]\) (0.4 g, 0.88 mmol) in CH2Cl2 (25 cm³) was treated with bromine in CCl4 (1.3 cm³ of 2% v/v) with rapid stirring. The solvent was removed as rapidly as possible in vacuo and the dichroic green solid dried briefly in vacuo. \([\text{Ni}(\text{PBu}_3)_2\text{Br}_3]\), \([\text{Ni}(\text{PPhMe}_2)_2\text{Br}_3]\), \([\text{Ni}(\text{PET}_2\text{Ph})_2\text{Br}_3]\) and \([\text{Ni}(\text{PMePh}_2)_2\text{Br}_3]\) were prepared similarly. Yields ca quantitative.

**Tribromobis(trimethylphosphine)nickel(III) \([\text{Ni}(\text{PMe}_3)_2\text{Br}_3]\)**

A solution of \([\text{Ni}(\text{PMe}_3)_2\text{Br}_2]\) (0.31 g, 0.84 mmol) in CH2Cl2 (20 cm³) was treated with bromine in CCl4 (1.2 cm³ of 2% v/v) with rapid stirring. The solution was filtered (Schlenk stick) and petroleum ether (40-60°C) (25 cm³) was added slowly. The resulting red-black precipitate was filtered off, rinsed with petroleum ether and dried in vacuo, 0.32 g (83%).

**Trichlorobis(phenyldiethylphosphine)nickel(III) \([\text{Ni}(\text{PPhEt}_2)_2\text{Cl}_3]\)**

A solution of \([\text{Ni}(\text{PPhEt}_2)_2\text{Cl}_2]\) (0.2 g, 0.43 mmol)
in CH₂Cl₂ (20 cm³) was cooled to -78°C, and excess NOCl condensed in, with vigorous stirring. The colour changed from red to dark blue. The solvent and excess NOCl were removed in vacuo the mixture being allowed to warm to room temperature. After brief drying in vacuo at ambient temperature, the product was stored at -20°C under dinitrogen. The other Ni(III) chlorocomplexes were prepared similarly. Yields ca quantitative.

**Attempted preparation of [Ni(PPh₂)₂Cl₂]**

Green [Ni(PPh₃)₂Cl₂] was recrystallised from CH₂Cl₂ to produce the red planar isomer. This was cooled to -78°C, and pure NOCl condensed onto it, the colour changing to dark green. After a few minutes, the excess NOCl was pumped away. The product is a green solid which decomposes very rapidly at room temperature. Found C = 61.3, H = 4.4, N = 0.5%. Required for CₓHₓClₓNiₓ C = 62.7, H = 4.4, (N ≈ 0%).

7.72 \([\text{Ni}(L-L)X₃]^-\)

(a) Ni(L-L)Br₃ (L-L = Ph₂PCH₂CH₂PPh₂, Ph₂P(CH₂)₃PPh₂, cisPh₂PCHCHPPh₂).

**General Method:** A finely-ground suspension of [Ni(L-L)Br₂] (1 mmol) in dry CCl₄ (ca 2 cm³) was treated with ca 0.5 mmol of Br₂ in CCl₄ (1.35 cm³ of a 2% v/v solution) in a small conical flask under N₂. After stirring or shaking for 30 minutes the Ni(III) complex was filtered off quickly, rinsed with dry CCl₄ and dried in vacuo. The products were stored in small (ca 2 cm³) glass ampoules to avoid decomposition. Yields ca quantitative.
Tribromo(o-phenylenebis(diphenylarsine)nickel(III) \([\text{Ni}(\sigma-C_6H_4(\text{AsPh}_2)_2)\text{Br}_3]\)

To finely powdered \([\text{Ni}(\sigma-C_6H_4(\text{AsPh}_2)_2)\text{Br}_2]\) (0.75 g, 1 mmol) under \(N_2\) in a Schlenk apparatus, was added \(\text{Br}_2\) in \(\text{CCl}_4\) (1.4 cm\(^3\) of a 2% v/v solution; 0.5 mmol \(\text{Br}_2\)). After 10 minutes, \(\text{CCl}_4\) (20 cm\(^3\)) was added, the black precipitate was filtered off, rinsed with dry \(\text{CCl}_4\) (2 x 5 cm\(^3\)) and dried. Yield \(=\) quantitative.

Tribromo(o-diphenylphosphinophenylidiphenylarsine)nickel(III) \([\text{Ni}(\sigma-C_6H_4(\text{PPh}_2)(\text{AsPh}_2)_2)\text{Br}_3]\)

To \([\text{Ni}(\sigma-C_6H_4(\text{PPh}_2)(\text{AsPh}_2)_2)\text{Br}_2]\) (0.71 g, 1 mmol) in \(\text{CH}_2\text{Cl}_2\) (20 cm\(^3\)) was added a 2-fold excess of \(\text{Br}_2\) in \(\text{CCl}_4\) (2% v/v). The dark brown solution was rotatory evaporated to dryness, and the residue stirred with petroleum ether/diethyl ether (15 cm\(^3\), 2:1 v/v) for 30 minutes, filtered and dried. 0.55 g, 70%.

Tribromo(o-methylthiophenyldiphenylphosphine)nickel(III) \([\text{Ni}(\sigma-C_6H_4(\text{SMe})(\text{PPh}_2)_2)\text{Br}_3]\)

To \([\text{Ni}(\sigma-C_6H_4(\text{SMe})(\text{PPh}_2)_2)\text{Br}_2]\) (0.285 g, 0.54 mmol) in \(\text{CH}_2\text{Cl}_2\) (25 cm\(^3\)) under \(N_2\) and cooled to -20°C, was added a stoichiometric quantity of \(\text{Br}_2\) in \(\text{CCl}_4\) (2% v/v) with vigorous stirring. The solvent was pumped down to \(\text{ca} 5\) cm\(^3\) in \text{vacuo}, the black solid filtered off, rinsed with diethyl ether and dried briefly. 0.24 g, 72%. n.b. only partial oxidation occurs upon treatment of the \(\text{Ni}(\text{II})\) complex with \(\text{Br}_2/\text{CCl}_4\).

Tribromo(o-phenylenebis(diphenylphosphine)nickel(III) \([\text{Ni}(\sigma-C_6H_4(\text{PPh}_2)_2)\text{Br}_3]\)

To \([\text{Ni}(\sigma-C_6H_4(\text{PPh}_2)_2)\text{Br}_2]\) (0.29 g, 0.44 mmol) in
CH₂Cl₂ (80 cm³) was added a five-fold excess of Br₂. The black solution was evaporated to ca 15 cm³ and pentane (10 cm³) added dropwise. The black crystals were filtered off and dried in vacuo. 0.25 g, 76%.

(b) Ni(L-L)Cl₃; L-L = Ph₂PCH(CH₃)₂PPh₂, cis-Ph₂PCHCHPPh₂.

These complexes could be made either by careful treatment of the Ni(II) material with Cl₂ in CCl₄ suspension, or by NOCl oxidation. A typical example of each method is given.

**Trichloro(cis-1,2-bis(diphenylphosphinoethene))nickel(III)**
[Ni(Ph₂PCHCHPPh₂)Cl₃]

The orange [Ni(cis-Ph₂PCHCHPPh₂)Cl₂] (0.3 g, 0.57 mmol) was ground finely in an agate mortar (as used for the preparation of Nujol mulls for spectroscopy), then dried in vacuo for one hour in a 50 cm³ round-bottomed flask. The powder was covered in dry CCl₄ (5 cm³) and chlorine was gently bubbled through under an atmosphere of nitrogen. The mixture was stirred for fifteen minutes, then rapidly filtered. The dark green product was washed with CCl₄ and dried in vacuo. Yield essentially quantitative.

**Trichloro(1,2-bis(diphenylphosphino)ethane))nickel(III)**
[Ni(Ph₂PCH₂CH₂PPh₂)Cl₃]

Nitrosyl chloride was prepared from KNO₂ and POCl₃ and purified by redistillation in vacuo*. Excess NOCl was slowly

carried in a stream of dry nitrogen through a 0°C trap containing a stirred solution of $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2]$ (0.5 g, 0.95 mmol) in $\text{CH}_2\text{Cl}_2$ (25 cm$^3$). The yellow-orange solution turned dark green, the majority of the solvent was pumped off, and the green solid filtered and dried. 0.32 g, 60%.

**Trichloro(o-phenylenebis(diphenylphosphine))nickel(III)**

$[\text{Ni}(\text{o-C}_6\text{H}_4\text{PPh}_2)_2\text{Cl}_3]$ [87x584]

$[\text{Ni}(\text{o-C}_6\text{H}_4\text{PPh}_2)_2\text{Cl}_2]$ (0.325 g, 0.56 mmol) in $\text{CH}_2\text{Cl}_2$ (200 cm$^3$) was treated with excess NOCl as above. The solvent volume was reduced to ca. 20 cm$^3$ and cyclohexane (15 cm$^3$) added with stirring. The mixture was cooled overnight at -20°C, the green product filtered off, rinsed with $\text{CCl}_4$ and dried. 0.27 g, 80%.

**Trihalo(o-phenylenebis(dimethylarsine))nickel(III)**

$[\text{Ni}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_2\text{X}_3]$ [84x330]

$[\text{Ni}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_2\text{Cl}_2]$ (ca. 2 mmol, 0.8 g) was dissolved in cyclohexane (30 cm$^3$) under $\text{N}_2$, filtered and the cyclohexane removed in vacuo. The waxy crystals were redissolved in $\text{CH}_2\text{Cl}_2$ (25 cm$^3$) and a small excess of the appropriate halogen in $\text{CH}_2\text{Cl}_2$ added. Gas was immediately evolved, and a dark solid precipitated. This was filtered off, rinsed with $\text{CH}_2\text{Cl}_2$ and dried in vacuo. The products are very moisture sensitive and were transferred to sealed containers, and stored at -20°C. Yield ca. 80%.

**Trichloro(1,2-bisdimethylphosphinoethane)nickel(III)**

$[\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}_3]$ [84x146]

The yellow Ni(II) complex (0.2 g, .7 mmol) was finely
ground in an agate mortar and transferred to a 50 cm\textsuperscript{3} round-bottomed flask connected to a Schlenk filter stick. The apparatus was evacuated and the solid dried in vacuum for one hour. A freshly prepared dilute solution of Cl\textsubscript{2} in dry CCl\textsubscript{4} (ca 5 ml) was introduced onto the Ni(II) complex and the mixture was stirred for 30 minutes. The red product was filtered under nitrogen and dried in vacuum. It was extremely moisture-sensitive and, like the o-C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2} analogues, was transferred to glass ampoules in a glove box (< 10 p.p.m. H\textsubscript{2}O). The bromide was similarly prepared as an olive green solid.

7.73 [Ni(L-L)\textsubscript{2}X\textsubscript{2}]^+

The following complexes were satisfactorily prepared by literature methods; [Ni{o-C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}X\textsubscript{2}]Y (X = Y = Cl; 15)
 X = Y = Br; 15 X = C1,Br; Y = ClO\textsubscript{4}; 15) [Ni{o-C\textsubscript{6}H\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{2}]ClO\textsubscript{4}. 14 For X = Cl, Y = ClO\textsubscript{4}, however, the following method was more convenient and gave good results for L-L = o-C\textsubscript{6}H\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}, o-C\textsubscript{6}H\textsubscript{4}(AsMe\textsubscript{2})\textsubscript{2}, o-C\textsubscript{6}H\textsubscript{4}(PMe\textsubscript{2})(AsMe\textsubscript{2}), Me\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PMe\textsubscript{2} (Y = BF\textsubscript{4} also) and o-C\textsubscript{6}F\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2} for which it is described.

Dichlorobis(1,2-bis(dimethylphosphino)3,4,5,6-tetrafluorobenzene)nickel(III) perchlorate

[Ni{o-C\textsubscript{6}F\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{2}](ClO\textsubscript{4}). To a solution of [Ni{o-C\textsubscript{6}F\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{2}] (0.065 g, 0.1 mmol) and LiClO\textsubscript{4} (0.01 g, 0.1 mmol) in ethanol (25 cm\textsuperscript{3}) - MeCN(7 cm\textsuperscript{3}) was added a small excess of Cl\textsubscript{2}/CCl\textsubscript{4} solution, to produce a grass green solution. This was concentrated in vacuum to yield a green precipitate, which was filtered off, rinsed with cold 2-propanol and diethylether, and dried in vacuum 0.05 g, 78%. ([Ni{o-C\textsubscript{6}F\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}Br\textsubscript{2}]ClO\textsubscript{4} was made similarly from [Ni{o-C\textsubscript{6}F\textsubscript{4}(PMe\textsubscript{2})\textsubscript{2}}\textsubscript{2}Br\textsubscript{2}], LiClO\textsubscript{4} (1:1 mol ratio) and Br\textsubscript{2} in ethanol, and isolated as a brick-red solid. 88%).
For $L-L = \sigma C_6H_4(\text{PMe}_2)_2$, the published method, which is metathesis of the corresponding chloride in hot methanol with LiBr, was found to yield partially-reduced materials (Chapter 3). The following method avoids this problem. (It was also found generally to apply).

Dibromobis(o-phenylenebis(dimethylphosphine))nickel(III)perchlorate
\[ [\text{Ni}(\sigma C_6H_4(\text{PMe}_2)_2)Br_2]ClO_4. \]

A suspension of \([\text{Ni}(\sigma C_6H_4(\text{PMe}_2)_2)Br_2]ClO_4\) (0.24 g, 0.42 mmol) in CCl$_4$ was treated with the stoichiometric amount of Br$_2$, and the mixture shaken for 2 hours. The brown product was filtered off, and dried in vacuo. ca quantitative.

Other complexes were made by the following method.

Dibromobis(o-dimethylphosphinophenyldimethylstibine)nickel(III)perchlorate
\[ [\text{Ni}(\sigma C_6H_4(\text{PMe}_2)(\text{SbMe}_2)_2)Br_2]ClO_4. \]

\([\text{Ni}(\sigma C_6H_4(\text{PMe}_2)(\text{SbMe}_2)_2)Br_2]ClO_4\) (0.36 g, 0.44 mmol) in CH$_3$CN (25 cm$^3$) was treated with Br$_2$ (0.04 g, 0.25 mmol) in CCl$_4$ (10 cm$^3$). The solution was concentrated to ca 10 cm$^3$, diethyl ether added until crystallisation began, and the solution cooled to -20°C for 48 hours. The red-brown solid was collected, rinsed with diethyl ether and dried. 0.31 g, 78%.

\([\text{Ni}(\sigma C_6H_4(\text{PMe}_2)(\text{AsMe}_2)_2)Br_2]ClO_4\) was prepared similarly.
7.74 Multidentate Ligand Complexes of Ni(III)

Trihalo(bis(2-diphenylphosphinoethyl)phenylphosphine)nickel(III)

\[ \text{[Ni}\{\text{PhP(CH}_2\text{CH}_2\text{PPPh}_2\}_2\}X_3] \]

These complexes were made in Schlenk apparatus by a method exactly analogous to that used for the complexes \[ \text{[Ni(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\}_2\}X_3] \], and handled similarly under atmosphere of dry nitrogen. They were extremely moisture-sensitive.

Tribromo(bis(3-dimethylarsinopropyl)methylarsine)nickel(III)

\[ \text{[Ni(MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_2\}Br_3] \]

Bromine (0.022 g, 0.15 mmol) in CH\(_2\)Cl\(_2\) was added to \[ \text{[Ni(MeAs(CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2\}_2\}Br_2] \] (0.19 g, 0.3 mmol) in CH\(_2\)Cl\(_2\) (20 cm\(^3\)) under nitrogen. The solvent was rapidly pumped off, until a red-brown solid precipitated. This was separated and dried, 0.12 g, 60%.

7.8 Nickel(III) and Nickel(II)-Nickel(IV) Complexes of Diamine Ligands

The starting materials \[ \text{[Ni(L-L)}_2\}X_2 \] (L-L = H\(_2\)NCH\(_2\)NCH\(_2\)NH\(_2\) (en), H\(_2\)N(CH\(_2\))\(_3\)NH\(_2\) (pd), H\(_2\)NCH(Me)CH\(_2\)NH\(_2\) (pn); X = Cl,Br), and \[ \text{Ni(L-L)}_2\}X_2 \], were prepared by the literature method.\(^{26}\)

(A) Ni(III) Complexes

(1) \[ \text{[Ni(en)}_2\}Cl_2\}Cl \]

A saturated solution of \[ \text{[Ni(en)}_2\}Cl_2\} \] in MeOH was obtained by boiling excess \[ \text{[Ni(en)}_2\}Cl_2\} \] with the solvent, cooling to room temperature and filtering. Chlorine gas was passed quickly through the solution with rapid magnetic stirring, resulting
in immediate deposition of a yellow precipitate. This was filtered off, washed well with MeOH, then diethyl ether, and dried in vacuo. Cautious treatment with 30% HCl followed by washing with MeOH resulted in a smaller yield of purer material.

(ii) \([\text{Ni(en)}_2\text{Cl}_2]\text{Cl}_4\)

Prepared by the method of Babaeva et al., by metathesis of \([\text{Ni(en)}_2\text{Cl}_2]\text{Cl}\) with 20% \(\text{HClO}_4\).

(iii) \([\text{Ni(tn)}_2\text{Cl}_2]\)\(\text{Cl}\)

Prepared in an analogous fashion to \([\text{Ni(en)}_2\text{Cl}_2]\text{Cl}\).

(iv) \([\text{Ni(en)}_2\text{Br}_2]\)\(\text{Br}\)

To a suspension of finely ground \([\text{Ni(en)}_2\text{Br}_2]\) (0.5 g, 1.5 mmol) in a small volume of dry \(\text{CCl}_4\) was added a slight excess of 3% v/v \(\text{Br}_2\) in the same solvent. After standing for 2 hours the resultant brown solid was filtered off, washed repeatedly with small volumes of \(\text{CCl}_4\), then dried in vacuo. Yield = quantitative.

(v) \([\text{Ni(tn)}_2\text{Br}_2]\)\(\text{Br}\)

Prepared analogously from \([\text{Ni(tn)}_2\text{Br}_2]\).

(B) \(\text{Ni(II)}/\text{Ni(IV)}\) Mixed Valence Complexes

(i) \([\text{Ni(en)}_2\text{Ni(en)}_2\text{Cl}_2]\text{Cl}_4\)

A saturated solution of \([\text{Ni(en)}_2\text{Cl}_2]\) was prepared in a 1:1 mixture of dry MeOH and dry EtOH. Dry \(\text{N}_2\) was passed over a dilute solution of \(\text{Cl}_2\) in \(\text{CCl}_4\) and the resultant dilute \(\text{Cl}_2/\text{N}_2\)
mixture slowly bubbled through the \([\text{Ni(en)}_2\text{Cl}_2]\) solution. The colour changed from dark blue through light green to dark green over ca 30 minutes. After a further five minutes, dark green material slowly precipitated. This was filtered off, washed with dry EtOH, then diethyl ether, and dried in vacuo.

(ii) \([\text{Ni(pn)}_2\text{Ni(pn)}_2\text{Cl}_2]\) \(_4\-

Prepared as very dark blue-green microcrystals as described by Babaeva et al. 28

(iii) \([\text{Ni(en)}_2][\text{Ni(en)}_2\text{Cl}_2] (\text{ClO}_4)_4\-

Freshly prepared \([\text{Ni(en)}_2\text{Cl}_2]\) \(_1\) (0.5 g, 1.75 mmol) was finely ground, dried in vacuo for one hour, then suspended in a small volume (ca 3 cm\(^3\)) of \(\text{CCl}_4\). A few drops of 70\% \text{HClO}_4 (CARE! explosion hazard) were added and the mixture shaken gently for a few minutes. The aqueous layer was removed by pipette and more acid added. The process was repeated several times. Finally the very dark-coloured product was filtered, washed several times with \(\text{CCl}_4\), then dried in vacuo. Yield 0.41 g, 57\%.

(iv) \([\text{Ni(pn)}_2][\text{Ni(pn)}_2\text{Br}_2]\) \(_4\-

Dry nitrogen was passed over neat \(\text{Br}_2\) in a flask, then bubbled slowly through a saturated solution of \(\text{Ni(pn)}_2\text{Br}_2\) in 1:1 dry MeOH/ETOH. Khaki-green reflective microcrystals precipitated, which were filtered off, washed with diethyl ether and dried in vacuo.
7.9 Polyiodide Complexes of Nickel(II)

(a) Ni(L-L)$_2$I$_6$

(i) Bis(o-phenylenebis(dimethylarsine))nickel(II)

triiodide(1-) [Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$(I$_3$)$_2$]

A saturated solution of [Ni(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$I$_2$] in MeCN (20 cm$^3$) was treated with excess I$_2$ (Ni:I$_2$ = 1:5) in CH$_2$Cl$_2$ (20 cm$^3$). On cooling slowly to -20°C, greenish-black crystals formed. These were filtered off, rinsed with diethyl ether (5 cm$^3$) and dried briefly in vacuo. Yield essentially quantitative.

[Ni(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$I$_2$] and [Ni(o-C$_6$H$_4$(PMe$_2$(AsMe$_2$)$_2$)$_2$I$_2$] were made analogously.

(ii) Bis(triiodo)bis(2,5-diselenahexane)nickel(II)

[NI(MeSeCH$_2$CH$_2$SeMe)$_2$(I$_3$)$_2$]

To [NI(MeSeCH$_2$CH$_2$SeMe)$_2$I$_2$] (0.15 g, 0.2 mmol) in CH$_2$Cl$_2$ (25 cm$^3$) was added I$_2$ (0.254 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm$^3$). On cooling to -25°C for 48 hours a black powder was obtained. This was collected, rinsed with diethyl ether and dried in vacuo. Yield 0.22 g, 90%.

(iii) Bis(triiodo)bis(2,5-dithiahexane)nickel(II)

was made analogously.

(iv) [NI(H$_2$NCH$_2$CH$_2$NH)$_2$I$_2$]$_2$ was made by the method of Nyholm.
(b) Ni(L-L)I$_4$

(i) Ni$_2$C$_6$H$_4$(AsMe)$_2$I$_4$.

Dicarbonyl(o-phenylenebis(dimethylarsine)nickel(0) (0.2 g, 0.5 mmol) was recrystallised under dinitrogen from cyclohexane and redissolved in CH$_2$Cl$_2$. Iodine (0.64 g, 2.5 mmol) in CH$_2$Cl$_2$ (20 cm$^3$) was added with vigorous stirring, and the resulting black solid filtered off in a Schlenk tube, rinsed with CH$_2$Cl$_2$ and dried in vacuo. Found C = 13.8, H = 2.2, C$_{10}$H$_{16}$As$_2$I$_4$Ni requires C = 14.1, H = 1.9%.

(ii) Ni[o-C$_6$H$_4$(AsPh)$_2$]$_4$I$_4$.

A solution of [Ni{o-C$_6$H$_4$(AsPh)$_2$}I$_2$] (0.17 g, 0.2 mmol) in CH$_2$Cl$_2$ (20 cm$^3$) was added to iodine (0.254 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm$^3$). On standing at -20°C for 2 days a black powder precipitated. This was filtered off, washed with n-pentane and dried. 0.175 g, 80%. Found C = 32.4, H = 2.6, I = 44.9; C$_{30}$H$_{24}$As$_2$I$_4$Ni requires C = 32.7, H = 2.2, I = 46.1%. $\mu$ = 0.5 BM (Gouy).

(c) Ni(L-L)$_2$I$_3$

Ni[o-C$_6$H$_4$(AsMe)$_2$]$_2$I$_3$.

(1) A solution of [Ni[o-C$_6$H$_4$(AsMe)$_2$]$_2$Cl$_2$]ClO$_4$$_8$ (0.15 g, 0.19 mmol) in MeCN (35 cm$^3$) was added to excess aqueous KI (40 cm$^3$, 0.1 M) with stirring. The khaki-green precipitate was filtered off and dried to give a green-black solid.

(2) A solution of [Ni[o-C$_6$H$_4$(AsMe)$_2$]$_2$Cl$_2$](ClO$_4$)$_2$*

* See chapter 5
(0.2 g, 0.22 mmol) in CF₃CO₂H (15 cm³) was filtered into an excess of aqueous KI (40 cm³). The precipitate was filtered off, rinsed well with water, and dried.

Ni{o-C₆H₄(PMe₂)(AsMe₂)}₂ was prepared by method (1) above.

7.10 Complexes of Nickel(IV). [Ni(L-L)₂X₂][CIO₄]₂

**General Method** (X = Cl, Br; L-L = o-C₆H₄(AsMe₂)₂, o-C₆H₄(PMe₂)₂, o-C₆H₄(PMe₂)(AsMe₂), o-C₆F₄(PMe₂)₂.

Conc. nitric acid was added dropwise to a mixture of [Ni(L-L)₂](CIO₄)₂ (0.5 mmol) and the appropriate conc. HX (2-3 drops) at 0°C until all the complex had dissolved. The deep red or green solutions produced were stirred at 0°C, whilst 70% HClO₄ was added dropwise to precipitate the required complex. [CARE Explosion Hazard. No explosions were experienced in this work, but high oxidation state metal perchlorates are often explosive]. The solid was filtered off and washed quickly with a small quantity of 10% HClO₄ (distilled water caused slight decomposition of the arsine complexes) and dried in vacuo at room temperature for 48h. The Ni(IV) complexes were stored in glass ampoules at -20°C after drying; physical and spectroscopic results were obtained on freshly prepared samples (< 48 hours old).

[Ni(Me₂PCH₂CH₂PMe₂)₂Cl₂](BF₄)₂

Finely ground [Ni(Me₂PCH₂CH₂PMe₂)₂](BF₄)₂ (0.53 g, 1 mmol) in a Schlenk apparatus was treated with a small excess (ca 1.2 mmol) of chlorine in dry CCl₄ with stirring. The light purple product was filtered off after 2 hrs and dried in vacuo. Yield 90%. The complex is deliquescent and turns green on exposure to air in less than 1 minute.

* Other Ni(II) starting materials [Ni(L-L)₂X]Y, Ni(L-L)₂X₂, or the Ni(III) complexes [Ni(L-L)₂X₂]Y (X = Cl, Br; Y = CIO₄) can be used as starting materials also.
7.11 Miscellaneous Complexes of Other Metals

(a) Palladium

Dichlorobis(1,2-bis(dimethylphosphino)3,4,5,6-tetrafluorobenzene) palladium(II)

\[ \text{[Pd\{o-C_6F_4(PMe_2)_{2}\}_2Cl_2].} \] The ligand (0.27 g, 1 mmol) was added to a gently refluxing solution of \( \text{Na}_2\text{PdCl}_4 \) (0.15 g, 0.5 mmol) in ethanol (40 cm\(^3\)). After stirring for 1 hr, the solvent was removed, and the residue recrystallised from \( \text{CH}_2\text{Cl}_2 / \text{diethylether} \). 0.27 g, 75%.

Dichlorobis(1,2-bis(dimethylphosphino)tetrafluorobenzene)palladium(IV) perchlorate. \( \text{[Pd\{o-C_6F_4(PMe_2)_{2}\}_2Cl_2(ClO}_4\} \).

\( \text{Pd\{o-C_6F_4(PMe_2)_{2}\}_2Cl}_2 \) (0.36 g, 0.5 mmol) was dissolved in the minimum volume of \( \text{CHNO}_3 \) at 0°C with magnetic stirring giving a deep yellow solution. The product was precipitated by the slow dropwise addition of chilled 70% \text{HClO}_4 (CARE) as a yellow solid, filtered, washed with 10% \text{HClO}_4 and dried in vacuo 0.34 g, 76%.

Attempts to synthesise a planar \( \text{[Pd\{o-C_6F_4(PMe_2)_{2}\}_2Cl}_2 \) by the reaction of the ligand and \( \text{[Pd(\text{CH}_2\text{CN})}_2\text{Cl}_2] \) in a 1:1 mole ratio in \( \text{ClCH}_2\text{CH}_2\text{Cl} \) resulted only in formation of \( \text{[Pd(ligand)}_2][\text{PdCl}_4] \) (far i.r. evidence). This Magnus salt was not susceptible to rearrangement to the desired product in boiling dimethylformamide. In this respect the behaviour of the \( \text{o-C}_6\text{F}_4\text{(PMe}_2\text{)}_{2} \) complexes is similar to those of \( \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2 \) and \( \text{o-C}_6\text{H}_4\text{(PMe}_2\text{)}_{2} \).

(b) Cobalt

Dichlorobis(1,2-bis(dimethylphosphino)benzene)cobalt(III) hexafluorophosphate \( \text{[Co\{o-C}_6\text{H}_4\text{(PMe}_2\text{)}_{2}\}_2\text{Cl}_2]PF}_6 \). (See overleaf) ...
The ligand (0.2 g, 1 mmol) was added with stirring to a solution \([\text{Co(H}_2\text{O)}\text{]Cl}_2\) (0.12 g, 0.5 mmol) and \(\text{NaPF}_6\) (0.84 g, 5 mmol) in ethanol (25 cm\(^3\)) - water (3 cm\(^3\)) under nitrogen. After warming for five minutes, the dark green solution was stirred in air for 3 hours. The solution changed to purple-green, and was concentrated in vacuo to small volume, whereupon a violet powder precipitated. This was washed with cold ethanol (5 cm\(^3\)) and diethyl ether (5 cm\(^3\)) and dried in vacuo 0.15 g, 45%.

**Dichlorobis(1,2-bis(dimethylphosphino)tetrafluorobenzene)cobalt(III) chloride** \([\text{Co} \cdot \text{C}_6\text{F}_4(\text{PMe}_2)_2\text{Cl}_2]\)

The ligand (0.27 g, 1 mmol) was added to a solution of \([\text{Co(H}_2\text{O)}\text{]Cl}_2\) (0.12 g, 5 mmol) in warm propan-2-ol (20 cm\(^3\)). On cooling to room temperature, light green crystals precipitated. These were rinsed with diethyl ether and dried in vacuo. They were finely powdered, suspended in dry \(\text{CCl}_4\) (ca 5 cm\(^3\)) and treated with a small excess of chlorine. After standing for 2 hrs, the resulting light purple powder was filtered off, washed with \(\text{CCl}_4\) (10 cm\(^3\)) and dried in vacuo 0.2 g, 50%.

### 7.12 Ligands - their Preparation and Sources

#### 7.12.1 Ligands containing Nitrogen Donor Atoms

Dimethylamine, Analar pyridine, N,N,N',N'-tetramethylethylene-diamine(1,2(dimethylamino)ethane) (Aldrich Chemical Co. Ltd.), Analar 2,2'-bipyridyl and 1,10-phenanthroline (Koch-Light Laboratories Ltd) were used as supplied. The diamines 1,2-propanediamine and 1,3-propanediamine were used as supplied (B.D.H. Chemicals Ltd). The 1,2-ethanediamine was dried over CaH\(_2\) and distilled prior
to use, as it was also used for preparations of Ir(III) complexes requiring pure ligand.

The $\text{o-C}_6\text{H}_4(\text{NMMe}_2)_2$ was prepared by an adaptation of the method of Brown, using $\text{Me}_2\text{SO}_4$ instead of MeI. This involves base-catalysed methylation of $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ (Aldrich Chemical Co. Ltd).

7.122 Ligands Containing Phosphorus Donor Atoms

(a) Monodentate Ligands

Triphenylphosphine (Aldrich Chemical Co. Ltd.) was used as supplied. Trimethylphosphine was prepared by treatment of a diethyl ether solution of $\text{PCl}_3$ at $-20^\circ\text{C}$ with MeLi. After hydrolysis, the ether layer was dried and used directly for complex preparation. Triethylphosphine was obtained commercially (Strem Chemical Co.) and tri-n-butylphosphine was supplied by Dr. W. Levason. Tricyclohexylphosphine was made by the vacuum pyrolysis of its $\text{CS}_2$ adduct, available commercially. Dimethylphenylphosphine, diethylphenylphosphine and diphenylmethylphosphine were made by the treatment of $\text{PhPCl}_2$ or $\text{Ph}_2\text{PCl}$ with the appropriate Grignard reagent and were purified by distillation in vacuo.

Trimethyl- and triethylphosphite were obtained from Aldrich Chemical Co. Ltd. and used as supplied.

(b) Bidentate ligands (including 'mixed' donor ligands with phosphorus)

The ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, 4, 5$) and cis-$\text{Ph}_2\text{PCHCHFPPh}_2$ were obtained by the standard literature routes, or slight modifications thereof, viz;
The ligand o-C\(_6\)H\(_4\)(PPh\(_2\))(SMe) was conveniently prepared from o-C\(_6\)H\(_4\)Br(SMe)\(^{36}\), by a modification of the literature procedure.\(^{37}\) This involves lithiation of the o-C\(_6\)H\(_4\)Br(SMe) followed by treatment with Ph\(_2\)PCl.

\[
\begin{align*}
\text{o-C}\,\text{H}_4\,\text{Br(SMe)} & \xrightarrow{\text{nBuLi,ether}} \text{o-C}\,\text{H}_4\,\text{Li(SMe)} & \xrightarrow{\text{Ph}_2\text{PCl}} & \text{o-C}\,\text{H}_4\,(\text{PPh}_2)(\text{SMe}).
\end{align*}
\]

Previously, the synthesis of o-C\(_6\)H\(_4\)(PPh\(_2\))\(_2\) has involved tedious multi-stage preparations.\(^{38,39}\) Recently, however, it was found that it could be synthesized in a "one-pot" reaction utilising o-C\(_6\)H\(_4\)F\(_2\) and NaPPh\(_2\) in liquid NH\(_3\), in a yield of 35%.\(^{40}\) The following rather more convenient procedure was used to prepare this ligand, using the same methodology.

**Preparation of o-C\(_6\)H\(_4\)(PPh\(_2\))\(_2\)**

Lithium metal (4.2 g, 0.7 mmol) was hammered into thin sheets, and cut into strips under petroleum ether. These
strips were then chopped into a 500 cm$^3$ three-neck round bottomed flask under nitrogen, falling directly into a solution of PPh$_3$ (67 g 0.26 mmol) in dry THF (300 cm$^3$). After approximately ten minutes a faint straw colour appeared and this gradually deepened to dark red upon stirring overnight under nitrogen. The mixture was then refluxed briefly, cooled and filtered from excess lithium through a short length of neoprene tubing, containing a plug of glass wool, between two cone tubing adaptors, into another three-neck flask. To destroy the phenyl lithium generated by the reaction, Bu$^+$Cl (16.65 g 19.8 ml 0.18 mol) was added dropwise to the stirred solution at 0°C. After an hour stirring at room temperature, the mixture was re-cooled and o-C$_6$H$_4$F$_2$ (10 g 88 mmol) was added cautiously dropwise. On warming to room temperature a vigorous reaction ensued. When it subsided, the purple solution was refluxed for thirty minutes, cooled and hydrolysed with dilute NH$_4$Cl solution (ca 100 cm$^3$). The layers were separated, the aqueous layer washed once with CH$_2$Cl$_2$ (120 cm$^3$) and the organic layers combined and dried overnight over MgSO$_4$. Upon concentration, a pale yellow wax separated. This was shaken with cold methanol, whereupon a white solid precipitated, then stored at -20°C for 3 days. The product was filtered off and dried in vacuo 25.5 g, 65%. (Identified by low resolution mass spectrometry: M = 446 (P$^+$), 369 (P-Ph)$^+$. $^{31}$P$^{1H} = 2.21$ (ppm relative to H$_3$PO$_4$). (No signals due to Ph$_3$P or Ph$_2$PH observed).

(c) Methyl-Substituted Bidentates

The methyl-substituted bidentate phosphine ligands Me$_2$PCH$_2$CH$_2$PMe$_2$ and o-C$_6$H$_4$(PMe$_2$)$_2$ were prepared by literature methods;
The ligand \( \sigma\)-C\(_6\)H\(_4\)\(\left(\text{NMe}_2\right)\)(PMe\(_2\)) was prepared by the literature procedure,
\(^{42}\) which is similar to the preparation of \( \sigma\)-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\) but utilises \( \sigma\)-C\(_6\)H\(_4\)(NMe\(_2\))Br in place of \( \sigma\)-C\(_6\)H\(_4\)BrCl. The former is easily prepared from \( \sigma\)-C\(_6\)H\(_4\)(NH\(_2\))Br (Aldrich Chemical Co. Ltd.) and MeI in basic conditions. The arsine-phosphine \( \sigma\)-C\(_6\)H\(_4\)(PMe\(_2\))(AsMe\(_2\)) was available from earlier studies \(^{42}\),
as was the corresponding stibine-phosphine \( \sigma\)-C\(_6\)H\(_4\)(PMe\(_2\))(SbMe\(_2\)).

These compounds are very oxygen-sensitive and were prepared and handled under nitrogen using techniques which have been fully described previously. \(^{41,42}\)

The effect on the donor properties of ligands of fluorine substitution has, as described in Chapter 2 (page 33), been of considerable interest in co-ordination chemistry. To study the effect of such substitution on the ability of \( \sigma\)-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\) to stabilise high oxidation states, particularly Ni(IV) and Fe(IV), it was desired to synthesise \( \sigma\)-C\(_6\)F\(_4\)(PMe\(_2\))\(_2\). The usual route to such ligands, namely halide displacement by LiPMe\(_2\)
in THF, was not attempted in view of the fact that the less powerful nucleophile LiPPh$_2$ reacted with aryl-F groups, in particular in the successful synthesis of $\alpha$-C$_6$H$_4$(PPh$_2$)$_2$. It was therefore necessary to use the reverse nucleophilic process, viz. the reaction of the appropriate aryl anion with Me$_2$PCl. (A similar route has been used to prepare $\alpha$-C$_6$F$_4$(PPh$_2$)$_2$). A prerequisite was the preparation in good yield and purity of moderate quantities of Me$_2$PCl. A literature procedure 44 was modified to this end;

$$
\begin{align*}
2\text{PSCl}_3 & \xrightarrow{\text{Et}_2\text{O}} 6\text{MeMgl,} \\
\text{SS} & \xrightarrow{\text{excess PhPCl}} \text{Me}_2\text{P-PMe}_2 \\
\text{Me}_2\text{P-PMe}_2 & \xrightarrow{220^\circ\text{C}} \text{Me}_2\text{PCl}
\end{align*}
$$

This was prepared using the literature procedure 45.
which involves the reaction of MeMgl with PSCl$_3$ at low temperature. The original preparation was on a very large scale (1 mole PSCl$_3$) and recommends an acetone slush bath (-78°C) for cooling. However, explosions have been encountered in such reactions, probably because over-efficient cooling caused the reaction to stop temporarily. If the literature route is followed on a smaller scale (0.25 moles PSCl$_3$) using an efficient mechanical stirrer and ice-salt (ca -15°C) cooling, no problems are encountered.

(ii) Me$_2$PCl

This was prepared by a modification of the method of Parshall. A 100 cm$^3$ round-bottomed 3-neck flask, fitted with a nitrogen inlet, and a short Vigreux column connected to a still-head, condenser and tared receivers, was charged with Me$_4$P$_2$S$_2$ (18.6 g, 0.1 mol) and PhPCl$_2$ (60 g, 0.27 mol). Under a stream of dry nitrogen, the mixture was heated until it became homogeneous (ca 200°C), the product boiling between 40-75°C being collected. 12.6 g 65% 1H NMR 1.63(d) $J_{P-H} = 8$ Hz. It was pure enough to be used directly in the next stage.

(iii) o-C$_6$F$_4$PMe$_2$.

Under nitrogen, the apparatus consisting of a 250 cm$^3$ three necked flask, fitted with nitrogen inlet, "Suba seal" septum cap, and reflux condenser, was charged with dry diethyl ether (100 cm$^3$) and 1,2-dibromotetrafluorobenzene (5 g 0.016 mol). The mixture was cooled to -85°C, and Bu$_3$Li (10.9 cm$^3$ of 1.49M solution) added dropwise via a syringe over a period of ca 20 min. After warming briefly to -20°C, the mixture was cooled to -85°C, and Me$_2$PCl (1.56 g 0.016 mol) added slowly via a syringe, the mixture becoming

* Joints were sealed with PTFE tape since Me$_2$PCl reacts with most Vacuum greases.
** Available commercially from Fluorochem. Ltd.
red in colour. After stirring for 30 min, the mixture was allowed to warm to room temperature. The mixture was cooled again to -85° and treated successively with Bu\(^\text{NLi}\) (11 cm\(^3\)) and Me\(_2\)PCl (1.7 g) as before and allowed to warm up over ca 1 hr. Hydrolysis was effected with deoxygenated aqueous NH\(_4\)Cl solution (35 cm\(^3\)) at 0°C, the organic layer separated, the aqueous layer extracted with diethyl ether (25 cm\(^3\)), and the combined organic layers dried (Na\(_2\)SO\(_4\)). The ether was distilled off, and the residue fractionated in vacuo. After a short fore-run (BP 51-54°C/0.4 mm Hg) the main fraction boiled at 60-85°C/0.5 mm Hg. 1.9 g 43%. Redistillation gave BP 73°C/0.5 mm. Mass Spectrum M/Z 270 (11)P\(^+\), 255 (100) P-Me\(^+\), 240 (23) P-2Me\(^+\). \(^1\)H NMR (CD\(_3\))\(_2\)SO \(\delta = 1.50\) mult. \(^{31}\)P \(\delta = -37.9\) ppm (H\(_3\)PO\(_4\) ref.).

(iv) Methiodide o-C\(_6\)F\(_4\)(PMe\(_2\))(PMe\(_3\))\(^+\)I\(^-\)

o-C\(_6\)F\(_4\)(PMe\(_2\))\(_2\) (0.135 g, 0.5 mmol) was added dropwise to a warm solution of MeI (0.3 g, 2 mmol) in acetone (30 cm\(^3\)) with stirring. The solvent was removed in vacuo and the white gummy solid recrystallised from acetone-diethylether twice. Found; C = 31.8, H = 3.7; C\(_{11}\)H\(_{15}\)F\(_4\)IP\(_2\) requires C = 32.0, H = 3.7%. M.P. 174-177°C. (decomp.) \(^1\)H n.m.r. \((\delta) = 1.4(d;5 Hz)[6H], 2.28(d,14 Hz)[9H]. (Both show evidence of further coupling under high resolution). (CD\(_3\))\(_2\)SO.

\(^{31}\)P \(\delta = 31.75;\) Me\(_3\)P\(^+\) = 31.75; Me\(_2\)P\(^-\) = -34.6 ppm (relative to H\(_3\)PO\(_4\)).

Although the ligand o-C\(_6\)H\(_4\)(PMe\(_2\))(SMe) has previously been prepared by the reaction of o-C\(_6\)H\(_4\)Br(SMe) with LiPMe\(_2\) in THF, it was found convenient to use the available starting material Me\(_2\)PCl. The following method was therefore employed for the synthesis of o-C\(_6\)H\(_4\)(PMe\(_2\))(SMe).
(e) o-(Dimethylphosphino)thioanisole

Under nitrogen, the apparatus (a 250 cm$^3$ three-neck flask fitted with nitrogen inlet, "suba-seal" septum cap and reflux condenser) was charged with dry diethyl ether (100 cm$^3$) and o-bromothioanisole (13.4g, 66 mmol). The mixture was cooled to -30°C (acetone-liquid nitrogen) and Bu$^n$Li in hexane (44 cm$^3$ of a 1.50M solution; 66 mmol) was added dropwise via syringe. After stirring for one hour, Me$_2$PCl (6.4g, 66 mmol) was added dropwise. The mixture was allowed to warm to room temperature and hydrolysed with dilute NH$_4$Cl solution (30 cm$^3$). The layers were separated, the aqueous layer washed with diethyl ether (20 cm$^3$) and the combined organic layers dried over anhydrous MgSO$_4$ overnight. The ether was distilled off and the residue distilled in vacuo. After a short fore-run (BP. 23°C/0.1 mmHg) the product distilled over at 50°C/0.4 mmHg. Mass spectrum M/Z = 184 P$, 169$(P-Me)$^+$ (100). $^1$H nmr $\delta = 2.4$ (3H,s)(-SMe); 1.5,1.3 (both d; 3H each; -PMe$_2$).

(f) Multidentate Phosphorus Ligands

The ligands (Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$)$_2$, P(CH$_2$CH$_2$PPh$_2$)$_3$, CH$_3$C(CH$_2$PH$_2$)$_3$ and Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$ were all obtained commercially (Strem Chemicals Inc) and used as supplied.

7.123 Ligands Containing Arsenic Donor Atoms

(a) Monodentate ligands

Triethyl arsine was made by the reaction of AsCl$_3$ with EtMgBr. Trimethylarsine was made by the reaction of MeLi with AsCl$_3$, and used in a manner similar to Me$_3$P (page 334).
(b) **Bidentate ligands with phenyl substituents**

The ligands cis-Ph₂AsCH₂AsPh₂⁴⁸ and Ph₂AsCH₂CH₂AsPh₂⁴⁷ were synthesised by literature procedures and their purity assessed by ¹H n.m.r. and mass spectroscopy.

(i) Li/THF

\[
\begin{align*}
\text{Ph}_3\text{As} & \xrightarrow{\text{Li/THF}} \text{Ph}_2\text{AsLi} \\
\text{Ph}_2\text{AsLi} & \xrightarrow{0.35 \text{ moles}} \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2
\end{align*}
\]

(ii) 0.7 moles Bu⁺Cl (ca70%)

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{Br}} \text{Br} \\
\text{or} & \xrightarrow{\text{Cl}} \text{Cl} \\
\text{or} & \xrightarrow{\text{Ph}_2\text{AsAsPh}_2}
\end{align*}
\]

₀-Phenylenebis(diphenylarsine) (₀-C⁶H₄(AsPh₂)₂) was supplied by Dr. W. Levason.

(c) **Bidentate ligands with methyl substituents**

The ligands ₀-C⁶H₄(AsMe₂)₂⁴⁹ and Me₂As(CH₂)₃AsMe₂⁵₀ were prepared by literature procedures:

\[
\begin{align*}
\text{Me}_2\text{AsO}_2\text{SO}_2^- \xrightarrow{\text{SO}_2/\text{KI}/\text{HCl}} \text{Me}_2\text{AsI} & \xrightarrow{\text{Na}/\text{THF}} \text{Me}_2\text{AsNa} \\
\text{Me}_2\text{AsNa} & \xrightarrow{0.5 \text{ equiv. } ₀-C⁶H₄\text{Cl}_2 \text{ or } \text{Cl}(\text{CH}_2)_3\text{Cl}/\text{THF}} ₀-C⁶H₄(\text{AsMe}_2)_2 \text{ or Me}_2\text{As(CH}_2)₃\text{AsMe}_2
\end{align*}
\]
(d) Multidentate ligands containing arsenic donors

The ligands \( \text{Me}_n\text{As}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3-n \) (\( n = 0, 1 \)) and \( \alpha-\text{C}_6\text{H}_4[\text{As(\text{Me})CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2]_2 \) were available from earlier studies. 42ii

7.124 Ligands Containing Antimony Donors

The ligands \( \text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2 \) and \( \alpha-\text{C}_6\text{H}_4(\text{SbMe}_2)_2 \) were prepared by adaptations of procedures described in the literature. The method is described for \( \alpha-\text{C}_6\text{H}_4(\text{SbMe}_2)_2 \).

\[
\begin{align*}
\text{NH}_2 & \quad \text{NaNO}_2/\text{H}_2\text{O} \\
& \quad 0^\circ\text{C} \\
\text{Br} & \quad \text{SbCl}_2/\text{cHCl} \quad \text{glycerine} \\
& \quad \text{NaOH, R.T.} \\
\text{Br} & \quad \text{MeMgI, Et}_2\text{O} \\
& \quad (64\%) \\
\text{Br} & \quad \text{SO}_2/\text{cHCl} \\
\end{align*}
\]

(The above reactions were carried out by A. L. Hale and D. J. Gulliver 42ii)

\[
\begin{align*}
\text{SbCl}_3 & \quad (i) \text{MeMgI} \\
& \quad (ii)\text{Br}_2 \\
\text{Me}_3\text{SbBr}_2 & \quad (\text{ca} 20\%) \\
\text{Br} & \quad (i) \text{Na}/\text{NH}_3(1) \\
& \quad (ii)\text{Br}_2 \\
\text{Br} & \quad \text{or Me}_2\text{Sb}(\text{CH}_2)_3\text{C} \\
& \quad \text{SbMe}_2 (\text{ca} 50\%)
\end{align*}
\]
Preparation of o-phenylenebis(dimethylstibine)

Ammonia (ca 500 cm$^3$) was condensed into a 1000 cm$^3$ three necked round bottomed flask fitted with condenser and bubbler, mechanical stirrer and nitrogen/ammonia inlet. Sodium (19.3g 0.84 mmol) was cut into small pieces under petrol, then added to the ammonia. After 30 minutes all the sodium had dissolved, and Me$_3$SbBr$_2$ (68.6g 0.21 mol) was added to the dark blue solution. This turned red over ca 1 hour and was left for a further hour. The stibide solution was then transferred under nitrogen to a pressure equalising dropping funnel insulated with aluminium foil containing crushed Dry Ice, and added portionwise to a solution of o-C$_6$H$_4$(SbMe$_2$)Br (30.0g 0.1 mol) in THF (100 cm$^3$) at -40°C over ca 3 hours. The mixture was then allowed to warm to room temperature with stirring and the ammonia allowed to evaporate. Diethyl ether (150 cm$^3$) followed by aqueous NH$_4$Cl (150 cm$^3$) were added, the layers separated under nitrogen, the aqueous layer washed with diethyl ether (50 cm$^3$) and the combined organic layers dried over MgSO$_4$ overnight. The solvents were distilled off under nitrogen and the organic residue fractionated in vacuo. The two major impurities, tetramethyldistibine (1.5g) (B.P. 46 °C/0.5 mmHg) and PhSbMe$_2$(2g) (B.P. 66-80°C/0.5 mmHg) were followed by the desired product, 5.5 g 22% (B.P. 114°C/0.2 mmHg) $^1$H nmr; δ = 0.92(s), 6.9(m) (12H,4H respectively).
References


CHAPTER 8

SOME PRELIMINARY STUDIES IN IRON(IV) CHEMISTRY

WITH NEUTRAL DONOR LIGANDS
8.1 Introduction

Although iron(IV) is not the highest known oxidation state of iron, its chemistry is even more restricted than that of nickel(IV), especially where neutral ligands are concerned. This investigation was initiated as a logical continuation of work performed with nickel(IV), so that the complexes of the two metals could be compared in this high oxidation state, and also as part of a wider study of Ru and Os chemistry.

A range of Fe(III) complexes \([\text{Fe}(L-L)_2X_2]\text{BF}_4\) (\(L-L = \text{o-C}_6\text{H}_4(\text{EMe}_2)(\text{E'}\text{Me}_2); E = \text{P}, \text{As}; \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2, \text{o-C}_6\text{H}_4(\text{PMe}_2)_2\) and \(X = \text{Cl}, \text{Br}\), \([\text{Fe}(L-L)_2X_2]\text{[FeX}_4\text{]}\) (\(L-L = \text{o-C}_6\text{H}_4(\text{PMe}_2)(\text{SMe}), \text{Me}_2\text{As}(\text{CH}_2)_2\text{AsMe}_2\) and \(\text{Fe(II)}\) complexes \(\text{Fe}(L-L)_2X_2\) (\(L-L = \text{1,10-phenanthroline, 2,2'-bipyridyl, o-C}_6\text{H}_4(\text{PPh}_2)_2, \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2, \text{cis-Ph}_2\text{PCHCHPPh}_2; X = \text{Cl}, \text{Br}\)) have been prepared, some for the first time, and attempts have been made at their oxidation to Fe(IV) materials.

With the great recent interest in biochemically relevant Fe(IV) complexes of porphyrins, which can contain \(\text{Fe = O}\) units, attempts were made to utilise the reactions of \(\text{K}_2\text{Fe}^{\text{VI}}\text{O}_4\) with some hard donor ligands (less reducing than phosphines and arsines) to examine the possibility of isolating similar complexes with simpler ligands.

The results of this study obtained to date will be outlined in this chapter, and a brief examination of the relevant literature is included for comparison.
8.2 Survey of Relevant Literature

8.21 Iron(II) and Iron(III) Phosphine and Arsine Complexes
(Bidentate Ligands)

Complexes of Fe(II) and Fe(III) are of interest as starting materials for oxidation to Fe(IV), and some of their properties may be of relevance to their behaviour on oxidation. This section summarises details of the preparation and spectroscopic properties of complexes prepared in this study only, including new complexes.

Iron(II) complexes of phenyl-substituted phosphines are rare, and have only recently been the subject of investigation. The complexes \([\text{Fe(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]\text{Cl}_2]\) and \([\text{Fe(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]\text{Br}_2]\cdot\text{H}_2\text{O}\) were reported to be the products obtained by combining the Fe(II) salts and the ligand in ethanol or ethanol-acetone, in a 1:1 mole ratio. The octahedral \([\text{Fe(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]\text{Cl}_2]\) was made by refluxing the ligand and the anhydrous \(\text{FeCl}_2\) in toluene; it dissociates in solution (to \([\text{Fe(L-L)}\text{Cl}_2]\) + L-L) in polar solvents.

The ligand \(\text{cis-Ph}_2\text{PCHCHPPh}_2\) was found to react with iron(II) salts in ethanol to yield \([\text{Fe(L-L)}\text{Cl}_2]\)\(_X\)\(_2\). Depending on \(X\), and on whether the complex is solvated or not, these complexes can exhibit spin crossover behaviour between the singlet and quintet states, whereas similar complexes of methyl substituted phosphines (for example \(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\), \(\text{C}_6\text{H}_4\text{(PET}_2\text{)}\)\(_2\)) are low spin at room temperature. This is probably a consequence of the weaker \(\sigma\)-donor strength of the aryl phosphines, and the longer Fe-P bond distances in these complexes than observed in, for example, \([\text{Fe(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2}\text{Cl}_2]\).

The ligand \(\text{o-C}_6\text{H}_4\text{(PPh}_2\text{)}\)\(_2\) was found, in the course of
this study, to yield high-spin \([\text{Fe}(L-L)_2X_2]\) with anhydrous FeX_2 in benzene, and the products could be recrystallised without decomposition from CH_2Cl_2/ethanol (Table 8.211). Other spectroscopic data showed that the complexes were in all respects similar to those of cis-Ph_2PCHCHPPh_2 (high spin form). Data on all the complexes agreed closely with that found in the literature.

Nyholm first synthesised \([\text{Fe}\{\alpha-C_6H_4(AsMe_2)\}_2\_2Cl_2]\) [FeCl_4] in 1950. This complex is easily metathesised to \([\text{Fe}(L-L)_2Cl_2]Y\) (Y = ClO_4, BF_4) by treatment of acetone solutions with a few drops of the appropriate concentrated aqueous acid. This method was reported not to work for analogous complexes of phenyl-substituted phosphines (e.g. cis-Ph_2PCHCHPPh_2), and incomplete replacement of FeCl_4 occurs. (It was for this reason that Fe(II) complexes of these ligands, rather than the more simply prepared Fe(III) materials, were made in this study for attempted oxidation). The phosphine complexes \([\text{Fe}(L-L)_2X_2]Y\) (L-L = Me_2PCH_2CH_2PMe_2, X = Cl; Y = FeCl_4, L-L = o-C_6H_4(PMe_2)_2; X = Cl, Br; Y = ClO_4, ReO_4), of importance to this study, have also been isolated. All these complexes are low-spin, d^5, and are presumed on the basis of far-infra red and electronic spectroscopic data to have trans(D_2h) geometry. They are dark red (X = Cl) or dark green (X = Br). Apart from \([\text{Fe}(\text{cis-Ph}_2\text{PCHCHPPh}_2)_2\_2Cl_2]\)[FeCl_4], no phenyl-substituted diphosphine or diarsine complexes of Fe(III) have appeared in the literature.

A range of similar complexes \([\text{Fe}(L-L)_2X_2]FeX_4\) (L-L = Ph_2PCH_2CH_2PPh_2, cis-Ph_2AsCHCHAsPh_2, Me_2As(CH_2)_3AsMe_2, o-C_6H_4(PMe_2)(AsMe_2)) has more recently been prepared. In addition, during this study the complexes \([\text{Fe}(L-L)_2X_2]Y\) (L-L = o-C_6F_4(PMe_2)_2, o-C_6H_4(PMe_2)(SMe); X = Cl, Br; Y = BF_4, FeCl_4) were made. Spectroscopic data obtained (Table 8.211) confirms that all these complexes are low-spin, d^5 and probably of trans-geometry.
(a) $\nu_{\text{Fe-X}}$

(b) $\nu_{\text{FeCl}_4^-$, $\nu_{\text{Fe-Cl}}$ (cation) respectively.

(c) Recorded using S.P.700 instrument on nujol mull or CH$_2$Cl$_2$ solution.

(d) In CH$_3$CN solution except

(e) CH$_2$Cl$_2$, (f) diffuse reflectance

(G) Gouy, (E) Evans method.
Rather surprisingly, no X-ray crystallographic examination of any Fe(III) complex of these bidentate ligands has been undertaken, although it was found that crystals could readily be obtained by slow cooling of acetone solutions of the Fe(III) complex in the presence of a little 25% HBF$_4$. Currently, the crystal structure of [Fe($\sigma$-C$_6$F$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]BF$_4$, obtained in this way, is being elucidated as part of this work.

8.22 Miscellaneous Fe(II) and Fe(III) Complexes of Other Ligands

Also prepared to enable attempts at their oxidation, chemically or electrochemically, were [Fe(L-L)$_3$]X$_2$, [Fe(L-L)$_2$X$_2$]. (L-L = 1,10-phenanthroline, 2,2'-bipyridyl, X = Cl,Br), the former by precipitation from aqueous solutions of the sulphate with excess NaX, the latter by pyrolysis in vacuo of [Fe(L-L)$_3$]X$_2$.$^{17}$ The tris-ligand complexes are low spin, while the [Fe(L-L)$_2$X$_2$] are high-spin.

8.23 Complexes of Iron(IV)

8.231 Biologically-Related Compounds

A primary reason for interest in Fe(IV) chemistry is the implication of transitory Fe(IV) species in processes involving iron-containing oxygen transport proteins (for example, haemoglobin, myoglobin).$^{5,6}$ Although such intermediates were first postulated many years ago, it is only recently that firm chemical evidence has been obtained. In particular, Mossbauer spectroscopy, combined with esr and n.m.r. comparisons with model compounds, established the presence of Fe$^{IV}$ = 0 sites in H$_2$O$_2$-treated myoglobin.$^5$

* This survey is not intended to be comprehensive, except for Group Vb ligands, but rather is to illustrate aspects of the chemistry of iron(IV) with other, charged, ligands and to draw attention to comparisons with the chemistry of nickel(IV).
The model compounds used were iron complexes of di-anionic porphyrin ligands and the products of their reactions with O$_2$ and H$_2$O$_2$. For example, the following sequence of reactions has been established (P = (m-tolyl)$_4$porphyrin).\(^2-4\)

\[
\text{Fe}^{II}P \xrightarrow{H_2O_2} \text{PFe}^{III}-O-O-\text{Fe}^{III}P
\]

\[
PFe^{III}-O-O-\text{Fe}^{III}P \xrightarrow{2B} 2\text{BFe}^{IV}(P)=0.
\]

\(-80^\circ C\)

\[B = \text{nitrogen base, eg imidazole}.\]

The magnetic and spectroscopic (\(^1\)H n.m.r., Mössbauer, infra red, electronic) data for BFe(P)= 0 seem to exclude any other possibility (for example, that the complex could be a low-spin Fe(III) complex of a radical-cation ligand).\(^2-4\) The chemical behaviour rules out the continued existence of the O-O bridge; the bridged Fe(III) complex does not react with Ph$_3$P, but a fast catalytic reaction ensues between Ph$_3$P and BFe$^{IV}(P)=0$, with formation of Ph$_3$P = 0, at -80°C. Also, on combining a 1:1 ratio of the Fe(IV) and the original Fe(II) complex the bridged species PFe$^{III}-O-O-\text{Fe}^{III}$P is formed and the base (imidazole) recovered.\(^5\) It has been suggested that similar ferryl (Fe IV = 0) complexes could serve as precursors in the synthesis of magnetically intriguing mixed metal compounds (e.g. Fe IV = 0 + Cu I → Fe III -O-Cu II).\(^4\)

Recently, a most interesting Fe(IV) complex with hemiphorphyrazine has been isolated, in which the Fe atoms are bridged by O$^{2-}$ (see Figure 8.231).\(^6\) Again the variable-temperature magnetic behaviour of the polymer ruled out an Fe(III)-oxidised ligand formulation.
Figure 8.231  (A) Molecular structure of [(hemiporphyrazine)FeO]_n and (B) the arrangement of the chains of molecules in the overall structure, from reference 6.
8.232 Charged Sulphyr and Selenium Donors

The great majority of Fe(IV) co-ordination complexes are those involving charged S or Se donor atoms.\(^1\)

The 1,2-dithiolene ligands (Chapter 2, page 46), as the dianions, form \([\text{Fe}(\text{S}_2\text{C}_2\text{R}_2)_3]^{2-}\) when combined with \(\text{FeCl}_3.6\text{H}_2\text{O}\) in ethanol,\(^{18}\) in the correct mole ratio. These complexes (\(\text{R} = \text{CF}_3, \text{CN}\)) have not attracted the same interest in their charge distribution as, for example, the formally Ni(IV) species \([\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]\), or \([\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_3]^{2-}\). The esr experiments which shed light on the "Ni(III)" systems (Chapter 2) are not applicable to the Fe system. However, the consensus of opinion seems to be that these complexes are best described as Fe(III), with an anion-radical ligand.

In contrast, 1,1-dithiolenes form \([\text{Fe}(\text{S}_2\text{C}_2\text{R}_2)_2]\), and on air oxidation, Fe(IV) complexes can be isolated. In particular, the ligands \((\text{ROOC})_2\text{C}=\text{CS}_2^{2-}\) are effective in stabilising Fe(IV), and one such complex (\(\text{R} = \text{Et}\)) has been the subject of X-Ray crystallographic study.\(^{19}\) Magnetic and Mössbauer results show that these materials are similar to corresponding dithiocarbamate complexes (q.v.) which are certainly best described as Fe(IV), and, further, the ligand structural parameters are similar to those in the corresponding Ni(II) complex.\(^{19}\) The geometry about Fe is best described as a trigonal prism, with individual small rotations of the ligands about the \(C_2\) axis, one of which is larger than the other two so that overall symmetry is reduced to \(C_2\). (Figure 8.232).

The neutral \([\text{Fe}(\text{dtc})_3]\) (dtc = dithiocarbamate; Chapter 2, page 53) are also easily oxidised, by BF\(_3\) in air in a rather unusual reaction, to \([\text{Fe}(\text{dtc})_3]\text{BF}_4\).\(^{20}\) The magnetic moments (3.37 - 3.15 B.M.)
and Mössbauer spectra are consistent with an Fe(IV) ion with the low spin $d^4$ configuration. As in the Ni(IV) complex, the frequency of the C-N stretching vibration increases by 30-40 cm$^{-1}$ on oxidation, as the resonance form $R_2^N = CS_2^{2-}$ increases in significance over $R_2N-CS_2^-$.

The structure of $[\text{Fe(pyroldithiocarbamate)}_3]ClO_4$ has been determined, and the coordination geometry is octahedral, distorted substantially towards a trigonal prism in a very similar manner to $[\text{Fe}((\text{EtOOCC})_2 C = CS_2)_3]^+$ (Figure 8.232).

Recently this chemistry has been extended to cover selenium donor atoms, and the crystal structure of $[\text{Fe}((C_6H_5CH_2)_2NCSe_2)_3]BF_4$ has been determined. This is in all respects very similar to the corresponding Fe(dtc)$_3^+$ complexes, and the deviation from octahedral geometry is almost identical in the two cases. (Figure 8.232).

In comparison with the Ni(IV) dtc complexes, the Fe(IV) materials exhibit greater distortion from octahedral symmetry (14.5° for $[\text{Ni}((\text{Bu}^n\text{N})_2\text{NCS}_2)_3]\text{Br}$; 24° for $[\text{Fe}((C_6H_5CH_2)_2\text{NCSe}_2)_3]BF_4$). Their magnetic moments are lower than the 3.6 B.M. expected for a spin paired $d^4$ system, but this has been rationalised as due to the deviations from $O_h$ symmetry, which reduce the orbital moment contribution.

8.233 Iron(IV) Complexes with Neutral Ligands

Currently, the only complexes of Fe(IV) with neutral ligands are $[\text{Fe}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2X_2]Y_2$ ($X = \text{Cl}, \text{Br}; Y = \text{FeCl}_4, \text{BF}_4$), first made by Nyholm in 1956, and $[\text{Fe}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)_2\text{Cl}_2][\text{ReO}_4]_2$.
Perspective view of the cation in $[\text{Fe(Se}_2\text{CN(CH}_3\text{C}_6\text{H}_4)_2}_2\text{]}^{-}\text{BF}_4(4)$ looking down the three-fold axis.
The FeCl salts were isolated by the addition of FeCl$_3$ to nitrobenzene solutions of the Fe(IV) complex, themselves generated by addition of HNO$_3$ to solutions of the Fe(III) material. However, these were impure, and unsuitable for magnetic measurements as the anion FeCl$_4^{-}$ has a large magnetic moment (ca 5.9 B.M.). As the perchlorate salts were found to be particularly sensitive, detonating when struck or warmed above room temperature, the tetrafluoroborates were isolated for characterisation. The rather low magnetic moments ($X = Cl; 2.76$ B.M. $X = Br; 3.14$ B.M. at room temperature, falling linearly to 2.64 and 3.02 at 123K) compared with that expected for a d$^4$ ion in an octahedral field of 3.6 B.M., was rationalised as due to tetragonal distortion. However it was not clear whether the Fe-X bonds were extended or compressed to provide this distortion.

Warren and Bennett claimed that Nyholm's original measurements were in error, probably owing to contamination of the sample with the Fe(III) complex, and reported a magnetic moment of 3.38 B.M. for [Fe(o-C$_6$H$_4$(AsMe$_2$)$_2$]Cl$_2$][ReO$_4$]$_2$, and 3.61 B.M. for [Fe(o-C$_6$H$_4$(PMe$_2$)$_2$]Cl$_2$][ReO$_4$]$_2$. However, since in D$_{4h}$ symmetry there must of necessity be some tetragonal distortion, the latter figure seems high. No X-ray crystallographic examination of the complexes has been reported, not surprising in view of their instability.

The far infra red spectra of the Fe(IV) complexes show one band which varies with X, at 389 cm$^{-1}$ and 300 cm$^{-1}$ (X = Cl, Br respectively; o-C$_6$H$_4$(AsMe$_2$)$_2$ complexes). This compares with values of 380 and 341 cm$^{-1}$ for the Fe(III) (d$^5$) complexes (low-spin in both cases); a marked contrast to the changes observed in the Ni(III) to Ni(IV) (d$^7$ to d$^6$) oxidation, where a $\sigma$-antibonding electron is removed from the $d^2_z$ orbital (Chapter 3).
Mössbauer data has been recorded using 90% $^{57}$Fe-enriched complexes of Fe(IV). The values of the isomer shifts for $[^{57}\text{Fe}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)\text{X}_2][\text{BF}_4]_2$ (X = Cl, Br) were comparable to those obtained for other low-spin Fe(III) and Fe(II) complexes. The quadrupole splitting was about 3.2 mmsec$^{-1}$ for both complexes, and independent of temperature down to 4.2K. Further, detailed studies were consistent with a strong axial compression of the ligand field along the z direction, and significant ππ→dσ bonding between halide and iron IV.

Finally, it was suggested that the product of the reaction between $[\text{Fe(CO)}_3(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2]$ and CHCl$_3$ contains Fe(IV), on the basis of Mössbauer spectroscopy, but few details were given and the Fe(IV) formulation seems chemically unlikely. An interesting, but preliminary, report mentions the synthesis of $[\text{Fe}(\text{o-C}_6\text{F}_4(\text{AsMe}_2)_2)_2\text{Cl}_2]^{2+}$, but no spectroscopic or magnetic data was obtained.

8.234 Other Complexes of Fe(IV)

No report has yet appeared of the synthesis of the FeF$_6^{2-}$ ion, in contrast to the well-known NiF$_6^{2-}$ species, although attempts have been made to obtain it. It is possible that, with developments in fluorine technology, the ion may be obtained (for example, by the high-pressure fluorination of CsCl + FeCl$_3$ mixtures).

Oxime complexes of Fe(IV) also appear to be unknown, although this could be due to the unavailability of suitable Fe(II) or Fe(III) starting materials, rather than any inherent instability of Fe(IV).

Iron(IV)-periodate complexes are also unknown.
whereas Ni(IV) complexes exist (Chapter 2). Well-defined Fe(IV) oxide complexes are also rather rare. The only alkali metal metaferrate (IV) is Li$_2$FeO$_3$, the product of heating K$_2$FeO$_4$ with excess LiOH and extracting the excess LiOH with alcohol. The corresponding silver salt can be made from AgNO$_3$ and K$_2$FeO$_4$.

The discrete FeO$^{4-}$ ion is thought to exist in Ba$_2$FeO$_4$, formed when Ba$_3$[Fe(OH)$_6$)$_2$ is heated with Ba(OH)$_2$ in oxygen at ca 800°C.  

8.235 Fe(V) and Fe(VI)

In contrast to nickel, iron displays oxidation states higher than IV. Iron(V) is very rare, well-defined examples being restricted to K$_3$FeO$_4$, said to contain discrete FeO$_3^{3-}$ units, and the recently-prepared La$_2$LiFeO$_6$, containing Fe$^{V^6}$ octahedra.

Iron(VI) chemistry is confined to the ferrates(VI). The M$_2$FeO$_4$ (M = K,Rb,Cs) are best made by ClO$^-$ oxidation of Fe(NO$_3$)$_3$ in very concentrated aqueous alkali. The deep purple materials have been investigated by infra red, esr, Mossbauer and electronic spectroscopy. The chemistry of the FeO$^{2-}$ ion has been little-studied, being confined to thermal decomposition, and reaction with various reducing agents. It will oxidise arsenite, Cr$^{III}$, I$^-$, SO$_4^{2-}$, H$_2$O$_2$, I$^-$, NH$_4^+$ and alcohols, and has been investigated as an oxidant in water treatment (Chapter 1, page 3). Its reaction with HSO$_3$X (X = Cl,F) and HF could result in the preparation of new oxide-halides (cf Mn,Cr), although this does not appear to have yet been examined.
8.3 Results and Discussion

8.3.1 Reactions of $\text{K}_2\text{FeO}_4$

The iron(VI) oxoanion was made according to the published procedure, except that the final purification by washing with benzene, methanol and diethyl ether was omitted. Instead, the crude product was purified by precipitating it from 2M KOH solution with saturated aqueous KOH containing a little ClO\(^-\) ion. It was dried in vacuo and stored under nitrogen at -20°C, in which condition it was stable for ca 2 weeks. Its purity was assessed by iodometric titration, and from its electronic spectrum.

Attempts were made to carry out reactions of $\text{K}_2\text{FeO}_4$ with potential donor ligands under various conditions, with the intention of isolating any complexes of Fe(IV) which might thereby be formed. However, none of these reactions was successful; the only iron-containing material isolated from any of them was a flocculent brown-red gel or precipitate, containing no organic material and presumed to be FeO.OH in a hydrated form.

A possible alternative route to Fe(IV) oxo-complexes may be by reaction of suitable Fe(II) or Fe(III) materials with iodosyl benzene, C\(^6\)H\(_5\)I0. This reagent has already been successfully employed in generating the Cr\(^V\) = O species [O = Cr(SALEN)]PF\(_6\) (Chapter 1, page 7), and a similar reaction with [Fe\(^{III}\)(SALEN)]\(_2\)O or [Fe(SALEN)\(_2\)I] may be worthy of investigation.
8.32 Iron(IV) Complexes with Neutral Donors

8.321 Syntheses

Examination of the available literature suggested that the oxidation by nitric acid of $[\text{Fe}(L-L)X_2]^+$
($L-L = \sigma-C_6\text{H}_4(\text{AsMe}_2)_2; X = \text{Cl,Br}$, $L-L = \sigma-C_6\text{H}_4(\text{PMe}_2)_2; X = \text{Cl}$)
and subsequent isolation of the Fe(IV) cation by precipitation with inert anions gave somewhat variable results. Whereas
Nyholm found that the arsine complexes were best isolated as $\text{BF}_4^-$ salts (as the $\text{ClO}_4^-$ salts were unfortunately explosive
and the ReO$_4^-$ salts invariably contained N), Warren and Bennett
preferred ReO$_4^-$ as the counter ion as the salts so obtained appeared
not to be hygroscopic.

Accordingly, a variety of other strong oxidants was first tried, to see if Fe(IV) complexes could consistently
be generated pure without the incorporation of N (as NO$_3^-$ or as NO). Nitrosyl chloride was unsuitable, as it has earlier been found
that NO$_2^+$ is only capable of oxidising Fe(II) to Fe(III) in these systems. Other oxidants tried were $K_2\text{CrO}_4$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (catalysed
by AgNO$_3$) and Ce$^{4+}$, all in aqueous solution, but although colour
changes characteristic of Fe(II) $\rightarrow$ Fe(III) $\rightarrow$ Fe(IV) were sometimes observed, it was not possible to devise conditions under which solid products
could be isolated. The solubilities of the oxidants and Fe(III)
complexes were incompatible, and suspensions of the Fe(III)
complexes were not oxidised by aqueous solutions of the oxidants.

Recourse was therefore made to concentrated nitric acid. It was found that the best procedure for isolating essentially
nitrogen-free Fe(IV) materials was to dissolve the Fe(III) complexes
in the minimum volume of HNO$_3$ containing a small amount of HX ($X = \text{Cl}$; 3 drops conc. HCl in 10 ml conc. HNO$_3$, $X = \text{Br}$; 1 drop conc. HBr
in 10 ml conc. HNO₃) at ca -5°C (ice-salt bath). The solution was then filtered rapidly into a cold (-20°C) flask and 45% HBF₄ filtered dropwise, with shaking, into the acid solution. A purer product was invariably obtained if a little of the Fe(IV) complex remained in solution after the product was filtered off. It proved possible to wash the product very briefly on the sinter with a small volume of ice-cold distilled water, providing that it was then immediately dried in vacuo in a darkened desiccator.

In this way, the complexes [Fe(L-L)₂X₂][BF₄]₂ (L-L = o-C₆H₄(AsMe₂)₂, o-C₆H₄(PMe₂)₂, o-C₆H₄(PMe₂)(AsMe₂); X = Cl,Br) have been prepared dry and nitrogen-free (infra red spectral and analytical data; Table 8.321).

Attempts to prepare [Fe(Me₂PCH₂CH₂PMe₂)₂X₂][BF₄]₂ in the same way have so far failed. The Fe(IV) complexes undoubtedly form in nitric acid solution, but are extremely soluble even at temperatures marginally above the freezing point of the acid. The 45% HBF₄ failed to precipitate the complexes, as did the addition of large excesses of NaBF₄. Concentrated (ca 70%) HClO₄ and HPF₆ (ca 60%) also failed to give precipitates. This situation is very similar to that encountered with the corresponding Ni complex, but in this case, chlorine oxidation in suspension as used to prepare [Ni(Me₂PCH₂CH₂PMe₂)₂Cl₂][BF₄]₂ is of no use as Cl₂ is incapable of oxidising any of the Fe(III) complexes in suspension.

The opposite problem was encountered with the o-C₆F₄(PMe₂)₂ complexes. These were insufficiently soluble in the acid mixture at low temperature. Further efforts to isolate these complexes are in progress.
<table>
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<tr>
<th>COMPLEX</th>
<th>ANALYSES&lt;sup&gt;a&lt;/sup&gt;</th>
<th>μ&lt;sub&gt;eff&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (B.M.)</th>
<th>I.R.&lt;sup&gt;-1&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
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<tbody>
<tr>
<td>[Fe(o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;][BF&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>27.6(27.5) 3.8(3.7) -</td>
<td>3.05</td>
<td>390(vs)</td>
</tr>
<tr>
<td>[Fe(o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(AsMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;][BF&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>24.7(25.0) 3.4(3.4) 17.0(16.6)</td>
<td>2.84</td>
<td>303(m)</td>
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<td>[Fe(o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;][BF&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>35.0(34.5) 4.7(4.6) 10.0(10.2)</td>
<td>3.01</td>
<td>384(s)</td>
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<td>[Fe(o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;][BF&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>30.3(30.6) 4.2(4.1) 20.4(20.4)</td>
<td>2.71</td>
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<td>30.3(30.6) 4.1(4.1) 9.0(9.5) 3.22</td>
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<td>26.9(27.5) 3.9(3.7) -</td>
<td>3.27</td>
<td>294(m)</td>
</tr>
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(a) Calculated values in parentheses.
(b) Gouy method, at 295K.
Table 8.322. Spectroscopic Data for $[\text{Fe}(L-L)_2X_2]^{2+}$

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>Diffuse Reflectance $(10^{-3} \text{ cm}^{-1})$</th>
<th>Electronic Spectra (CF$_3$COOH solution) $(10^{-3} \text{ cm}^{-1} \text{ (t, dm}^3\text{ mol}^{-1}\text{ cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{AsMe}_2)_2\text{Cl}_2][\text{BF}_4]_2$</td>
<td>13.3(br), 16.7, 17.9, 24.0, 26.6, 28.6</td>
<td>12.5(sh)(510), 13.44(1150), 18.05(3650)</td>
</tr>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{AsMe}_2)_2\text{Br}_2][\text{BF}_4]_2$</td>
<td>12.5, 16.3, 17.5, 18.5(sh), 22.4, 26.2</td>
<td>11.66 (940), 12.59 (2740), 17.24 (3340).</td>
</tr>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{PMe}_2)_2\text{Cl}_2][\text{BF}_4]_2$</td>
<td>12.3, 13.3, 16.8(sh), 18.1, 19.1, 23.8, 26.5, 28.6</td>
<td>12.66(sh) (700), 13.74(1640), 20.01 (3480)</td>
</tr>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{PMe}_2)_2\text{Br}_2][\text{BF}_4]_2$</td>
<td>12.5, 15.4(sh), 16.5, 17.6, 23.8, 26.3, 29.4</td>
<td>11.68(700), 12.64(1980), 16.84(sh) (2260), 17.30(2360)</td>
</tr>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2))_2\text{Cl}_2][\text{BF}_4]_2$</td>
<td>12.3(sh), 13.4, 13.8(sh), 16.6, 17.4, 18.2(sh), 19.2(sh), 22.7(sh), 24.0, 28.9</td>
<td>12.5(sh)(1180), 13.55(2770), 18.52(7830)</td>
</tr>
<tr>
<td>$[\text{Fe(o-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2))_2\text{Br}_2][\text{BF}_4]_2$</td>
<td>12.5(br) v 15.4(sh,br), 16.9, 18.3, 24.9, 30.7</td>
<td>11.7(530), 12.66(1570), 16.66(sh) (1450), 17.54(1710)</td>
</tr>
</tbody>
</table>
As found for the nickel system, \( \sigma\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SMe}) \) is incapable of stabilising Fe(IV), and \([\text{Fe}\{\sigma\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SMe})\}_2\text{Cl}_2]\) \([\text{FeCl}_4]\) was decomposed by conc. HNO\(_3\). Distibine ligands such as Me\(_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\) are halogenated by FeX\(_3\), so that they are also incapable of stabilising Fe(IV). However, \( \sigma\text{-C}_6\text{H}_4(\text{EMe}_2)(\text{SbMe}_2) \) (E = P,As) give Fe(III) complexes, \(^{15,37}\) and the oxidation of these is also currently under investigation.

The iron(II) complexes with phenyl-substituted phosphine ligands \([\text{Fe}(L-L)X_2]\) (L-L = Ph\(_2\text{PCH}_2\text{CH}_2\text{PPh}_2\), cis-Ph\(_2\text{PCH}_2\text{CH}_2\text{PPh}_2\), o-C\(_6\text{H}_4(\text{PPh}_2)_2\); X = Cl,Br) decomposed on treatment with HNO\(_3\) to light green-brown oils. On treatment with BF\(_3\) in CH\(_2\)Cl\(_2\) in air, the solutions turned black, but the green \([\text{Fe}(L-L)\text{Cl}_2]\)BF\(_4\) (L-L = Ph\(_2\text{PCH}_2\text{CH}_2\text{PPh}_2\)) was the only product, recovered impure with boric acid. (This reaction was tried as corresponding reactions with \([\text{Fe}(\text{dithiocarbamate})_3]\) give Fe(IV) complexes. \(^{20}\))

8.322 Spectroscopic and electrochemical results

Criteria used to assess the purity of the Fe(IV) complexes were their analyses (C, H, N and X) and infra red spectra. The six complexes all had good C and H analyses, and little (\(< \text{ca} 0.1\%) or no N. Changes in the infra red spectra (4000 - 180 cm\(^{-1}\)) on oxidation from Fe(III) to Fe(IV) were restricted to slight increases in \(\nu\text{Fe-X}\) (Table 8.321) and small changes in ligand modes. In particular, new bands assignable to NO\(_3^-\) (at 1320 and 770 cm\(^{-1}\)) or NO\(^-\) (1800-1550 cm\(^{-1}\)) were not observed.

Diffuse reflectance spectra were obtained in the usual way (chapter 7), and solution spectra were recorded in CF\(_3\)COOH. In this solvent, little decomposition was noted over the time taken to prepare and run the samples. Repetitive scans showed only slow decomposition. The bromides decomposed noticeably faster than the chlorides.
The Fe(IV) spectra are distinctive, with two low-energy bands of moderate intensity and a broad band of higher energy and intensity (Table 8.322, Figure 8.323). It is not possible to assign these bands with any confidence. Comparison with other 3d<sup>4</sup> systems is difficult, as low-spin d<sup>4</sup> complexes are rare. The energies of all the bands show slight variation with the donor set, viz. Cl > Br; P > As, with the differences between Cl and Br larger than those between P and As. Assuming that the transitions are of d-d character (as is most likely, at least for the low-energy bands, even in this high oxidation state), this indicates that donor sets of Cl and P give a marginally greater ligand field than those containing Br and As, as previously observed for Ni(IV) (Chapter 6). The diffuse reflectance spectra show bands at approximately the same energies as the solution spectra, and the slight splitting of the broad bands at ca 1700 cm<sup>-1</sup> in solution are resolved as two peaks in the solid state spectra.

Iron(IV) complexes of dithiocarbamate and diselenocarbamate complexes display very intense (ε = ca 10,000) bands at > 18,000 cm<sup>-1</sup> and the d-d bands are not observed, making comparison with the arsine and phosphine complexes impossible.

Comparison of the data of Nyholm et al. for \([\text{Ni}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_2X_2][\text{BF}_4]_2\)\(^{12}\) with that obtained in this study for Fe(III) and Fe(IV) complexes, it seems that in nitromethane, the solvent used by Nyholm,\(^ {12}\) considerable decomposition to Fe(III) has occurred, since several of the bands reported coincide exactly in position with those of the corresponding Fe(III) complexes,\(^ {12}\) and are not the same as the bands found in this study, in CF<sub>3</sub>COOH solution.

Magnetic moments were recorded by the Gouy method
of samples of the Fe(IV) complexes within 24h of their preparation (Table 8.321). The values found, while lower than those of Warren and Bennett, are comparable with values obtained by Nyholm, and it seems probable that Nyholm's proposal of tetragonal distortion is valid for all the complexes. The higher values obtained by Warren and Bennett could be due to iron oxide impurities in the sample, only a very small amount of which could cause artificially high readings. Attempts to confirm the Gouy measurements using the Evans method on CF₃COOH solutions of the more stable complexes are in progress.

Cyclic Voltammetry

Cyclic voltammetry was performed in CH₃CN solution as described earlier for the Ni(IV) complexes, using the Fe(III) cations. The Fe(II)-Fe(III)-Fe(IV) system has the advantage that pseudo-octahedral stereochemistry is maintained throughout, and, in line with expectation, one-electron reversible processes were observed both for oxidation and reduction (Table 8.324, Figure 8.325) for most of the ligands.

Comparing the observed oxidation potentials with those of the corresponding Ni(III) → Ni(IV) system, it can be seen that the potentials are significantly higher for Fe(III) → Fe(IV) and that differences between ligands are more marked for iron. Particularly notable is the very large difference between the potential for Me₂PCH₂CH₂PMe₂ (+1.22V vs S.C.E.) and o-C₆F₄(PMe₂)₂ (+1.69 V vs. S.C.E.) and the corresponding difference in the Fe(III) → Fe(II) reduction which is greatly favoured by o-C₆F₄(PMe₂)₂ (+0.35V) compared with Me₂PCH₂CH₂PMe₂ (-0.18V, irreversible).

Further studies in the electrochemistry of the corresponding
Table 8.324. Electrochemical Data - Fe(III) - Chloro Complexes

<table>
<thead>
<tr>
<th>STARTING COMPLEX</th>
<th>Fe(III) → Fe(II) (mV vs S.C.E.)</th>
<th>Fe(III) → Fe(IV) (mV vs S.C.E.)</th>
<th>ΔP^a mV</th>
<th>HOX/H^red</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(_\text{C}_6\text{H}_4\text{(AsMe}_2\text{)}\text{]}_2\text{Cl}_2\text{]}\text{BF}_4</td>
<td>+ 1440</td>
<td>70</td>
<td>0.88</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Fe(_\text{C}_6\text{H}_4\text{(PMe}_2\text{)}\text{]}_2\text{Cl}_2\text{]}\text{BF}_4</td>
<td>+ 1430</td>
<td>90</td>
<td>1.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(_\text{C}_6\text{H}_4\text{(PMe}_2\text{)(AsMe}_2\text{)}\text{]}_2\text{Cl}_2\text{]}\text{BF}_4</td>
<td>+45</td>
<td>70</td>
<td>1.07</td>
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<td></td>
</tr>
<tr>
<td>[Fe(_\text{C}_6\text{F}_4\text{(PMe}_2\text{)}\text{]}_2\text{Cl}_2\text{]}\text{BF}_4</td>
<td>+ 1690</td>
<td>85</td>
<td>1.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(_\text{C}_6\text{H}_4\text{(PMe}_2\text{)}\text{]}_2\text{Cl}_2\text{]}\text{BF}_4</td>
<td>+ 1220</td>
<td>80</td>
<td>1.09</td>
<td>irreversible</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Electric potential difference

\(^b\) Oxidation/Reduction potential
Figure 8.323 A. CF$_3$COOH solution spectrum of $[\text{Fe}^{\text{o-C}_{6}H_{4}(\text{PMe}_{2})_{2}}\text{Br}_{2}][\text{BF}_{4}]_{2}$.

B. With $\text{S}_{2}\text{O}_{4}^{2-}$ ion added to generate the Fe(III) complex, for comparison.
Figure 8.325. 1. Oxidation waves and 2. Reduction waves for (A) \([\text{Fe}\{\text{C}_6\text{F}_{14}\{\text{PMe}_2\}_2}\}_2\text{Cl}_2]\text{BF}_4\) and (B) \([\text{Fe}\{\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\}_2\text{Cl}_2]\text{BF}_4\), showing the large differences in potentials for these complexes.
bromides is in progress and it is hoped that the electrochemistry of some of the complexes with phenyl-substituted donors will be investigated in CH$_2$Cl$_2$.

Conclusions

The isolation and characterisation of these Fe(IV) complexes further illustrates the remarkable ability of the neutral ligands o-C$_6$H$_4$(EMe$_2$)(E'Me$_2$)(E = E' = P, As; E = P, E' = As) to stabilise complexes of the 3d metals in unusually high oxidation states. The electrochemical results indicate that it should prove possible to obtain further Fe(IV) complexes of the related ligands o-C$_6$F$_4$(PMe$_2$)$_2$ and Me$_2$PCH$_2$CH$_2$PMe$_2$ if the chemical problems of their synthesis can be overcome. The electronic spectral and cyclic voltammetry data indicate that once again o-C$_6$H$_4$(PMe$_2$)$_2$ is a slightly better $\sigma$-donor than o-C$_6$H$_4$(AsMe$_2$)$_2$, and that substitution of fluorine into the aryl backbone has a greater effect on the donor power of o-C$_6$X$_4$(EMe$_2$) than substitution of As for P. With the limited amount of data currently available, direct comparison of the stability of the d$^6$ Ni(IV) and d$^4$ Fe(IV) complexes is difficult, although the electrochemistry and the observed 'shelf-life' of the complexes do suggest that the Ni(IV) complexes are slightly easier to generate and more robust.

Nyholm reported that Fe(II) and Co(II) complexes of the ligand o-C$_6$F$_4$(AsMe$_2$)$_2$ appeared easier to oxidise than complexes of o-C$_6$H$_4$(AsMe$_2$)$_2$, although no quantitative data to support this observation was given. This is contrary to what is observed for o-C$_6$X$_4$(PMe$_2$)$_2$ (X = H,F); electrochemically it is easier to generate the Fe(II) complex of o-C$_6$F$_4$(PMe$_2$)$_2$ from the Fe(III) complex than it is for o-C$_6$H$_4$(PMe$_2$)$_2$ (Table 8.324). Chemically it was found that chlorine oxidation of Co{o-C$_6$F$_4$(PMe$_2$)$_2$)$_2$Cl$_2$ was necessary in order to generate Co(III), whereas the corresponding Co(II) complex of o-C$_6$H$_4$(PMe$_2$)$_2$ is oxygen-sensitive.
References


3. Ibid., idem 102 4334.

4. Ibid, idem 102 5945.


10. (a) Ibid, idem. 20 3430.


